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Optical Sensing Properties of PVC Membrane Incorporating Lipophilic 8-Hydroxyquinoline Derivative

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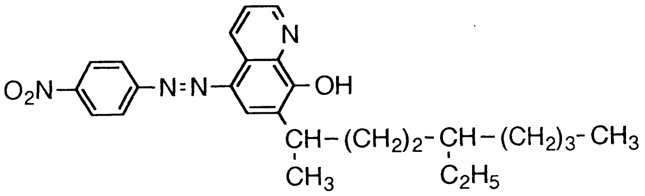
Optical properties of poly(vinyl chloride)(PVC) membrane incorporated with chromophore quinoline derivative were studied. The absorbance of the sensor increased with OH^- concentration (0.001 - 1 mol dm^{-3}) at 613 nm; and with Cu^{2+} concentration (5×10^{-6} - 10^{-3} mol dm^{-3}) at 580 nm due to deprotonation and complexation with Cu^{2+} ions.

Optical sensors for chemical species have become of interest in many analytical fields because they offer certain advantages over the electrochemical ones.[1-2] Chromogenic and fluorogenic reagents such as morin,[3] 8-hydroxyquinoline-5-sulfonic acid,[4] polyether antibiotic,[5] crown ether,[6-7] indonaphthol,[8] pH dyes[9-10] which upon selective complexation with cations or upon loosing a proton, are employed for developing ionic and molecular sensors. The changes in absorbance, fluorescence or other properties of the reagents when they react with the target species were detected as optical signals. The reagents were immobilized[2-4] on the sensor surface by covalent binding, adsorption, entrapment in Langmuir-Blodgett films, or incorporated into plasticized PVC membranes.[7,10] Optical fibers have been often used to transfer the optical signals.

In our work, we found that a newly synthesized compound, 5-(4-nitrophenyl-azo)-7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (HNEQ) formed a complex with copper(II) ion.[11] We are interested in developing optical sensors by incorporating lipophilic chromogenic reagents in PVC membrane using simple absorption spectrophotometry as a signal detector. This letter reports the optical properties of HNEQ in thin PVC membranes.



HNEQ

The ligand HNEQ was prepared according to the method described perviously.[11] Other membrane materials, bis(2-ethylhexyl)sebacate (DOS), PVC and tetrahydrofuran (THF) were from Fluka (Buchs, Switzerland). Sodium hydroxide (96.0%, 1.6% of Na_2CO_3), $Cu(NO_3)_2 \cdot 3H_2O$ and other inorganic salts were commercial products and were used without further purification. Aqueous solutions were prepared with distilled-deionized water.

The sensing membrane was prepared by casting the membrane mixture (7.1 mg of HNEQ, 220 mg of DOS and 110 mg of PVC in 3 ml of THF) on quartz glass slides 9 x 45 mm^2, 1 mm thick. The slides coated with membrane were inserted into quartz cuvettes (1 x 1 x 4.5 cm^3) and placed in a double beam UV/VIS absorption spectrophotometer (Hitachi, Tokyo, Japan). The coated membrane was equilibrated in 0.01 M NaH_2PO_4 or H_2SO_4 solutions for 10 minutes before the measurements.

The results showed that when the membrane was placed in pH buffer solutions (sulfuric acid , acetate or phosphate), no obvious changes in absorption spectrum in the pH range of 1 - 11 were observed. In high concentration of hydroxide ion solution, there was a bathochromic shift from 427 to 613 nm. Figure 1 shows the spectra in the range of 300 - 800 nm with the sensor in five different OH^- solutions. The absorbances at 613 nm (depicted in Fig. 2) continuously increased with OH^- concentration in the range of 10^{-3} - 1 mol dm^{-3}. The deprotonation constant (Ka) of the chromophore in the membrane medium can be predicated from Fig. 2 on the order of 10^{-13} mol dm^{-3}. Unlike many of the pH dyes, this new ligand deprotonated only in strong alkaline solitions.

