J. Iran. Chem. Soc., Vol. 6, No. 4, December 2009, pp. 857-862.

JOURNAL OF THE
Iranian
Chemical Society

Optical pH Sensor Based on Calcon Immobilization Membrane

S. Rastegarzadeh* and Z. Moradpour
Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

(Received 12 July 2008, Accepted 15 January 2009)

An optical pH sensor was developed by immobilizing Calcon on a porous cellulosic polymer film. The color of the membrane in acidic to basic medium changes from pink to blue, which can be used for determination of pH by spectrophotometry. The sensor response to the pH changes at two wavelengths 510 and 670 nm was investigated. The optical sensor can be used for repetitive and reversible pH measurement in the pH range of 4-9 with a response time of 5 min at 510 nm. The relative standard deviation (R.S.D) was less than 0.51% for seven times alternative measurements of pH from 7 to 8. The sensor was successfully applied to the determination of pH in tap and waste water samples.

Keywords: pH optical sensor, Calcon, Triacetylcellulose, Methyltrioctylammonium chloride

INTRODUCTION

Recently the development and application of optical chemical sensors (optodes) have grown rapidly [1-3]. In many frequently performed analyses the use of optodes has made measurements feasible which were otherwise difficult to monitor and perform efficiently. From among all sensors, optical pH sensors have received the most attention because the measurement and control of pH is very important in chemistry, biochemistry, clinical chemistry and environmental science. These sensors offer further advantages such as freedom from electrical noise and ease of miniaturization, as well as possibility of remote sensing. Also, they are suitable for applications where conventional electrodes cannot be used because of their size or because of the risk of electric shock during the *in vivo* measurements [4].

The optical pH sensors usually use certain indicators immobilized on solid support with pH-dependent changes of absorption or fluorescence [5-7]. The immobilization of sensing reagents in/on a solid support is an important step in the development of optodes. The reagents are normally adsorbed onto [8], entrapped into [9] or bounded to the supporting matrices by covalent bonds [10]. This requires identifying and testing a variety of polymeric materials [11] that could serve as porous support structures to minimize barriers to mass transport. Also, it is important for the search for colorimetric reagents that possess the requisite optical and chemical properties to improve both the sensitivity and the long-term stability of the response. The optical properties of some reagents are very sensitive to the environment, thus, often these reagents will experience spectroscopic shifts when immobilized in a solid support [12]. In order to be efficiently encapsulated in the support matrix, the reagent must be soluble in the support material. To enhance solubility, an ion-pairing approach can be used.

Most indicators are only sensitive to changes in pH values over the range of 2-4 pH units which limit the application of pH optodes to narrow pH range. Therefore, it is suggested to make pH optodes with extended pH range, for example using fluorescent indicator [13], indicators with varying acidic

*Corresponding author. E-mail: rastegarz@scu.ac.ir

groups or mixtures of multiple pH indicators [14,15].

In this paper, we describe the fabrication of a pH optical sensor based on immobilization of Calcon-methyltrioctyl-ammonium ion pair on triacetylcellulose membrane using a simple method. The characteristics of the proposed sensor were investigated by spectrophotometry, and the dynamic working range of pH for sensor at two wavelengths was obtained.

EXPERIMENTAL

Apparatus

A GBC UV-Vis spectrophotometer model Cintra 101 was used for the recording of the spectra, and the absorbance measurements were made using a Perkin-Elmer UV-Vis spectrophotometer model 550S. The sensing membrane was placed in a glass cell, and all measurements were performed in a batch mode.

A Metrohm model 632 pH-meter with a combined glass electrode was used after calibration against standard Merck buffers for pH determinations.

Reagents and Solutions

All reagents used were of analytical grade and double distilled water was used throughout.

McIlvaine buffer for solution of pH range of 2.2-8.0 was prepared by mixing appropriate amount of 0.1 M citric acid (Merck) and 0.2 M Na_2HPO_4 (Merck) solutions. The buffer solutions at pH range of 8.5-10.0 were prepared from 0.025 M $Na_2B_4O_7$ (Merck) and adjusting the pH by addition of 0.1 M hydrochloric acid or sodium hydroxide solutions [16].

Preparation of Optical Sensor

The following procedure for the preparation of sensor was performed in order to immobilize Calcon on triacetylcellulose membrane. For this purpose, the transparent triacetylcellulose membrane was produced from waste photographic film that had been previously treated with commercial sodium hypochlorite in order to remove colored gelatinous layers [17]. This clean and dry membrane was placed in the solution containing 0.025 g Calcon (Merck), 0.04 g methyltrioctylammonium chloride (Merck) and 10 ml ethylenediamine (Merck) for 10 min at ambient temperature.

