

Optical Sensors for OH⁻ and Cu²⁺ Based on 8-Hydroxyquinoline Derivative

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Optical properties of plasticized poly (vinyl chloride) (PVC) bulk membrane which are incorporated with a chromoionophore 8-hydroxyquinoline derivative and lipophilic anion excluder have been investigated. The optical sensor responds to the high selectivity of OH⁻ and Cu²⁺ ions. The measuring range was found to be 0.01 - 3 M for OH⁻ depending upon deprotonation, and 10⁻⁶ - 10⁻³ M (pH 2.5) for Cu²⁺ upon complexation. The pH values of Cu²⁺ ion solutions affected the dynamic range. Selectivity factors, reproducibility and response times of the optical sensor (optode) system are also presented.

Key words: optode system, chromoionophore, 8-hydroxyquinoline derivative, deprotonation, OH⁻ and Cu²⁺ ions

1. Introduction

Optical sensors (optodes) for chemical species have become a very big interest area in analytical chemistry, because they offer certain advantages over electrochemical sensors [1,2]. Chromogenic and fluorogenic indicators which upon selective complex formation with cations or upon losing a proton are employed for developing ionic and molecular sensors [3-13]. This deprotonation or complexation causes an optical property change in the indicator molecule which is immobilized on the sensor film by adsorption and covalent binding. Optical fibers are often used for the transfer of light to and from the sensor area.

Chromoionophores and fluoroionophores incorporated into PVC membranes have recently been used for developing alkali and alkaline earth metal ion sensors [14-17]. These ionophoric based sensors provide high selectivity and reproducibility. In addition, PVC membranes based on sensing materials are easy to fabricate into various shapes and thicknesses homogeneously. With thin ones in the range of 2-20 μ m, the response is fast.

In our work, we have designed an optical sensor system based on the newly synthesized lipophilic chromoionophore 5-(4-nitrophenylazo)-7-(4-ethyl-

1-methyloctyl)-8-hydroxyquinoline (HNEQ) [18]. PVC membrane coated on glass slides was used for fabricating the sensing material for the basic studies. It was found that the response time to the OH⁻ and Cu²⁺ ion was fast and had good reproducibility in various concentrations.

2. Experimental

Reagents The ligand HNEQ was prepared according to the method described previously [18]. Membrane plasticizer bis (2-ethylhexyl) sebacate (DOS), additive potassium tetrakis (p-chlorophenyl) borate (KTCBPB), PVC and solvent tetrahydrofuran (THF) were obtained from Fulka (Buchs, Switzerland). All inorganic reagents were of analytical reagent grade. Distilled and deionized water was used throughout.

Membrane preparation Membrane mixture containing 5.1 mg of HNEQ, 3.8 mg of KTCBPB, 220 mg of DOS and 110 mg of PVC was dissolved in 3 ml of THF. The 0.5 ml of the membrane solution was then poured on a quartz glass slide 9 \times 45 mm², and then withdrawn again with a pipette. The remaining membrane solution was allowed to dry at room temperature for 4 h. An alternative way of coating the membrane is dipping the glass slides in the membrane/THF solutions twice and drying them under the same conditions. The coated membrane sensor was conditioned by an equilibration in 0.1 M NaH₂PO₄ or H₂SO₄ for 10 min before the measurements were recorded.

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Apparatus UV/VIS absorbance measurements and spectra of the PVC membranes were taken using a double-beam absorption spectrophotometer (Hitachi, Tokyo, Japan).

Experimental procedure The slides carrying membrane were mounted in quartz cuvettes for UV/VIS spectrophotometry. Sample solutions were changed manually. Whole spectra were taken from 300 to 800 nm. For calibration, response time and interference measurements, the absorbance was measured at a fixed wavelength of 613 and 560 nm for the OH⁻ and Cu²⁺ ions respectively. Test solutions of Cu²⁺ ion were prepared by a series dilution of the stock solution, and mixed with buffers in a ration of 5:1. Solutions for measuring the interference of the foreign ions were mixed in solutions of 5×10^{-5} M of Cu²⁺ ions (pH 2.5). Hydroxide solutions were prepared with sodium or potassium salts.

