Optical Sensor for Amine Vapors Based on Dimer–Monomer Equilibrium of Indium(III) Octaethylporphyrin in a Polymeric Film

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A novel transduction chemistry for the development of a polymer film-based optical sensor that responds reversibly to gas-phase amine species at sub-ppm levels is described. The sensor is based on the equilibrium of a indium(III) octaethylporphyrin hydroxide ion-bridged dimer species with corresponding monomeric porphyrins within a thin poly(vinyl chloride) film as a function of the level of volatile amine in the surrounding gas phase. The presence of amines causes the dimeric species to be converted to monomer via the ligation of the amine with the In(III) center of the porphyrin structure. This yields a significant change in the visible absorption spectrum of the In(III) center of the porphyrin structure. This yields a significant change in the visible absorption spectrum of the film, with a decrease in the intensity of the Soret band (I_max = 390 nm) and a concomitant increase in the Soret band for the monomer (I_max = 406–408 nm). Response to different amines is based on their relative partition coefficient into the polymer film and their strength of axial ligation reactions, with a selectivity pattern of 1-butylamine > 1-propylamine > pyridine > triethylamine > ethylamine > methylamine > diethylamine > tert-butylamine. It is further shown that a significant concentration of dimeric species within the polymer film can only be achieved if appropriate amounts of lipophilic anionic sites are also incorporated into the polymer in the form of a tetraphenylborate derivative and the resulting film is equilibrated briefly with water prior to gas-phase measurements. With optimized film compositions, 1-butylamine can be detected in the gas phase to levels approaching 0.1 ppm, while less lipophilic amine can be monitored down to 10 ppm, with fully reversible responses to each species. A simple mathematical model for the response of the amine sensor is presented and shown to predict the optical behavior observed.

The rapid detection of amine species in aqueous solutions and in gas phases is of great importance not only for environmental and industrial monitoring applications but also for the quality control of food products.1–3 Among a variety of new analytical tools under development, chemical sensors capable of continuously monitoring ammonia and organic amine species are especially attractive. Electrochemical devices for detection of amines are usually based on the oxidation of amines on various anode materials including carbon,4 gold,5 diamond,6 and metal oxides7,8 or on chemically modified electrodes with functional groups9 as well as polymer and DNA layers.9,10 Amperometric biosensors for amines with immobilized amine oxidases11–13 or amine dehydrogenases14 have been reported based on either a direct or a mediated electron-transfer pathway. Host–guest interactions have also been applied for devising amine sensors, usually between neutral carriers and given organic ammonium ions. Such chemistry has been investigated using a variety of transduction modes including ion-selective electrodes,15–17 ion channel sensors,18,19 and piezoelectric quartz crystal sensors.20

Optical transduction methods have also been employed in the design of chemical sensors that respond to ammonia and organic amines. For example, Charlesworth and MCDonald described a fiber-optic fluorescence sensor for amine vapors based on a film of the pH-sensitive molecule 2-naphthol, hydrogen-bonded to a poly(ethylene oxide) matrix.21 Diamond et al. assessed a calix4-[...]

arene bearing nitrophenylazophenol chromogenic moieties complexed with lithium to form an acid ligand, which was immobilized onto filter paper for the colorimetric detection of gaseous trimethylamine. Moreover, metalloporphyrins have also become widely used as novel ionophores for the preparation of liquid/polymeric membrane electrodes and optodes that display unique potentiometric anion selectivities. In the case of the potentiometric electrodes, in some instances (e.g., films doped with (M(III)), Sn(IV), In(III), and Ga(III) porphyrin species), it has been found that the resulting sensors exhibit a “super-Nernstian” response owing to a unique dimer–monomer equilibrium that occurs within the polymer membrane phase. Indeed, it has been observed that these given metalloporphyrins are capable of forming, spontaneously, hydroxide ion-bridged dimeric structures when used as anion ionophores within organic polymer films. Interestingly, such a dimer–monomer equilibrium can also cause a large shift in the $\lambda_{\text{max}}$ of the Soret band for the metalloporphyrins, which suggests a new optical transduction chemistry for sensing anions and other species, via the ability of a given analyte to break metalloporphyrin dimers, via selective axial ligation reactions with the central metal ion, into monomers within the organic films. In such sensing systems, there is no need for a second chromophore, which is required for conventional optical ion sensors.

