pH-Sensitive Polymer Matrix with Immobilized Indicator Ion Pairs[*]

GUO Liang-qia, NIE Qiu-yan, XIE Zeng-hong[**], CHEN Yi-ting and CHEN Guo-nan

Department of Chemistry, Fuzhou University, Fuzhou 350002, P.R. China

CHEN Xi and WANG Xiao-ru

Department of Chemistry, Xiamen University, Xiamen 361005, P.R. China

A new sensor material for monitoring pH in aqueous solutions is described· It is based on lipophilic ion pairs consisting of an anionic pH indicator Bromocresol Green and a quaternary ammonium cation cetyltrimethylammonium· The ion pairs are homogeneously distributed inside the plasticized PVC membrane· The change of pH in an aqueous solution causes the change of optical property of the indicator immobilized on the plasticized PVC membrane· The plasticized PVC membrane is sensitive in a pH range from 4.0 to 6.0.

Keywords Bromocresol green, pH, PVC membrane

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Introduction

Since the first fiber optic pH sensor was developed by Peterson *etc*.[1] for *in vivo* measurements, many optical fiber pH sensors have been described for different pH ranges· Optical sensors for pH are usually obtained by immobilizing a pH indicator on a solid support for monitoring the optical properties. The solid supports include ion exchangers[2—4], cellulose membranes[5—11], porous glass[12,13], polyacrylamide[1,14,15], polypyrrole[16], sol-gel glass[17—19], styrene-divinylbenzene copolymer[20] *etc*· The covalent linking of the dye on the suitable matrix seems to be the most efficient immobilization method since the membranes are almost free of dye leaching. Although good results have been obtained with most of these pH optodes, they require a long and tedious preparation, which involves matrix treatment and dye immobilization·

In this work, we applied the ion pair technique to modifying the indicator, which can enhance the hydrophobicity of the sensitive dye. PVC membranes were largely applied to pH modificatory electrodes[21], however, PVC membranes as the matrix for pH sensitive membranes have rarely been reported except for our early work[22—24]. We immobilized pH indicator bromocresol green in ion pairs on the plasticized PVC membrane, forming a pH sensitive membrane· And by this way the amount of sensitive dye in the matrix can be changed conveniently. The behavior of the sensitive membrane was investigated. The result was satisfied·

Experimental

1 Apparatus and Reagents

A UV-1100 UV-Vis spectrophotometer(Bejing Rayleigh Analytical Instrument Company in China) was used for recording the visible spectra. The spectrophotometric measurements at a fixed wavelength were made on a 722-Raster Spectrophotometer(the Third Analytical Instrument Factory of Shanghai of China). The standard buffer solutions(HAc-NaAc buffers) were calibrated by a (pHS-2) pH meter (Shanghai Leichi Instrument Factory of China). The mixture solution for preparing sensitive membranes was mixed with a vortex mixer(Jiangshu Haimen City Qilin Medical Factory of China).

Bromocresol green was from Koch-light laboratories Ltd. Cetyltrimethylammonium (CTA) bromide was from Shanghai Chemical Reagents Corporation of China· PVC powder was supplied by the Second Chemical Plant of Fuzhou of China. All the other reagents were of analytical reagent grade. All the aqueous solutions were prepared with doubly de-ionized distilled water.

2 The Synthesis of the Ion Pairs

The ion pairs of the sensitive dye were synthesized *via* the method as described in the literature[22]· They were preserved in a desiccator with calcium chloride as the drying agent.

3 The Preparation of PVC Sensitive Membrane

The ion pairs of 2.0 mg, 100.0 mg of PVC

powder and 60. 0 mg of dibutyl phthalate were dissolved in 4. 0 mL of tetrahydrofuran. The solution was mixed homogeneously with a vortex mixer. The mixture was spread as a thin film into a plane glass trough (25. 5 mm × 75. 5 mm). After the tetrahydrofuran was volatized and the sensitive membrane was shaped. The membrane was homogeneous and transparent.