3. Results and Discussion

3-1 Absorption spectra

The ligand HNEQ extracts the Cu²⁺ ion in chloroform from water solution by forming a strong complex [18]. It deprotonates in an alkaline medium. The maximum absorption of neutral, deprotonated and Cu-complex forms of HNEQ in ethanol are at 455, 596 and 499 nm, respectively. With DOS/PVC membrane without KTCPB, the corresponding values appear 427, 613 and 580 nm [19].

The present membrane sensor with KTCPB gave similar color change when immersed in OH⁻ or Cu²⁺ solution. The maximum absorption band of the membrane shifted from 470 nm for HNEQ to 614 nm and 540 nm respectively in 0.5 M OH⁻ and 10^{-4} M Cu²⁺ (pH 2.5) solutions. The spectra of the membrane in 0.02 M H₂SO₄, and 1.0 M OH⁻ solutions are depicted in Fig. 1, and the ones in Cu²⁺ solutions in Fig. 2. The ligand and its Cu²⁺ complex are electrically neutral in the membrane. Their absorption bands largely shifted due to the changes of membrane composition, while the deprotonated ligand (anionic) almost gave the same bane as it did without KTCPB [19].

Figure 2 also shows that the pH values of the Cu²⁺ solutions influence the absorbance as well as the spectral pattern. Under the same Cu²⁺ concentrations, the maximum absorption shifted towards a longer wavelength when the pH value rose up. Furthermore,

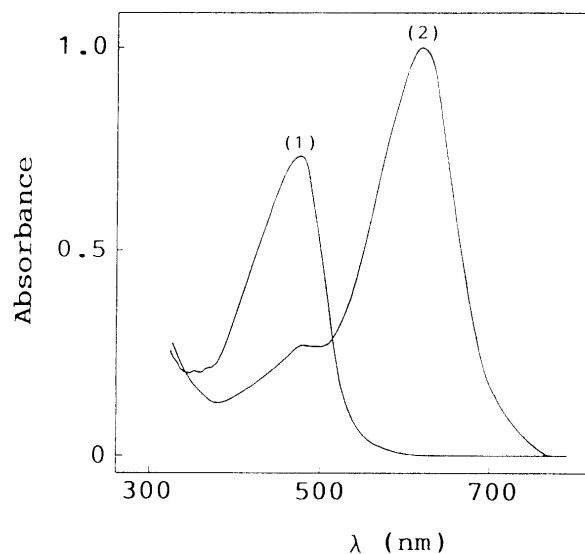


Fig. 1 Absorption spectra of the membrane incorporated with HNEQ after equilibrated with (1) 0.02 M H₂SO₄ and (2) 1.0 M OH⁻.

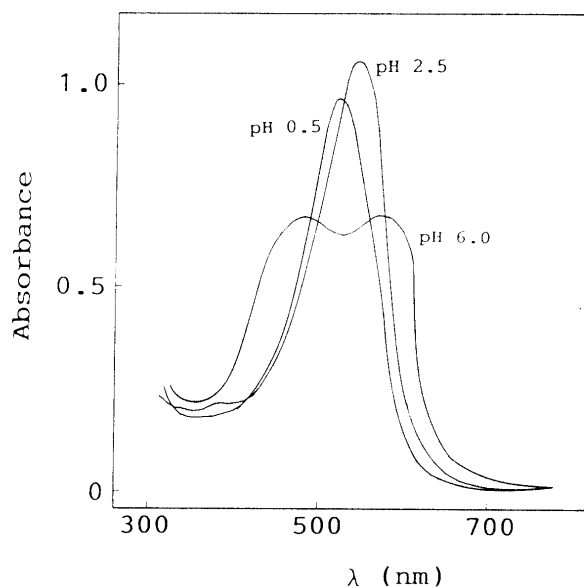


Fig. 2 Absorption spectra of the sensor after equilibrated with 2×10^{-4} M of Cu²⁺ ion solutions at pH 0.5, 2.5 and 6.0.

at pH 0-3, the absorption spectrum has only one peak which shifted with Cu²⁺ concentration. This is again very different from the membrane without KTCPB which gave broad spectra similar to the one at pH 6 (Fig. 2) and was not influenced by the pH of solutions [19].