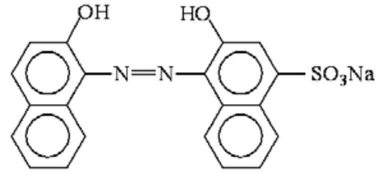

Fig. 1. Structure of Calcon.

Then, it was washed with water for removing the additional reagents. The obtained membrane was stored under water when not in use.

RESULTS AND DISCUSSION

Response Spectra and Membrane Composition

Calcon is a sodium salt of 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid (Fig. 1), which is known as water soluble colorimetric reagent for Al^{3+} [18].

The preliminary experiment showed that the Calcon can not be immobilized on triacetylcellulose membrane. The use of methyltrioctylammonium chloride can help immobilizing Calcon on the membrane by formation of a lipophilic ion pair. So, addition of a small amount of methyltrioctylammonium chloride to solution of Calcon in ethylendiamine changed the membrane color which indicated the adsorption of Calcon-methyltrioctylammonium ion pair on triacetylcellulose membrane.

The characteristic spectra of Calcon in solution and immobilized on triacetylcellulose film as a function of pH are shown in parts a and b of Fig. 2, respectively. As can be seen, the immobilized and solution forms of the Calcon exhibit marked difference both in their optical properties and their acid-base reactivity. As shown in Fig. 2a, the solution absorption spectra has a maximum of 510 nm in acidic media and 567 nm in basic solution, and no distinct isobestic point is observed.

In Fig. 2b, the specific changes in the spectra of immobilized Calcon can be observed in comparison to its free form. Two absorbance maxima at 510 and 537 nm were seen in acidic solution (pH = 3-5), and the maximum absorbance shifts to about 670 nm as a result of an increase in the pH. It is important to note that the absorption spectra of the immobilized Calcon are red shifted in comparison to those of

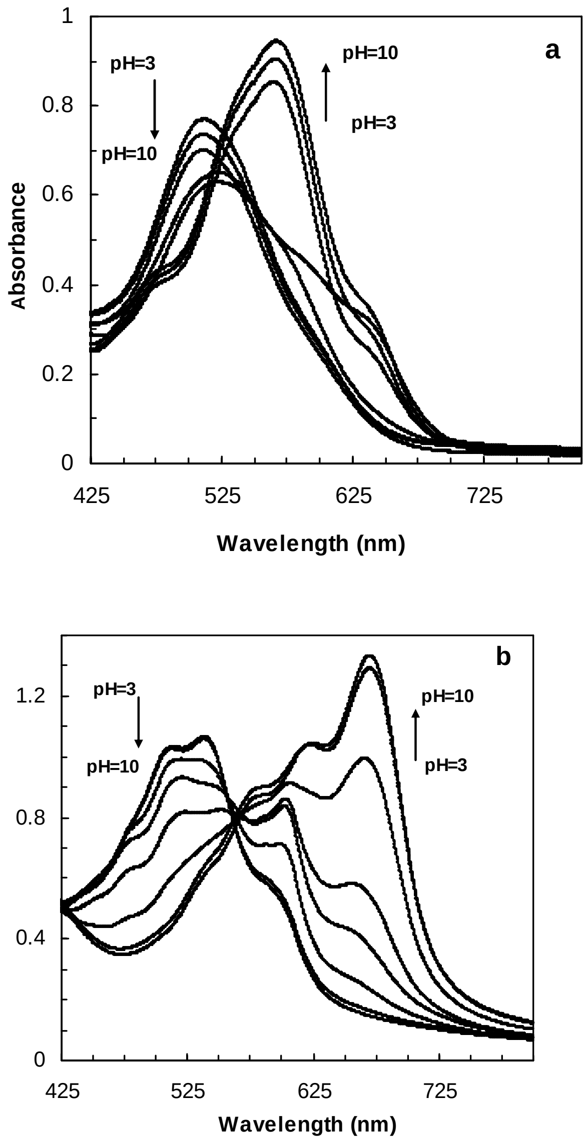

Fig. 2. Absorption spectra for Calcon in solution (a) and immobilized on triacetylcellulose membrane (b), in buffer solutions with pH values: 3, 4, 5, 6, 7, 8, 9 and 10.

its soluble form. This suggests that the structural conformation of the immobilized Calcon is more planar than that of its solution analogue [12]. Furthermore, a clear isobestic point in spectra shows the presence of a simple equilibrium between protonated and deprotonated forms of the immobilized Calcon. The wavelengths of 510 and 670 nm were selected for measuring the absorbance of membrane in subsequent studies.