An optical chloride sensor based on such dimer–monomer equilibrium of indium(III) octaethylporphyrin in polymeric film has been demonstrated recently and successfully applied to reversible and accurate measurement of chloride levels in diluted serum samples. Herein, we describe initial efforts to extend the use of this novel metalloporphyrin dimer–monomer equilibrium chemistry to detect neutral species in the gas phase. It will be shown that thin polymer films doped with indium(III) octaethylporphyrin can be conditioned such that hydroxide ion-bridged dimer species can form spontaneously within the films and that such films then respond optically to various gas-phase amine species at sub-ppm levels based on monitoring the decrease in ammonia, pyridine, chlorine, hydrogen chloride, nitrogen dioxide, and nitrogen monoxide. Moreover, metalloporphyrins have also become widely used as novel ionophores for the preparation of liquid/polymeric membrane electrodes and optodes that display unique potentiometric anion selectivities. In the case of the potentiometric electrodes, in some instances (e.g., films doped with (M(III)), Sn(IV), In(III), and Ga(III) porphyrin species), it has been found that the resulting sensors exhibit a “super-Nernstian” response owing to a unique dimer–monomer equilibrium that occurs within the polymer membrane phase. Indeed, it has been observed that these given metalloporphyrins are capable of forming, spontaneously, hydroxide ion-bridged dimeric structures when used as anion ionophores within organic polymer films. Interestingly, such a dimer–monomer equilibrium can also cause a large shift in the $\lambda_{\text{max}}$ of the Soret band for the metalloporphyrins, which suggests a new optical transduction chemistry for sensing anions and other species, via the ability of a given analyte to break metalloporphyrin dimers, via selective axial ligation reactions with the central metal ion, into monomers within the organic films. In such sensing systems, there is no need for a second chromophore, which is required for conventional optical ion sensors.

A new type of optical sensor based on such reactants have been reported for real-time detection of amines in the gas phase. M etalloporphyrins are potentially useful chromogenic indicators for the development of novel optical sensors owing to their open coordination sites for axial ligation, large spectral shifts upon ligand binding, and intense coloration.Indeed, Rakow and Suslick recently reported on the use of changes in the visible absorption spectra of porphyrins adsorbed onto reversed-phase silica thin-layer chromatography plates, as a method to devise an array of optical sensors for detecting given organic vapors via pattern recognition techniques. Others have used immobilized porphyrins to devise optical gas sensors for oxygen, ammonia, pyridine, chlorine, hydrogen chloride, nitrogen dioxide, and nitrogen monoxide.
dimer or increase in monomer concentrations as the amine species ligate to the central In(III) ion of the metalloporphyrin structure.

EXPERIMENTAL SECTION

Reagents. All salts, NaOH, acids, and tetrahydrofuran (THF) were from Aldrich (St. Louis, MO). Poly(vinyl chloride) (PVC), sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), bis(2-ethylhexyl) sebactate (DOS), o-nitrophenyl octyl ether (o-NPOE), and [12-(4-ethylphenyl)dodecyl]-2-nitrophenyl ether (ETH 8045) were obtained from Fluka AG (Buchs, Switzerland). The chromogenic reactant hydroxol(2,3,7,8,12,13,17,18-octaethylporphyrinato)indium(III) (In\(^{III}[\text{OEP}]\)OH) was synthesized via metatation of the free porphyrin (MidCentury Chemicals, Posen, IL) and indium chloride in refluxing glacial acetic acid.\(^ {54}\) All other chemicals were analytical or reagent grade products. Aqueous solutions were prepared with freshly Milli-Q-deionized water (18.2 M\(\Omega\) cm specific resistance).

Polymeric Optical Sensor Membranes. The sensing films contained (in wt %) PVC (33%), plasticizer (66%), In\(^{III}[\text{OEP}]\)OH (1%), and various mole percents of NaTFPB relative to the reactant. The membrane components (totaling 100 mg) were dissolved in freshly distilled THF (2 mL). The sensing membranes were manually cast with a micropipet by evenly spreading the cocktail solutions (5 mL) over an inner wall of a glass cuvette (4 cm \(\times\) 1 cm \(\times\) 1 cm) used as a flow cell. After a 20-min evaporation period, a thin polymer film was formed that adhered to the glass surface, with a thickness of \(~5\) \(\mu\)m. Before measurements, the films were soaked in deionized water for 0.5–1 min to convert the In\(^{III}[\text{OEP}]\)OH monomer to the (In\(^{III}[\text{OEP}]\))\(^+\) dimer. When not in use, the optical sensing films were stored in the dark in an environment that had a relative humidity of 80%.