4   Measurement of the Spectrum

The sensitive membrane was fixed in a colorimetric cell, the behavior of the membrane at 405 and 620 nm in the buffer solutions at different pH values was recorded. The sensitive membranes were conditioned in a blank solution time after time to get rid of the superfluorous dye until the intensity of absorption leveled off before the first measurement was taken. The sensitive membranes were preserved under a dry condition when they were unused.

Results and Discussion

1   The Absorption Spectra

The optical properties of bromocresol green in a solution and immobilized on a plasticized PVC membrane are shown, as a function of pH in a buffer solution, in Figs. 1 and 2, respectively. It is evident that the immobilized form and soluble form of the indicator display marked differences in optical property. In solution, the maximal absorption wavelength of the acidic form of the indicator is violet shifted when the acidity in buffer solution increases, but that of its basic form is invariable. A clear and fixed isobestic point is shown in Fig. 1.
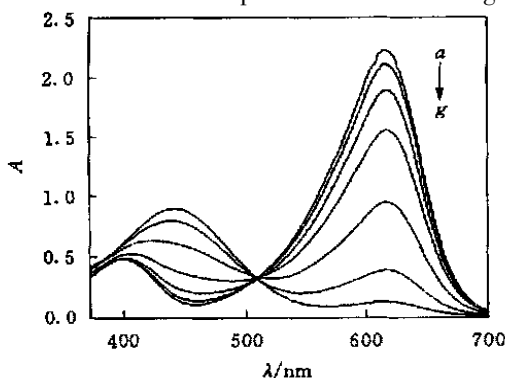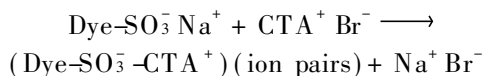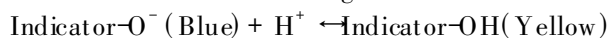

Fig. 1   The absorption spectra of bromocresol green in the solution.
pH: *a*. 7. 0; *b*. 6. 0; *c*. 5. 4; *d*. 5. 0; *e*. 4. 5; *f*. 4. 0; *g*. 3. 5.

Bromocresol green and Cetyltrimethylammonium(CTA) bromide are combined into lipophilic ion pairs *via* the following reaction:

$$Dye\text{-}SO_3^- Na^+ + CTA^+ Br^- \longrightarrow$$
$$(Dye\text{-}SO_3^- \text{-}CTA^+)(ion \ pairs) + Na^+ Br^-$$

The lipophilic ion pairs are homogeneously distributed inside the plasticized PVC membrane. When the hydrogen ions in the solution diffuse into the membrane, the following reaction occurs.

$$Indicator\text{-}O^- (Blue) + H^+ \leftharpoons Indicator\text{-}OH(Yellow)$$

It is a reversible equilibrium. From Fig. 2, the maximal absorption wavelength of the acidic form of the indicator at 405 nm is basically not influenced by pH; the maximal wavelength of the basic form of the indicator is red shifted to 620 nm in comparison to that of its soluble form in the solution. This suggests that when the indicator is immobilized on the plasticized PVC membrane, the change of the micro circumstances of the indicator makes its absorption wavelength shift.
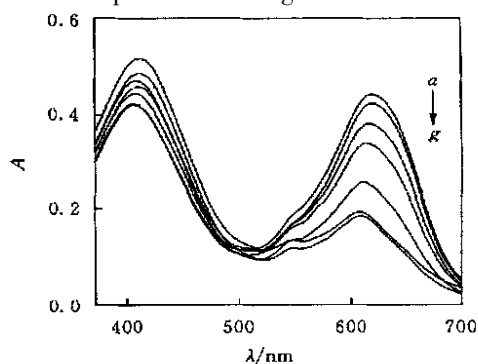

Fig. 2   The absorption spectra of bromocresol green on the plasticized PVC membrane.
pH: *a*. 7. 0; *b*. 6. 0; *c*. 5. 4; *d*. 5. 0; *e*. 4. 5; *f*. 4. 0; *g*. 3. 5.