3-2 OH⁻ ion response

The calibration graph was prepared by measuring the absorbance at 613 nm and 2 min after changing the samples. A typical plot of the absorbance against the logarithmic concentration is presented in Fig. 3. The absorbance of the sensor increased in the concentration range of 0.01 to 3 M. The shape of the calibration curve shows that the ligand deprotonated from pH 12 with a constant in the order of 10^{-13} - 10^{-14} M in membrane. This value differs from these of most of the other pH indicator based sensors [3-8]. The present one directly responds to high hydroxide concentrations. The measuring range was not affected by anions

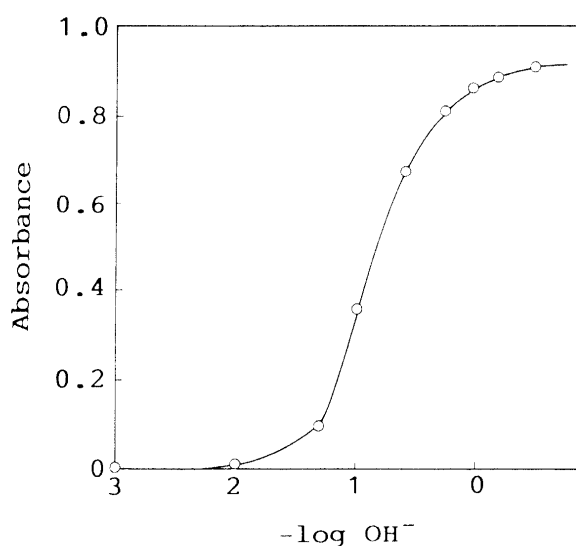


Fig. 3 Calibration graph for OH⁻ ion obtained with the sensor by measuring the absorbance at 613 nm.

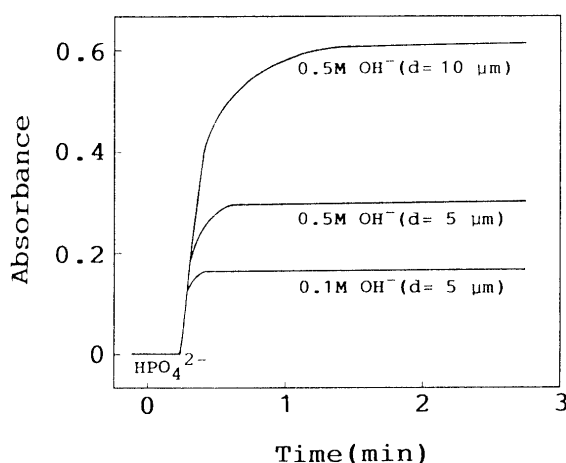


Fig. 4 Time responses of the sensor to OH⁻ ion solutions at different membrane thickness (*d*).

such as SO₄²⁻, Cl⁻, ClO₄⁻, SCN⁻, I⁻ (0.1 M) and alkali and alkaline earth metal ions.

The response of the sensor to OH⁻ was fast. The steady state absorption was reached in 12 and 23 s for 0.1 and 0.5 M of OH⁻ solutions with thin membrane of 5 μm (Fig. 4). For membrane of 10 μm thick, 95% of the absorption change was obtained within 60 s. The reproducibility of absorbance in 0.1 M OH⁻ solutions was to be within ± 0.008 .

The life time of the sensor was, however, limited due to the easy falling off of the membrane from the slides because the glass surface did not have a strong interaction with lipophilic membrane. With certain fabricating technique to lipophilize the supporting materials, the sensor is expected to have as long a life time as other DOS/PVC membranes for ion-selective electrodes. Under dry conditions, the sensor showed no absorption changes upon standing for 30 days.