Instrumentation. The complete flow-through optical sensor system employed for gas-phase amine detection is shown in Figure 1. Compressed nitrogen gas was used as the main carrier gas source at a flow rate of 2.63 L/min controlled by a flow meter. This gas stream was passed through several wash bottles containing deionized water to generate a nitrogen stream with a relative humidity of 80% as measured by a commercial electronic hygrometer. This humidified nitrogen flow was merged with a second nitrogen gas stream emanating from the amine diffusion tube. The diffusion device was prepared by incorporating a 15-cm length of microporous Gore-Tex tubing (W.L. Gore, Elkton, M.D) concentrically within a similar length of glass tubing. Another nitrogen gas stream at a lower flow rate of 0.08 L/min was utilized as recipient gas passing through the center of the inner porous tubing while a mixture of a given amine hydrochloride (e.g., ammonium chloride, 1-butylammonium chloride, etc.) and NaOH solutions was delivered by a peristaltic pump at a flow rate of 1.00 mL/min through the spacing between the two concentric tubes. The concentration of amines in the test atmosphere as a function of concentrations of amine hydrochloride and NaOH solutions used was determined by trapping of the gas-phase amines for a timed period into 100 mL of 0.001 M HCl solution and then measuring the pH changes of the collection solutions by a pH electrode (Fisher Accumet 620). Final concentrations of amine vapors were determined based on this determination and the mixing ratio of the two nitrogen streams. Changes in gas-phase concentrations to generate calibration data were carried out by using different concentrations of amine hydrochloride and NaOH solutions to create the gas-phase species in the flow-through diffusion tube. Similarly, interfering species such as CO\(_2\), SO\(_2\), and H\(_2\)S in the test atmosphere were prepared by mixing appropriate salts (i.e., NaHCO\(_3\), Na\(_2\)SO\(_3\), Na\(_2\)S) and hydrochloric acid in the diffusion tube, and their gas-phase concentrations were determined by trapping of the gas-phase species for a timed period into 100 mL of 0.05 M NaOH solution. The NO gas was generated by using excess KI in 1 M hydrochloric acid and NaNO\(_2\), and the concentrations were calibrated by a NO chemiluminescence analyzer (Sievers 280).

Measurements for dissolved amines in solutions were performed by using a commercial flow-through cell with an inside dimension of 10 mm \(\times\) 40 mm \(\times\) 0.1 mm (Hellma Cells, Inc.), as described previously.\(^ {54}\) Absorbance spectra of the sensing films coated in the flow cell were recorded by a UV–visible spectrophotometer (Beckman 640B) at ambient temperature (23 °C).

RESULTS AND DISCUSSION

Response Mechanism. It has been recently discovered that certain metalloporphyrin structures can spontaneously form hydroxide ion-bridged dimers within organic polymer films, especially when noncoordinating lipophilic anionic sites are added to the organic phase.\(^ {52}\) It has been further shown that these dimer–monomer equilibria can be utilized advantageously to devise new optical sensors for sensing anions in solution phase,\(^ {54}\) since breaking of the dimers by strong anionic ligands can yield a concomitant large bathochromic shift in the Soret absorbance band of the porphyrin structure.\(^ {46,55}\) It is known that neutral species such as amines can also coordinate strongly with metal ion centers of the metalloporphyrins\(^ {36,55,56}\) and thus can also potentially break
such dimer species into monomers within the polymer membrane phase. Therefore, this same sensing chemistry should be applicable for the measurement of certain neutral organic species in gas phases that surround the porphyrin-doped polymeric films.