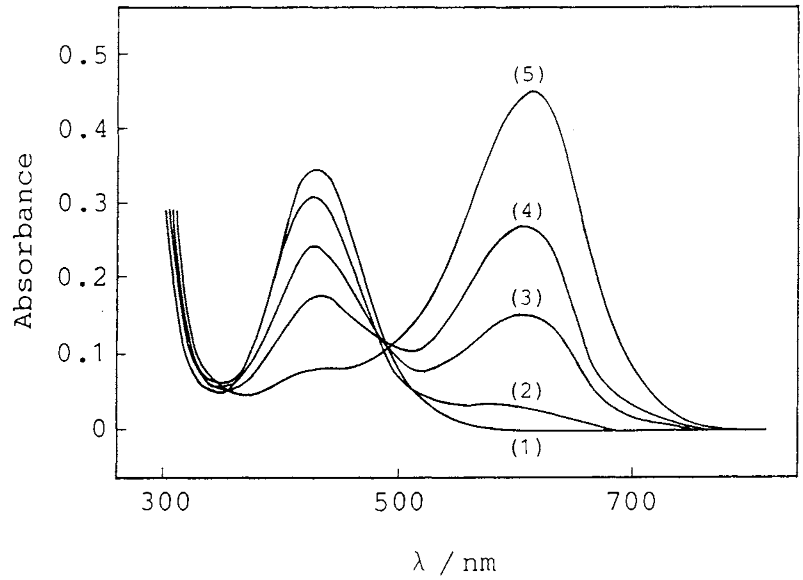


Fig. 1. Absorption spectra of the sensing membrane in OH^- solutions: (1) 0.001, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5 mol dm^{-3}.

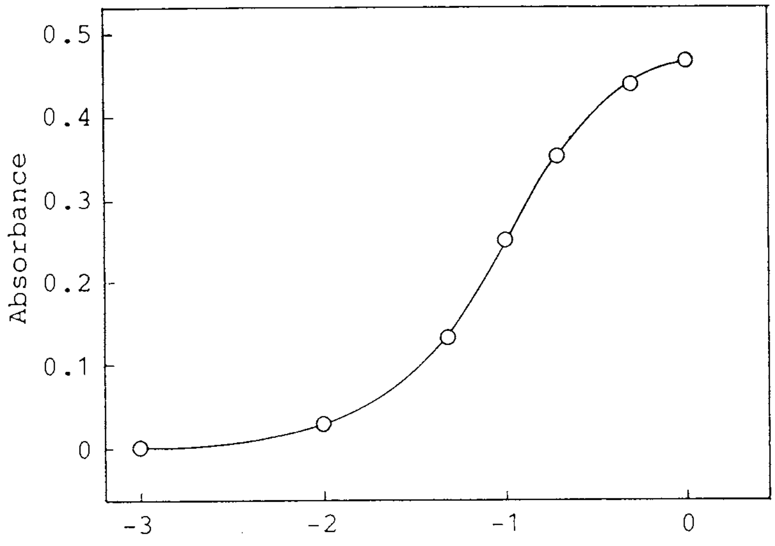


Fig. 2. Absorbances of sensing membrane at 613 nm as a function of log C for hydroxide ion.

The response time of the membrane to OH^- ions was studied at 613 nm. For membrane of 5-10 μm in thickness, a complete equilibrium was attained in 2 minutes. The reproducibility of the signals in 0.1 M OH^- solutions was within +0.01 in absorbance. These showed that the HNEQ held a reversible acid-base conversion, and was rather stable chemically and optically in PVC membrane.

The optical properties of the membrane in Cu^{2+} solution were of special interest. The membrane immersed in Cu^{2+} solutions showed that the spectrum differed from its deprotonated form. Figure 3 gives the absorption spectra with the membrane in four different Cu^{2+} concentrations at pH 2.5 adjusted with H_2SO_4. There was a drastic increase in absorption at 500 - 600 nm when the Cu^{2+} ions concentration increased in the range of 10^{-6} - 10^{-3} mol dm^{-3}. Similar to the response to OH^- ions, the plot of absorbance against the logarithmic concentration was again "S" shaped like the typical optical sensor.[6-10] The same absorption values in the range of 400 - 600 nm were also obtained at pH 6 (buffered with acetate) solutions. This means that in the experimental pH range, complexing reactions were completed in each Cu^{2+} concentration. For membranes of 5-10 μm in thickness, stable absorbances were obtained in 2 minutes.