In order to provide a transparent and homogeneous membrane with maximum change in absorbance, the effect of variables on the preparation of the optical sensor was investigated. The obtained results indicated that the hydrolyzed cellulose film in ethylendiamin as solvent shaped the porous structure in the polymer, which Calcon-methyltrioctylammonium ion pair effectively adsorbed on membrane. Consequently, the best optode was prepared by treating transparent triacetylcellulose membrane with a solution of 0.025 g Calcon and 0.04 g methyltrioctyl-ammonium chloride in 10 ml ethylendiamine for 10 min.

pK_a of Immobilized Reagent

The pK_a of indicators is usually calculated according to the equation:

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

where A_a and A_b are the absorbance values of indicator in its acid and conjugated base form, respectively, and A_x is the absorbance measured at a defined pH within the titration plot [7,19]. From the above equation the pK_a value of the immobilized Calcon on triacetylcellulose membrane was calculated as $pK_a = 6.47 \pm 0.14$.

Response Time and Dynamic Range

The absorbance changes of the membrane were recorded *vs*. time at 510 and 670 nm wavelengths, when the pH was changed from 5 to 6. As can be seen in Fig. 3, the absorbance reaches 90% of the steady state signal in about 3 min. It can be noted that well over 95% of the total response can be achieved within 5 min. The response time was shorter at low and high pH values.

For achieving a working dynamic range, the response of the optodes as a function of pH was studied at 510 and 670 nm wavelengths. As it is observed from Fig. 4, the sensor response was linear in the range of pH values of 4-9 with equation A = -0.1255 pH + 1.4613 (r = 0.9985) for 510 nm and in the range of 5-9 pH unit with equation of A = 0.2377 pH - 1.0474 (r = 0.9986) for 670 nm, where A is absorbance of sensor membrane.

A comparison between response of sensor in prepared

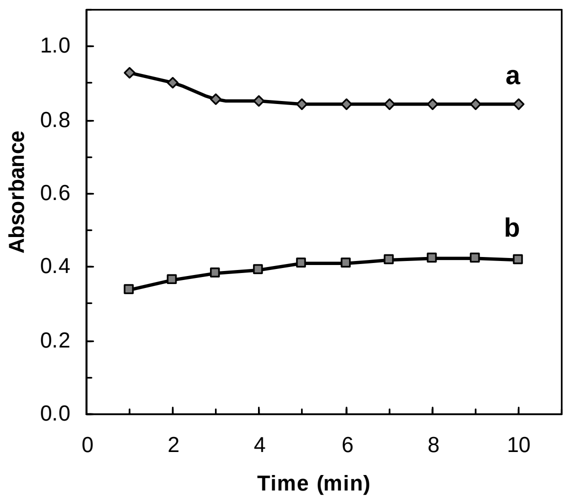

Fig. 3. Response time curve of sensor when pH changed from 5 to 6 at 670 nm (a) and 510 nm (b).

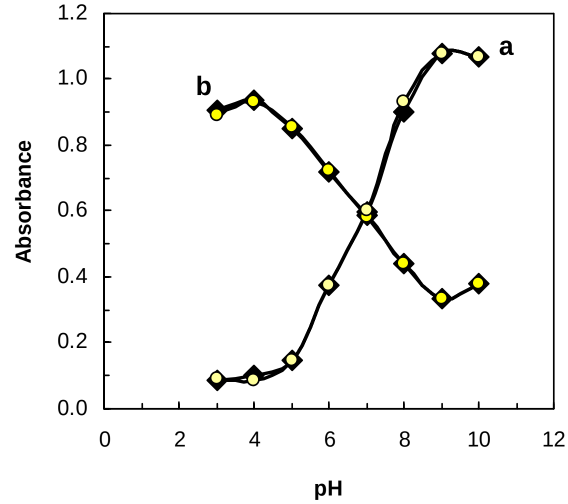

Fig. 5. The comparison of sensor response between different buffer solutions: (a) 670 nm and (b) 510 nm.