In preliminary studies for this work, it was found that many volatile amines can break several metalloporphyrin dimers such as \(\{\text{MnIII}\{\text{OEP}\}\}_{2}\text{OH}^{+}\), \(\{\text{GaIII}\{\text{OEP}\}\}_{2}\text{OH}^{+}\), and \(\{\text{InIII}\{\text{OEP}\}\}_{2}\text{OH}^{+}\) to their respective monomers within thin PVC films, thereby producing a large change in the visible absorbance spectra of the polymer coatings. By measuring the increase of monomer absorbance or the decrease of dimer absorbance bands, the concentration of amines can be quantified. In this paper, we focus on the most promising of these reactant systems, \(\{\text{InIII}\{\text{OEP}\}\}_{2}\text{OH}^{+}\).

**Optical Behavior of InIII{OEP}OH in Organic Solution and in Polymeric Films.** The changes in the UV-visible spectra of InIII{OEP}OH in a dichloromethane solution upon the addition of varying amounts of NaTFPB are shown in Figure 3. For the initial solution containing only the indium(III) porphyrin monomer, a Soret band at 405 nm and an additional small shoulder at 386 nm can be clearly observed (line A), indicating that the indium(III) porphyrin exists predominantly in the monomeric form within this solvent. Interestingly, when 50 mol % NaTFPB (relative to the indium(III) porphyrin) is added to this organic-phase solution, a new band corresponding to a dimeric species appears (line B). This is in contrast to similar experiments with Sn(IV), Ga(III), and Mn(III) porphyrins, in which the hydroxide ion-bridged dimers can only be generated by adding a very basic aqueous solution (0.4 M NaOH) into the organic porphyrin solution (yielding two phases) containing borate (line C). Indeed, isolation of \(\{\text{InIII}\{\text{OEP}\}\}_{2}\text{OH}^{+}\)-TFPB - single crystals that yield an X-ray structure corresponding to the hydroxide ion-bridged dimer can only be accomplished by adding borate to the organic phase. Therefore, the general dimer formation reaction for metalloporphyrins within the polymer film can likely be expressed as

\[
\text{M}^{III}\{\text{OEP}\}^{+} + \text{H}_2\text{O} + \text{R}^{-} \rightarrow \{\text{M}^{III}\{\text{OEP}\}\}_2\text{OH}^{+}\text{R}^{-} + \text{H}^{+}
\]

Since a proton is generated, it can be predicted that a higher pH would promote the formation of dimer from monomer. Indeed, such a pH effect has been observed in recent work with an optical sensing membrane for chloride based on the same dimer–monomer equilibrium of the indium(III) prophyrin. The basic

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**Figure 2.** Schematic of dimer–monomer equilibrium of indium(III) porphyrin in the presence of added lipophilic anion sites, R⁻, within polymeric films, and analyte gas-phase amine species that can enter film and interact with porphyrin as axial ligand.

**Figure 3.** Visible spectrum of 10⁻⁶ M InIII{OEP}OH in dichloromethane solution (A) and its changes upon the following successive actions: addition of 50 mol % NaTFPB (B); treatment with 0.4 M NaOH (C); and addition of 80 mol % NaTFPB (D).
The conditions required for dimer formation of the indium(III) porphyrin in organic solvents suggest that the dimerization constant ($K_{d}$) of indium(III) porphyrin is much weaker than formation constants for other metal(III) porphyrin dimer structures. Figure 3 also shows that further increases in the NaTFPB concentration lead to a new equilibrium species with $\lambda_{max} = 399$ nm (line D), which is probably due to a $\pi-\pi$ interaction between monomeric $\text{In}^{III}[\text{OEP}]^+$ and the borate species, thus forming an ion pair (e.g., $\text{In}^{III}[\text{OEP}]^+\text{TFPB}^-$).