The effect of the other metal ions was studied at pH 2.5 solutions. Within 5 minutes, no change in absorption spectra was observed with 10^{-2} mol dm^{-3} of alkali and alkali-earth metal ions, and 10^{-4} mol dm^{-3} of transition metal ions such as Fe^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, and Ag^+.

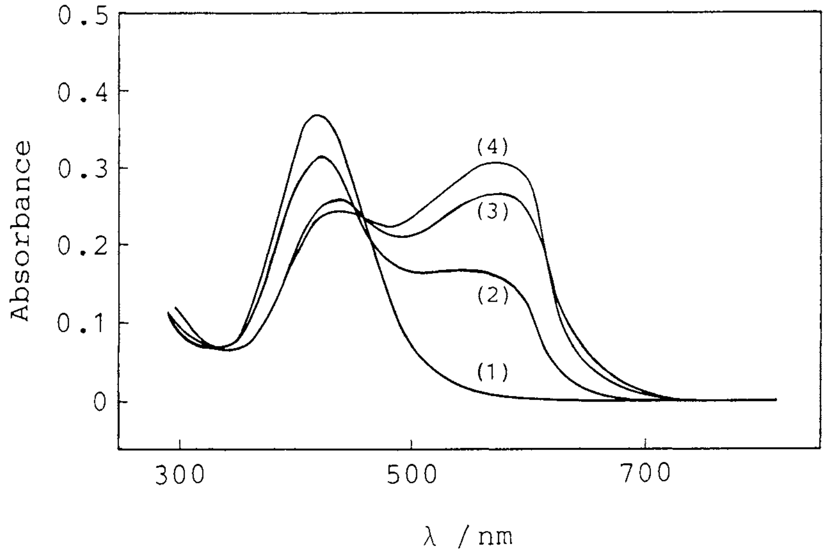


Fig. 3. Absorption spectra with membrane in Cu^{2+} concentrations at pH 2.5: (1) 10^{-6}, (2) 10^{-5}, (3) 10^{-4}, (4) 10^{-3} mol dm^{-3}.

In conclusion, the lipophilic chromophore HNEQ incorporated in PVC membrane showed spectral changes in OH^- and Cu^{2+} solutions in wide concentration ranges. The fast response of the optical signals indicated that this membrane is highly promising in developing optodes for these ions.

References

1) O.S.Wolfbeis, Fresenius J. Anal. Chem., 337, 522 (1990).
2) W.R.Seitz, CRC Crit. Rev. Anal. Chem., 19, 135 (1988).
3) L.A.Saari and W.R.Seitz, Anal. Chem., 55, 667 (1983).
4) Z.Zhujun and W.R.Seitz, Anal. Chim. Acta, 171, 251 (1985).
5) K.Suzuki, K.Tohda, Y.Tanda, H.Ohzara, S.Nishihama, H.Inoue, and T.Shirai, Anal. Chem., 61, 382 (1989).
6) D.C.Ashworth, H.P.Huang, and R.Narayanaswamy, Anal. Chim. Acta, 213, 251 (1988).
7) K.Miyazaki, K.Tohda, H.Ohzora, K.Watanabe, H.Inoue, and K.Suzuki, Bunseki Kagaku, 39, 717 (1990).
8) J.N.Roe, F.C.Szoka, and A.S.Verkman, Analyst, 115, 353 (1990).
9) M-R.S.Fuh, L.W.Burgess, T.Hirschfeld, G.D.Christian, and F.Wang, Analyst, 112, 1159 (1987).
10) K.Seiler, W.E.Morf, B.Rusterholz, and W.Simon, Anal. Sci., 5, 557 (1989).
11) H.Imura, H.Ikeda, and K.Ohashi, Proc. Symp. on Solvent Extraction, 1989, No. 101.

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