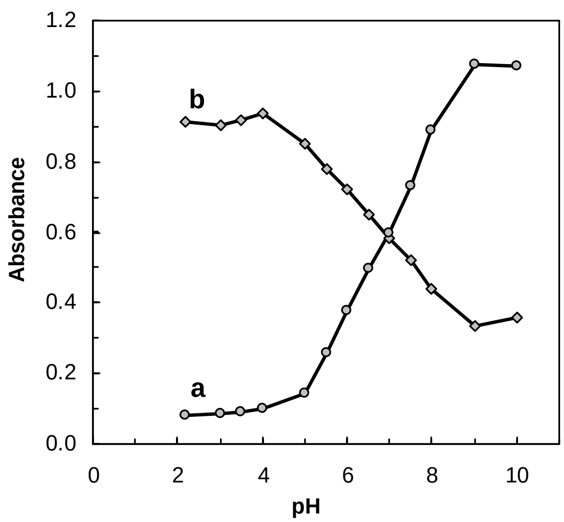

Fig. 4. Sensor response *vs*. pH at 670 nm (a) and at 510 nm (b).

buffer solutions [16] and standard Merck buffers was performed. Figure 5 shows that the obtained results in different buffer solutions are in good agreement.

Reproducibility and Stability

Figure 6 shows a typical response profile for the transition process as a result of change in the membrane medium to three successive pH values 4, 6 and 8 at 670 nm and 6, 7 and 8 at 510 nm. These results are evidence of highly reproducible and reversible response of the proposed pH sensor.

The reproducibility of the optical response was also evaluated by alternatively recording the absorbance change of the optode in going from pH 7 to 8 at 510 and 670 nm. The relative standard deviation (R.S.D) was less than 0.51% for seven pH measurements at each wavelength.

The stability of the sensor was studied by repeated measurements during certain time. The obtained results showed that the changes in the absorbance, after keeping the membrane in water for three weeks, were less than 4.5%.

Selectivity

The interference of metal ions on response of the sensor was investigated in solutions with pH 6 and 9 at two wavelengths; 510 and 670 nm. The tolerance limit was defined as the maximum concentration of cations causing an error of less than ±5% in the determination of pH. Some ions such as Cu^{2+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Cd^{2+} and Co^{2+} were in their precipitated hydroxide form at high pH values. The results are summarized in Table 1. The interference of Cu^{2+}, Zn^{2+} and Cd^{2+} at 510 nm was eliminated using 0.1 M glycin for Cu^{2+}, 0.06 M tartrate ion for Zn^{2+} and 0.1 M sodium chloride for

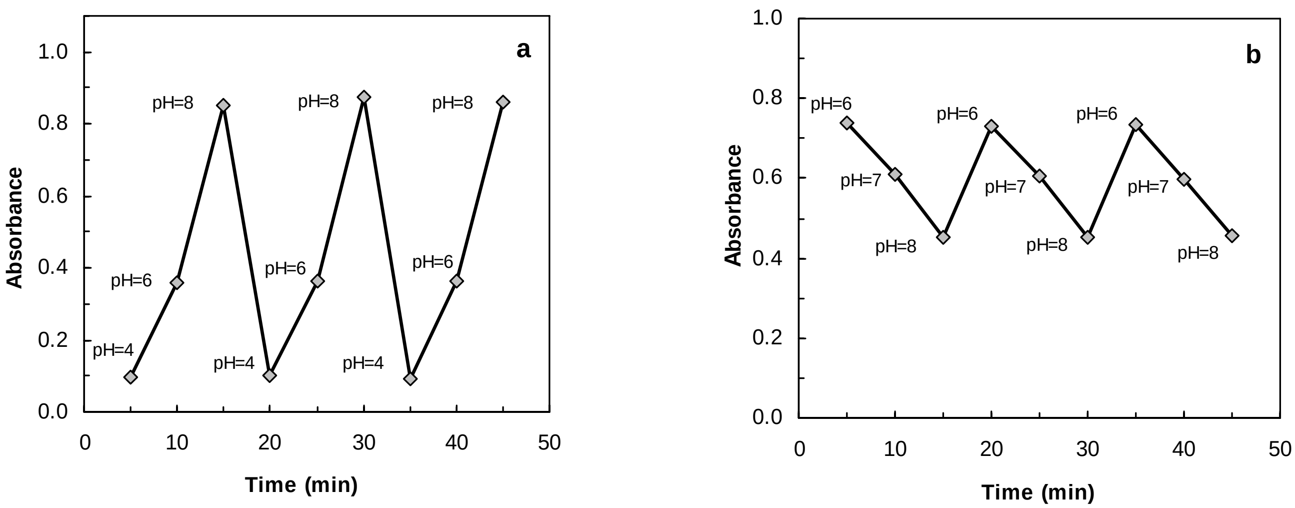

Fig. 6. Change in absorbance of the sensor for alternating the pH level from 4 to 8, at 670 nm (a) and 6 to 8 at 510 nm (b).