Figure 4 shows that a similar chemistry also occurs when the $\text{In}^{III}[\text{OEP}]\text{OH}$ monomer is doped within a thin PVC film used to prepare the amine optical sensor. Initially, there is only one monomer band, appearing at 406–408 nm for all of the dry films with different amounts of added borate. After the films are soaked in deionized water, a blue shift of the Soret band to 390 nm indicates the spontaneous formation of the hydroxide ion-bridged dimer. The absorbance of the dimer band increases and the absorbance of the monomer band decreases as the NaTFPB concentration added to the PVC film increases until 50 mol % relative to the indium(III) porphyrin. Further increases in the NaTFPB concentration yields the ion-pair band at 402 nm, as observed in the case of the experiments conducted in dichloromethane solutions (see Figure 3). The overall red-shift of the spectra compared with those in dichloromethane solution is probably due to a different solvent and dielectric constant; i.e., oNPOE is the solvent/plasticizer of the polymer film. It should be noted that dimer formation in the polymeric PVC film is apparently even more favorable than in dichloromethane solution since soaking the film in pure water with a neutral pH is adequate for the spontaneous conversion of the monomer to the dimer, whereas very basic solution is required in the analogous experiments carried out with the porphyrin in dichloromethane (see above). The optimal ratio of the absorbance values for dimeric to monomeric forms of the metalloporphyrin ($A_{406}$ and $A_{390}$ nm) for the films equilibrated with water was obtained for the film containing 50 mol % borate relative to the indium(III) porphyrin. Interestingly, drying the hydrated film with nitrogen gas causes the dimer species to disappear, suggesting that water molecules play an important role in the dimer–monomer equilibrium. Indeed, the X-ray structure for the analogous hydroxide ion-bridged Ga(III)tetraphenylporphyrin dimer has shown that a neutral water molecule is required at one of the open axial ligand sites of the dimer to help stabilize this structure. Therefore, in the case of the proposed amine sensor, it is necessary to maintain an adequate humidity within the surrounding gas phase when the sensor is operated, so that a trace level of water in the organic film is maintained to promote dimer formation. Indeed, Figure 5 shows that humidity has on the dimer–monomer equilibrium of the indium(III) porphyrin within the plasticized PVC film (with KFTPB also added at 80 mol % to porphyrin; see below). In a low humidity environment, very little dimer is observed (based on intensity of absorbance band at 390 nm). The dimer absorbance band increases and the monomer absorbance band decreases with an increase in the relative humidity of the surrounding gas phase. A high and stable dimer concentration is obtained in the organic film when the relative humidity is in the range of 60–90%. For optimal sensitivity and reproducibility, a relative humidity of 80% was chosen for all analytical sensing of gas-phase amines. This humidity was controlled by the amount of water inside the wash bottles. Figure 4 also shows that, in the presence of humidity instead of bulk water, the molar ratio of borate to indium(III) porphyrin required to achieve the greatest dimer/monomer ratio was shifted from 50 to 80 mol %. In fact, compared with being soaked in bulk water, films exposed to gas phases of different humidities likely contain much lower equilibrium concentrations of water, which decreases the dimer forma-

![Figure 4](image-url)
tion so that a higher concentration of borate is needed to enhance the formation of dimer in the polymer film (i.e., borate salt also can act to increase water content of the membrane phase\(^\text{60}\)). Under such conditions, protons likely serve as countercations for the excess borate sites.

Three different polymer film plasticizers with different polarities, DOS, ETH 8045, and o-NPOE ($\epsilon = 4.2, 13.4,$ and 24.3, respectively), were examined for their effects on the optical response of the amine sensor. It was found that o-NPOE, with the highest dielectric constant, yielded films with the optimal sensitivity; in contrast, a rather poor response was observed for films plasticized with DOS. This suggests that formation of the dimer species is not favored under nonpolar conditions, since almost no dimer could be observed in the visible spectrum of the film when formulated with DOS (data not shown). This is consistent with potentiometric data obtained previously showing that polymer membranes formulated with lower dielectric constant plasticizers yield more Nernstian response toward chloride (i.e., little or no dimer formation in the membrane).\(^\text{46,61}\)

Characteristics of the Optical Amine Sensor. A typical series of response spectra showing the dramatic changes in the conversion of dimer to monomer within the polymer film with increases in ethylamine concentration in the gas phase is shown in Figure 6. It can be seen that, at the absorbance band corresponding to the monomer species (406 nm), the sensor showed a more sensitive response than at the dimeric band at 390 nm owing to the great molar absorptivity of the monomer. An isobestic point for the equilibrium between the monomer and the monohydroxide ion-bridged dimer is observed at 397 nm in the concentration range from 0 to 85 ppm ethylamine. However, at higher concentrations of ethylamine, the response spectra are shifted to longer wavelengths. This behavior is observed for other primary amines as well, suggesting that at higher concentrations of amine (L) a second axial ligand binding reaction may occur with another amine molecule binding to the monomeric species ($\text{In}^{\text{III}}[\text{OEP}]\text{L}_2$)\(^+\) to form ($\text{In}^{\text{III}}[\text{OEP}]\text{L}_3$)\(^+\). Further evidence for such chemistry can be gleaned from the results obtained with other, more bulky secondary and tertiary amine analytes. With such species, steric hindrance may prevent axial ligation reactions on one side of the In(III). This situation is illustrated in Figure 7, where it can be seen that, in the case of triethylamine, a perfect isobestic point in the spectra can be obtained in response to this species even at higher gas-phase concentrations.