2   The Effect of Material Proportion

With the linearity scope of the response and the response slope as the target, the optimal proportion(PVC powder 100. 0 mg, dibutyl phthalate 60. 0 mg) was confirmed by changing the proportional of PVC powder and dibutyl phthalate.

3   The Effect of the Membrane Thickness

The thickness of the sensitive membrane was determined by the amount of the mixture for the preparation of the membrane. The thickness of the sensitive membrane can influence the response time and the sensitivity. The volume of 4. 0 mL is the optimal amount of the mixture for the preparation of the membrane according to our experiment.

4   The Relative Absorbance as a Function of pH at Two Wavelengths

According to the theory, on increasing the pH value from 4. 0 to 6. 0 in the solution, the absorbance of the acidic form of the indicator decreas-

es and that of the basic form of the indicator increases simultaneously· The dual-wavelength method was applied to minimizing the error· Applying dual-wavelength method, a plot of the relative absorbance intensity of the basic form and the acidic form as a function of pH is shown in Fig. 3. From Fig. 3, it can be seen that the membrane shows a sensitive response *vs.* pH from 4. 0 to 6. 0.
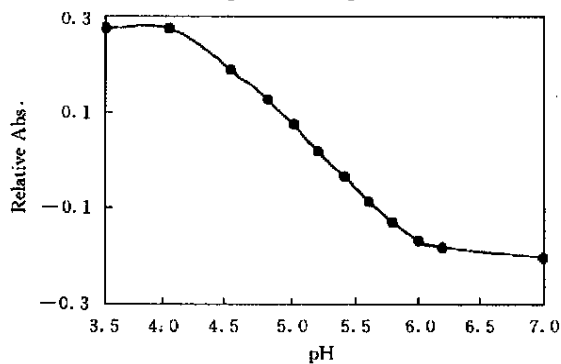

Fig. 3   **The relative absorbance as a functiion of pH at two wavelengths for the sensitive membrane.**

5   The Apparent pK_a Value

The apparent pK_a value of the indicator immobilized on the plasticized PVC membrane was determined from the absorbance at 620 nm in the buffer solution with different pH values. The apparent pK_a value is 5. 08± 0. 07, which is calculated with the aid of the following equation:

$$pK_a = pH + \log(A_x - A_b)/(A_a - A_x)$$

where A_x, A_b and A_a are the absorbances of the membrane, its basic form and its acidic form at a defined pH near the pK_a, respectively.

6   Response Time

Response time lies on the diffusion of hydrogen ions between the solution and the sensitive membrane and the reaction between hydrogen ions and the indicator immobilized on the plasticized PVC membrane. The sensitive membrane takes
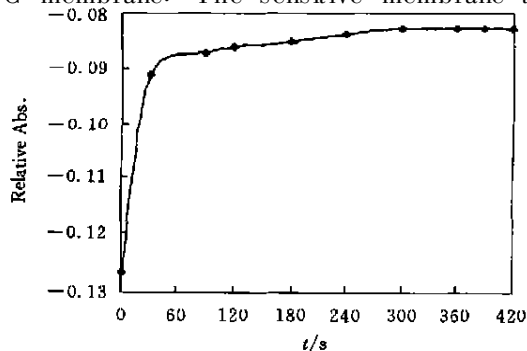

Fig. 4   **The response time of the sensitive membrane in the buffer's pH value range from 5. 8 to 5. 6.**

more time to reach the response equilibrium when the pH value in the buffer solution goes up than it takes when the pH value in the buffer solution goes down· Fig. 4 shows a typical curve for the response time measured at 620 nm· As can be seen, the output signal reaches 95% of the steady-state response within about 120 s.

