Optical Sensor for Ammonia Gas in Ambient using Bromocresol purplepoly (vinyl pyrrolidone) Composite Film

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For bromocresol purple-poly(vinylpyrrolidone) composites, the absorbance (Abs) at $\lambda max= 605$ nm increases with ammonia concentration and is proportional to [BCP][%RH][logC_{NH3}]. In humid conditions, several ppm levels ammonia could be detected.

Key Words: Gas sensor, Humidity, Ammonia, Bromocresol purple.

1. INTRODUCTION

Recently, several optochemical sensors have been widely investigated ¹⁻¹⁰. In general, most optical chemical sensors are based on the principles of either absorption or fluorescence of well known indicators dispersed in polymer matrices. The choice of the indicator (probe) and of the polymer as matrix is a key question in the development of this type of sensor.

In previous works, the optical properties of a series of sulphonephthalein dyes entrapped within polymer matrices have been examined. It has been found that the bromocresol purple(BCP)-poly(vinylpyrrolidone) composite is the most preferable sensing material for quantification of ammonia in ambient air ¹¹⁻¹³.

The commercial production of a convenient optical gas sensor requires that the applicable wavelength range should lie between 450 nm and 700 nm if an amorphous silicon photodetector is used.

In this work, the optical properties of composite with BCP and PVP were examined with respect to the quantification of low levels ammonia (<50 ppm) in ambient atmosphere.

2. EXPERIMENTAL

Reagent grade bromocresol purple (BCP), and poly (vinyl pyrrolidone) (PVP) were used. BCP and PVP were dissolved in a mixture of N,N-dimethylformamide (DMF) and ethanol. The solution was used to prepare films by coating on alumina substrates or quartz plates. The films were then heated at 80 °C in vacuum to remove the solvents.

The spectra of the element formed on alumina and quartz plates were measured in reflection and transmission n modes, respectively. Filtered light from a D_2/I_2 lamp (400 nm ~ 800 nm) was guided into a fiber and the collected light was analyzed using a spectromultichannel photodetector (MCPD-1000, Otsuka electronics). The spectrum (I₀) of the element in standard air was measured first and used as a reference for measuring the spectrum (I/I₀) of the film. The reflectance was defined as $100x(I/I_0)$. Log (I₀/I) was defined as the absorbance (Abs.). All measurements were performed at 30 °C. The humidity in the chamber was controlled by mixing standard air and humid air which was prepared by allowing standard air to bubble through water at 30 °C. The concentration of NH₃ was controlled by diluting 200 ppm NH₃ /N₂ with N₂. The flow rate was 200 cm³ and the volume of the test chamber was about 0.3 cm³.

3. RESULTS

The spectral changes as a function of ammonia concentration were examined for a BCP-PVP composite thin film and the results at 78% RH and 30 °C are shown in Fig.1. The absorbance at $\lambda max = 605$ nm due to the formation of the basic form of BCP, was slightly enhanced by the introduction of ammonia vapor even in dry air, while the λmax value was independent on the ammonia concentration. The changes were accelerated by the coexistence of water vapor. A good linear relationship between the absorbance and the logarithm of ammonia concentration was observed and the slope of the straight line (sensitivity) increased with increasing humidity (Fig.2 and 3).

Under humid conditions, it is expected that BCP exists as a mixture of acidic form [In A], basic form [In B] and hydrated form [In H], i.e

$\ln N + H_2 O \rightleftharpoons \ln H$	$K_1 = [\ln H]/[\ln N][H_2O]$	[1]
In H ≓ In B+In A	$K_2 = [\ln B] [\ln A]/[\ln H]$	[2]
InA+NH₃ ≓ InB	$K_3 = [In B]/[In A][NH_3]$	[3]
where [InN] is the concentration of neutral form, $\left[H_2O\right]$ and $\left[NH_3\right]$		
are the concentrations of sorbed water and ammonia, respectively.		

When the ammonia content is proportional to the logarithm of ammonia concentration in air, $[NH_3] = K_4 \log (C_{NE3})$, it is expected that the absorbance is proportional to the logarithm of C_{NE3} .

Furthermore, the water gain of PVP linearly increases with relative humidity, i.e. $[H_2O] = K_s$ [%RH]. When [In A] \gg [In B], the equation [2] can be replaced by Eq. [2]

In
$$H \rightleftharpoons In A$$
 $K_2' = [In A]/[In H]$ [2']
Finally, it is expected that the absorbance is proportional to

$[In N][\%RH][log C_{NHB}]$

The relationship between absorbance and [%RH][log C_{NFB}] was shown in Fig.4. The response behavior is also influenced by the humidity and the response time became faster with an increase in the humidity (Fig.5)





Fig.5. Response behavior for BCP-PVP composite films. BCP 5x10⁻⁵mol/g-PVP, 30°C

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