The selectivity of the In[OEP]OH-based optical amine sensor was examined by monitoring the visible spectra of the sensing film for nine separate amine gases at various concentrations. Based on the absorbance changes at 406 nm, the degree of monomer formation, $\alpha$, is calculated as follows:

$$\alpha = \frac{A - A_0}{A_1 - A_0} \quad (1)$$

where $A$ is the absorbance at the given concentration of amine, $A_0$ is the absorbance of the monomeric band when the film is exposed to humidity in the absence of any amine vapor, and $A_1$ is the absorbance at the same wavelength after the polymer film is in equilibrium with a very high concentration of amine gas.

The $\alpha$ values observed versus the logarithm of amine concentrations are shown in Figure 8. According to the proposed transduction chemistry illustrated in Figure 2, the optical selectivity of the present sensor should be determined by the ability of amine vapors to be extracted into the polymer film phase and further ligate directly to the central In(III) ion to break the porphyrin dimer into a monomer species. As illustrated in Figure 8, the selectivity sequence for the primary amines tested is


reported for another chromogenic reactant, ETH 4001, are also 1-butylamine at concentrations of the other amines to the concentration of the present sensor for these nine amines relative to 1-butylamine. Table 1 lists the optical selectivity coefficients strength of interaction as axial ligands of these amines due to primary amines. Again this is likely due to a decrease in the lipophilicity. Less response was observed for secondary, tertiary, and branched ammonia, which corresponds directly to the order of lipophilicity. Table 1. Comparison of the Selectivity Coefficients (log $K^{\text{opt}}$) for In(OEP)OH- and ETH 4001-Based Amine Sensors

<table>
<thead>
<tr>
<th>amine</th>
<th>In(OEP)OH$^a$</th>
<th>ETH 4001$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butylamine</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1-propylamine</td>
<td>-0.3</td>
<td>-0.5</td>
</tr>
<tr>
<td>pyridine</td>
<td>-0.9</td>
<td>-1.7</td>
</tr>
<tr>
<td>triethylamine</td>
<td>-1.0</td>
<td>-1.1</td>
</tr>
<tr>
<td>ethylamine</td>
<td>-1.1</td>
<td>-1.2</td>
</tr>
<tr>
<td>methylamine</td>
<td>-1.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>diethylamine</td>
<td>-1.7</td>
<td>-1.6</td>
</tr>
<tr>
<td>tert-butylamine</td>
<td>-1.8</td>
<td>-1.8</td>
</tr>
<tr>
<td>ammonia</td>
<td>-2.5</td>
<td>-2.3</td>
</tr>
</tbody>
</table>

$^a$ By the present sensor. $^b$ Given in ref 28.

1-butylamine > 1-propylamine > ethylamine > methylamine > ammonia, which corresponds directly to the order of lipophilicity. Less response was observed for secondary, tertiary, and branched primary amines. Again this is likely due to a decrease in the strength of interaction as axial ligands of these amines due to steric hindrance. The results are shown in Figure 9. It can be seen that the signal change in the measured absorbance up to 360 ppm, although an increase in monomer formation is observed at higher levels of this gas. Response toward $SO_2$ at 280 ppm was equivalent to 1 ppm ethylamine. The greater response toward $SO_2$ is probably due to a pH decrease within the PVC film owing to the presence of this more acidic gas, similar to what occurs for $CO_2$ at levels of $>360$ ppm, thus promoting the conversion of dimer to monomer. It was found that $H_2S$ and NO were also effective reactants to break the indium(III) porphyrin dimer to the monomer and result in a dramatic optical response toward both gases at concentrations higher than 5 ppm (equivalent to 0.3 ppm ethylamine). However, it should be possible to reduce or eliminate the effect of such species by using an outer coating on the polymer film that oxidizes or selectively adsorbs these potential interfering gases.