7   The Reversibility and Reproducibility

Fig. 5 shows a typical curve for the transition process as a result of the change of the absorbance of the sensitive membrane at 620 nm for the alternative change of pH value between 5. 0 and 4. 5. The relative standard deviations(n= 6) for the change of the membrane response are 1. 39% and 1. 05%, respectively. Fig. 6 shows a typical curve of the transition process as a result of the change of the absorbance of the sensitive membrane at 620 nm for the alternative change of pH value among 4. 8, 5. 0 and 5. 2. As can be seen, the sensitive membrane shows a reversible response *vs.* pH. An additional test of the response stability, based on monitoring the absorbance at 404 nm(pH= 5. 0), showed a change less than 0. 2% over a period of 3 h.
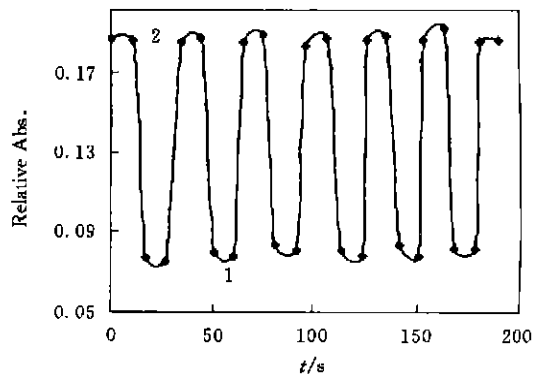

Fig. 5   **The change of the absorbance of the sensitive membrane at 620 nm for the alternative change of pH value between 5. 0(1) and 4. 5(2).**
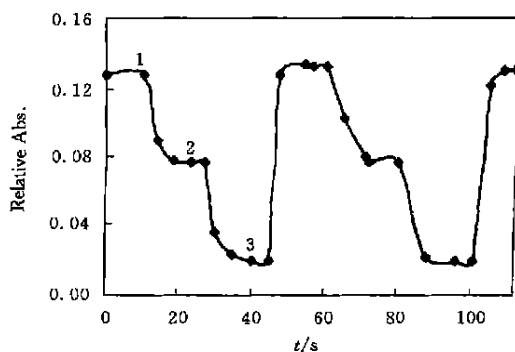

Fig. 6   **The change of the absorbance of the sensitive membrane at 620 nm for the alternative change of pH value among 4. 8(1), 5. 0(2) and 5. 2(3).**

8　The Factors Affecting Absorbance Intensity

A series of NaAc-HAc buffers was prepared, containing varying amounts of sodium chloride to vary the ionic strength, and all the buffers were adjusted to pH 5.0 with a pH meter. Sodium chloride was added to maintain the ionic strength in the range from 2.0 to 4.0. A linear relationship between the absorbance intensity of the sensitive membrane and the ionic strength was observed. This suggests that the sensitive membrane can be applied to the analysis of solutions with high ionic strengths. Several species were tested as interferences, including Cu^{2+}, Fe^{3+}, Co^{2+}, Al^{3+}, Mg^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, SO_4^{2-}, PO_4^{3-}, NO_3^- (all of them at 10^{-3} mol/L). None of them showed an observable effect on the absorbance intensity of the sensitive membrane.

9　The Analytical Application

The effluents in the mixture pool of the antibiotic factory (Fuzhou Antibiotic Group Corp.) were tested. The pH value determined with the sensitive membrane was $4.96\pm 0.05(n=6)$, which was $4.95\pm 0.01(n=6)$ determined with the pH meter for the same sample. This demonstrates that the effluent pH measurement result with the sensitive membrane is generally in agreement with that determined with the pH meter.

Conclusion

Bromocresol green as the pH indicator, which was modified by its reacting with the quarternary ammonium cation cetyltrimethylammonium to form ion pairs, can be homogeneously distributed in the plasticized PVC membrane. The sensitive membrane shows a reversible response $vs.$ pH. The response of the sensitive membrane covers a pH range between pH 4.0 and 6.0 in the high ionic strength solution. The further work will focus on the investigation of the possibilities for immobilizing other indicators and multiple indicators by this method. An effort to improve the response time should also be made.

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