3-3 Cu²⁺ ion response

The absorption spectra as well as the dynamic range of the Cu²⁺ response (Fig. 2) was heavily influenced by the solution pH. Figure 5 shows the response curves of the Cu²⁺ optical sensor at four pH levels. Above pH 3, the sensor responded to Cu²⁺ concentration in the range of 10^{-6} - 10^{-4} M; while at a lower pH, this range shifted towards higher ones. This corresponds to the results from the solvent extraction that the reaction of complex formation was complete above pH 3 [18].

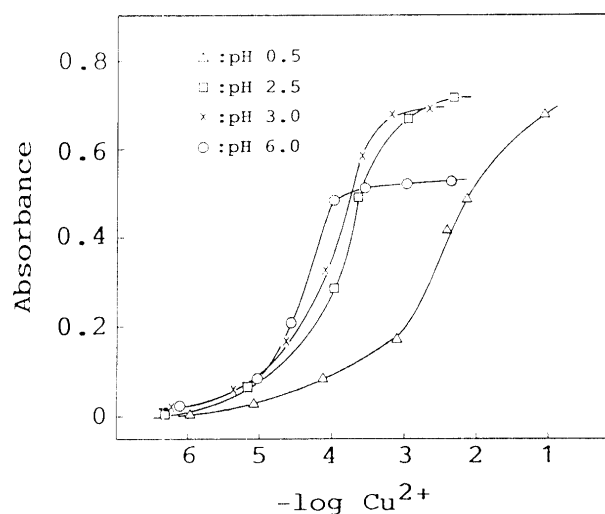


Fig. 5 Calibration graphs for Cu²⁺ ion at different pH levels. The absorbance were measured at 560 nm.

Table 1 Effect of different metal ions on the absorbance values of the optode membrane, in contact with a fixed concentration of 5×10^{-5} M $\text{Cu}(\text{NO}_3)_2$ at pH 2.5.

Metal ion	Concentration (mol/l)	Absorbance at 540 nm	
		Absorbance	Deviation(%)
Cu^{2+}	5×10^{-5}	0.2250	0.0
K^+	10^{-1}	0.2258	± 0.4
Na^+	10^{-1}	0.2261	± 0.5
Ca^{2+}	10^{-2}	0.2284	± 1.5
Mg^{2+}	10^{-2}	0.2291	± 1.8
Al^{3+}	10^{-3}	0.2254	± 0.2
Cr^{3+}	10^{-3}	0.2276	± 1.2
Fe^{3+}	10^{-3}	0.2297	± 2.1
Cd^{2+}	10^{-3}	0.2258	± 0.3
Mn^{2+}	10^{-3}	0.2259	± 0.4
Ag^+	10^{-4}	0.2324	± 3.3
Zn^{2+}	10^{-4}	0.2306	± 2.5
Ni^{2+}	10^{-4}	0.2383	± 5.9
Co^{2+}	10^{-4}	0.2807	± 24.7

The response time for the Cu^{2+} sensor was slightly slower than that of the OH^- sensor. For membrane of about $5 \mu\text{m}$ thick, a steady-state of the signal was obtained within 1 min of increasing Cu^{2+} ion concentrations. For a solution below pH 2.5, the signal recovered in 2 min. The reproducibility was found to be within ± 0.01 absorbance units.

The interference of the other metal ions was studied by observing the signal changes of the sensor in 10^{-4} M of Cu^{2+} solutions when metal ions of 10^{-3} M were present as background. The measured values of absorbance at 560 nm were shown in Table 1. For all the metal ion solutions tested, there were no significant change in an absorbance except where the Co^{2+} ion existed.

In conclusion, the present results have shown that the DOS/PVC membrane incorporated with the chromoionophore HNEQ is very well suited for developing optical sensors for OH^- and Cu^{2+} ions in view of the dynamic range, selectivity, response time and reproducibility.

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