It should be noted that the transduction chemistry employed in the current amine sensor is exactly the same as that employed to devise a solution-phase chloride optical sensor. Hence, one might anticipate that amine species in solution would interfere with the chloride response. However, it was shown in the earlier chloride sensor work that optimal responses toward chloride sensitivity can only be obtained in acidic solution phase (pH 3.0), where hydroxide activity is very low, allowing chloride to compete more favorably as axial ligand for the In(III) porphyrin. Hence, under such conditions, all amines would be protonated, greatly decreasing the extraction into and subsequent ligation of these species within the In(III)OEP OH- doped polymeric film.

As mentioned previously, an earlier optical sensor for amines was reported by Mohr et al., in which the reactant ETH 4001 was employed within a polymeric film. This sensor was only examined for detecting amines in an aqueous solution phase under basic conditions. Therefore, to directly compare the relative sensitivity of this earlier sensor with the proposed In(III)OEP OH- based amine-sensing films, the response of the new amine sensor in solution phase was also examined. This was accomplished by pumping the amine solutions in 0.1 M NaOH into the flow-through cell in contact with the optimized PVC film containing In(III)OEP-OH. The relative increase in the monomer absorbance upon changing from 0 to 25 mM 1-butylamine was 90% and a lower detection limit of 0.02 mM was found for 1-butylamine (at S/N = 3). In contrast, the sensor based on ETH 4001 has been reported to have a detection limit of 0.3 mM for 1-butylamine under the same basic solution conditions.

Reversibility of the sensor was evaluated by measuring the alternating responses to ethylamine gas at a high concentration (177.2 ppm) and a low concentration (0.3 ppm) with the spectrophotometer set at 406 nm, corresponding to the monomer species. The results are shown in Figure 9. It can be seen that the signal changes are fully reversible in both cases. For the high concentration measurement, the time to achieve 95% of the full-scale response is very fast (several seconds), whereas recovery to 95% of the initial value takes $\sim$15 min. Some of this lag is due to hysteresis within the lines of the gas delivery system. In contrast, response time toward low concentrations of amine is much longer (1.5 min), but the recovery time is considerably shorter (3 min). The sensor stability was assessed by monitoring the monomer absorbance signal from a gas sample of 0.3 ppm ethylamine. The results showed that, over a 30-min period, absorbance measurements taken every 6 min had a relative standard deviation less...
than 5%. The detection limit for ethylamine measurement is 50 ppb (at S/N = 3). The lifetime of the optical sensor was checked by measuring the response of ethylamine with the same optode membrane incorporating indium(III) porphyrin on different days. After a period of 25 days, a decrease in the absorbance of 10% was found owing to some crystallization of the dimer within the polymer film. However, the sensor still functioned in terms of its reversible response to all the amines tested. Obviously, the problem of decreased absolute signal due to porphyrin crystallization can be eliminated by referencing the monomer absorbance values to that found at the isobestic point.

Model for Optical Response. The sensing principle in the present optical gas sensor involves two reversible processes. One is the extraction of amine from the gas phase (g) into the organic polymer film phase (f) in accordance with the following equilibrium:

\[
\text{amine}_{(g)} \rightleftharpoons \text{amine}_{(f)}
\]

This equilibrium can be quantified by the partition coefficient of amine gas, \(K_p\):

\[
K_p = \frac{[\text{amine}]}{P_{\text{amine}}}
\]

where \(P_{\text{amine}}\) and \([\text{amine}]\) denote the partial pressure of amine in the gas phase and the concentration of amine in the film phase at equilibrium, respectively.