Table 1. Effect of Interfering Cations on Response of pH Sensor at pH 6 and 9

Ion	Tolerance limit ($\mu g\ ml^{-1}$)				
	pH	6		9	
	Wavelength (nm)	510	670	510	670
Ba^{2+}		200	200	100	100
Co^{2+}		100	100	[a]p	p
Mn^{2+}		50	1	50	1
Mo(IV), K^{+}		200	200	200	200
Ni^{2+}		50	50	30	1
Cr^{3+}		100	50	100	1
Pb^{2+}		100	1	p	p
Mg^{2+}		200	200	p	p
Ca^{2+}		100	5	100	100
Al^{3+}		100	1	100	100
[b]Cd^{2+}		100	1	100	1
[c]Zn^{2+}		50	5	50	5
[d]Cu^{2+}		20	1	20	1

[a]Precipitated. [b]masked by NaCl. [c]Masked by tartrate. [d]Masked by glycin.

Table 2. Determination of pH in Water Samples

Sample	pH found[a]	
	PH meter	Proposed method
Tap water	7.60 ± 0.04	7.10 ± 0.02
[b]Waste water	6.80 ± 0.03	6.58 ± 0.02

[a]Mean ± standard deviation (n = 4). [b]From petrochemical company Mahshahr, Iran.

Cd^{2+}.

Application of Optical Sensor to Water Samples

In order to check the applicability of the proposed pH sensor, it was applied to the determination of pH in tap and waste water samples. Due to higher selectivity at 510 nm, the absorbance was measured at this wavelength. The results given in Table 2 show that the pH values evaluated using the optical sensor are in good agreement with those obtained by the pH meter.

CONCLUSIONS

A pH optical sensor was developed by immobilization of Calcon-methyltrioctylammonium ion pair on triacetylcellulose membrane using a simple method. The major limitation of pH optodes is the narrow pH range. Attempts were made in order to extend the pH response range of optodes by employing several indicators with different acid constants [14,15]. One of the advantages of the proposed optode is that it responds to wide pH range about 5 pH units using only Calcon. In addition, the sensor response shows high reproducibility even in different buffer solutions.

ACKNOWLEDGEMENTS

The authors are grateful to Shahid Chamran University Research Council for financial support (Grant No. 227-1386).

REFERENCES

[1] M.I. Albero, J.A. Ortuno, M.S. Garcia, C. Sanchez-Pedreno, R. Exposito, J. Pharm. Biomed. Anal. 29 (2002) 779.
[2] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, S.B. Manohar, Anal. Chim. Acta 515 (2004) 311.
[3] S. Rastegarzadeh, Z. Moradpour, Anal. Lett. 40 (2007) 2993.
[4] Y. Kostove, S. Tzonkov, Anal. Chim. Acta 280 (1993) 15.
[5] H. Xu, O.A. Sadik, Analyst 125 (2000) 1783.
[6] P. Hashemi, R.A. Zarjani, M.M. Abolghasemi, A. Olin, Sens. Actuators B 121(2007) 396.
[7] A. Lobnik, I. Oehme, I. Murkovic, O.S. Wolfbeis, Anal. Chim. Acta 367 (1998) 159.
[8] A. Safavi, M. Sadeghi, Spectrochim. Acta Part A 66 (2007) 575.
[9] A. Song, S. Parus, R. Kopelman, Anal. Chem. 69 (1997) 863.
[10] Z. Liu, F. Luo, T. Chen, Anal. Chim. Acta 510 (2004) 189.
[11] B. Adhikari, S. Majumdar, Prog. Polym. Sci. 29 (2004) 699.
[12] T.P. Jones, M.D. Poter, Anal. Chem. 60 (1988) 404.
[13] D.R. Fry, D.R. Bobbitt, Microchem. J. 69 (2001) 25.
[14] A. Safavi, M. Bagheri, Sens. Actuators B 90 (2003) 143.
[15] J. Lin, D. Liu, Anal. Chim. Acta 408 (2000) 49.
[16] J.A. Dean, Analytical Chemistry Handbook, McGraw-Hill, New York, 1995, pp. 14.30-14.34.
[17] A. Safavi, M. Bagheri, Sens. Actuators B 99 (2004) 608.
[18] Z. Holzbecher, L. Divis, M. Kral, S. Ladislav, F. Vlacil, Handbook of Organic Reagent in Inorganic Analysis, Ellis Horwood, 1976, p. 621.
[19] C. Hazneci, K. Ertekin, B. Yenigul, E. Cetinkaya, Dyes Pigments 62 (2004) 35.