The second process is the subsequent axial ligation of amine species with the metal center of the indium(III) porphyrin to force the formation of monomers in the polymeric film:

\[
\begin{align*}
\text{In}^{III}[\text{OEP}]_2\text{OH}^+ + \text{amine} &\rightleftharpoons \\
\text{In}^{III}[\text{OEP}]\text{OH} + \text{In}^{III}[\text{OEP}]\text{amine}^+ 
\end{align*}
\]

Assuming the monomer absorbance spectra of the \(\text{In}^{III}[\text{OEP}]\text{OH}\) and \(\text{In}^{III}[\text{OEP}]\text{amine}^+\) species are the same, and no significant dissociation of the monomeric \(\text{In}^{III}[\text{OEP}]\text{OH}\) species occurs within the film during amine gas measurements, the above reaction can be simplified as

\[
\text{dimer} + \text{amine} \rightleftharpoons 2\text{monomer}
\]

with a given formation constant \(K_f\):

\[
K_f = \frac{[\text{monomer}]^2}{[\text{dimer}][\text{amine}]}
\]

where the concentration terms refer to the concentration of each species in the polymer film phase. Substitution of eq 2 into eq 3 yields,

\[
K_pK_f = \frac{[\text{monomer}]^2}{[\text{dimer}]P_{\text{amine}}}
\]

The film's optical response, \(\alpha\), may be defined as the ratio of the concentration of monomer generated to the total amount possible in the film, \([\text{monomer}]_{\text{total}}\), when excess amine is present, and is described by eq 5:

\[
\alpha = \frac{[\text{monomer}]}{[\text{monomer}]_{\text{total}}} = \frac{A - A_0}{A_1 - A_0}
\]

According to mass balance, the concentration of dimer in the membrane can be expressed as

\[
[\text{dimer}] = ([\text{monomer}]_{\text{total}} - [\text{monomer}])/2
\]

Thus, inserting eqs 5 and 6 into eq 4 gives

\[
K_pK_f = \frac{2\alpha^2[\text{monomer}]_{\text{total}}^2}{([\text{monomer}]_{\text{total}} - [\text{monomer}])P_{\text{amine}}}
\]

and after rearranging,

\[
P_{\text{amine}} = \frac{2\alpha[\text{monomer}]_{\text{total}}}{(1/\alpha - 1)K_pK_f}
\]

If \(K = 2[\text{monomer}]_{\text{total}}/K_pK_f\), then eq 8 can be further simplified to

\[
P_{\text{amine}} = \alpha K/(1/\alpha - 1)
\]

Two solutions for \(\alpha\) exist for this second-order equation, but only one is valid:
A series of theoretic curves for different $K$ values based on eq 10 can be generated. Figure 10 shows four such curves, along with experimental data for (■) 1-propylamine, (●) ethylamine, (▲) tert-butylamine, and (▲) ammonia. As shown, the theoretical curves for $K = 500$ fit the ammonia response data reasonably well, and $K = 100$ fits the data for tert-butylamine. The curves for $K = 15$ and $K = 1.5$ tend to fit the observed responses of ethylamine and 1-propylamine, respectively, but only at the higher concentration range. This general trend is as expected, since lower $K$ values correspond to higher $K_p$ values and, hence, more favorable partitioning of the amine into the polymer phase. At lower levels of amine vapor, however, the theoretical curves tend to predict a somewhat greater absolute absorbance and shallower optical response than observed experimentally. This is likely due to the fact that, at very low amine vapor levels, the pH within the organic polymeric film decreases somewhat, and the $\text{In}^{III}[\text{OEP}]-\text{OH}$ species dissociates to yield $\text{In}^{III}[\text{OEP}]^+$ with $\text{OH}^-$, TFPB$^-$, or both, as nonligated counteranions. This species has $\lambda_{\text{max}} = 402$ nm, which decreases the amount of observed monomer monitored at 406 nm.

**CONCLUSIONS**

A new optical sensing chemistry for detecting amine vapors at sub-ppm levels based on the use of $\text{In}^{III}[\text{OEP}]\text{OH}$ porphyrin within a thin PVC film has been described. This new sensing scheme demonstrates an additional analytical application for the newly discovered dimer—monomer equilibrium reactions that can occur when certain metalloporphyrins are doped, along with appropriate levels of lipophilic counteranions, within thin polymeric films. Although demonstrated here for the detection of amines, it is likely that other porphyrin dimer—monomer equilibrium reactions could be employed in a similar fashion to detect other neutral gases, including nitric oxide, carbon monoxide, etc., by choosing porphyrins with appropriate metal ion centers. Efforts to extend this sensing principle for detecting these other gases is currently in progress in this laboratory.

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