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Wide range pH measurements using a single H^+-selective chromoionophore and a time-based flow method

Afsaneh Safavi *, Abolfazl Rostamzadeh, Saeed Maesum

Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz 71454, Iran

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Abstract

A hydrophilic transparent triacetyl cellulose membrane was adopted as a pH optode by immobilizing highly selective and sensitive Nile blue indicator on the membrane. Contrary to the common procedure for determinations using optodes, in which a steady state response is measured, a new approach is introduced in which the dynamic response of the optode is used as the analytical signal. While in common procedures, pH optodes exhibit limited linear dynamic range (often 2–4 pH units only), it is shown that in a time-based flow method, an optode with only one acid-base indicator can be used for measurement in the pH range of 0–10. The procedure is simple, inexpensive and rapid.

Keywords: Wide range pH measurement; Dynamic method; Optode

1. Introduction

Optodes have been actively investigated for their potential in practical uses, such as clinical analysis, environmental analysis, biotechnology and process control. They are suitable for remote sensing and applications where conventional electrodes cannot be used because of their high cost, instability in aggressive or high pressure environments, large size, breakable nature, or the risk of electric shock during the in vivo measurements. Also, optical sensors have been developed for chemical analytes or physical parameters for which electrodes are not available [1]. The pH optodes mostly utilize pH indicator dyes in which several kinds of dye immobilization methods in the bulk or surface optode sensing phase were reported with unique techniques, such as trapping in dialysis tubing, adsorbing in polymer beads, covalently immobilizing on to porous glass or a cellulose membrane and ionically immobilizing on to an anion-exchange resin or sulfonated polystyrene surface [1,2]. Some pH optomembranes based on cellulose have been prepared for much useful applications [3–5]. In contrary to others, these hydrophilic membranes do not need any modification for response time or stability improvement.

A major disadvantage of using these types of sensors is that their responses exhibit limited linear dynamic range (often 2–4 pH units only). Several approaches have been proposed or employed in order to extend the pH range of these sensors. These include co-immobilizing indicators having complementary pH responses and multiplexing several optical pH probes [6]. The extension of pH response range of a sensor from its narrow linear range (pH 5–7.25) to the full calibration range (pH 2.51–9.76) has been performed using artificial neural network (ANN) [7]. A multilayer feed-forward (ANN) was used to model the input–output data of an optical-fiber pH sensor [8]. Recently, we described the development of an optical pH sensor based on immobilization of a mixture of two dyes on a triacetylcellulose membrane [9]. The sensor has a useful pH range at low and high pH values, where glass electrodes show acidic and alkaline errors, respectively. Application of a back-propagation artificial neural network model extended the measuring range of the proposed optode to the whole pH range.

While in batch assays, it is necessary to operate via steady state conditions, flow analysis methods have proved that this is not essential, allowing the treatment of optodes with samples in a controlled manner and under precise conditions gives reproducible, accurate and precise analytical results [2].

Although there are some reports on the dynamic model of the pH optodes [2,10], the quantitative studies of dynamic pH response of optodes have not been fully discussed in the past.

* Corresponding author. Tel.: +98 711 2284822; fax: +98 711 6305881.
E-mail address: safavi@chem.susc.ac.ir (A. Safavi).

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The response change of a poly-HEMA/Nile blue pH optode was simulated by applying Fick's law of diffusion via introduction of the diffusion factor variable with pH, D(pH) into a complicated theoretical response equation by Hisamoto et al. [2]. However, because both pK_a of immobilized pH indicator and *diffusion coefficient* through the membrane depend on other factors, such as temperature, ionic strength and composition of samples, more modification of the response equation seems to be necessary.

In this paper, we explain the development of a dynamic method to overcome the limited measuring range of previously reported pH optodes. The procedure involves measurement of the dynamic response of the optode. While in common procedures, pH optodes exhibit limited linear dynamic range (often 2–4 pH units only), it is shown that in a time-based flow method, an optode with only one acid-base indicator can be used for measurement in the pH range of 0–10.

2. Experimental

2.1. Instrumentation

Spectrophotometric measurements were performed with a flow cell mounted in a Philips PU8625 UV–vis spectrophotometer and a Philips PU4815 computing integrator attached to an IBM compatible personal computer. A Metrohm 632 pH meter with a Metrohm glass electrode was used for monitoring pH adjustments. A Watson Marlow 101F peristaltic pump and a Desaga PLG-Peristaltic pump were employed for pumping the solutions through the flow cell. A lab-made electrical power equipment driver with a computer interface was constructed for automatic control of the pumps.

2.2. Reagents

Nile blue hydrogen sulfate (NB) was supplied from Merck. Ethanol was used for alcoholic buffer preparation. Ethylene diamine (97%) and all other reagents were analytical grade (Merck or Fluka).

2.2.1. Buffer solutions

Universal aqueous pH buffer solutions were prepared from acetic/phosphoric/boric acids (0.04 M, respectively). The final pH was adjusted by the addition of 0.2 M sodium hydroxide or 4 M hydrochloric acid solutions.

2.2.2. Membrane

The transparent triacetylcellulose membranes were prepared from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove the colored gelatinous layers. It simply was treated with a clear solution of NB in ethylene diamine (5×10^{-3} g ml^{-1}) for 5 min (the optimum time) at ambient temperature. Then it was washed with water for removing ethylene diamine and loosely trapped dyes. This membrane was washed with hot ethanol for removal of extra dye, so that its absorbance at λ_{max} of 645 nm in acidic buffer solution (pH 1.8) was about 1.8. Finally, the membrane was washed with detergent solution and water and kept under water when not in use. The membranes prepared by this method were stable over several weeks of storage under pure water. Slight leakage (less than 1% decrease in absorbance at λ_{max}) of the dye was observed under flow conditions (flow rate of 14 ml min^{-1}) using the proposed buffer solutions for more than 60 min.

3. Results and discussion

It has been shown that Nile blue series chromoionophores in optode membranes are highly H^+-selective [11]. A highly sensitive Nile blue pH indicator with wide use in non-aqueous media has been recommended [12] as an excellent indicator for the pH range 9.0–10.4. Unfortunately, it suffers from the extreme insolubility of its basic form in water [12]. However, by the use of the proposed membrane it is possible to use NB indicator in aqueous media.

3.1. Static (batch) studies

Absorption spectra of NB optode (Fig. 1) and NB alcoholic solutions (6.5×10^{-5} g cm^{-3}) taken at different pH values were recorded at ambient temperature. The results show that the acidic maximum of absorption spectrum of the immobilized dye is red shifted in comparison to that of its solution form and has a maximum at 645 nm at the extreme pH values in comparison to the solution phase which has a maximum at 635 nm.

From the absorption of NB optode in buffer solutions with different pH values at steady state conditions, the pK' = 9.1 of Nile blue in the membrane was determined at the point of half-protonation (mid-point of pH measuring range). The pK' values of the NB pH indicator in the membrane (9.1) and water (9.7) [12] show that as expected [5,13], the acidity of the immobilized indicator is greater than that of its solution form.

The two limiting activities at which the slope of the response function (dependence of absorbance signals on pH values of samples) reduces to quarter of its maximum value have been used to quantify the practical measuring range (7.3–10.8) of the pH optode described herein. Estimation of best fitting curve

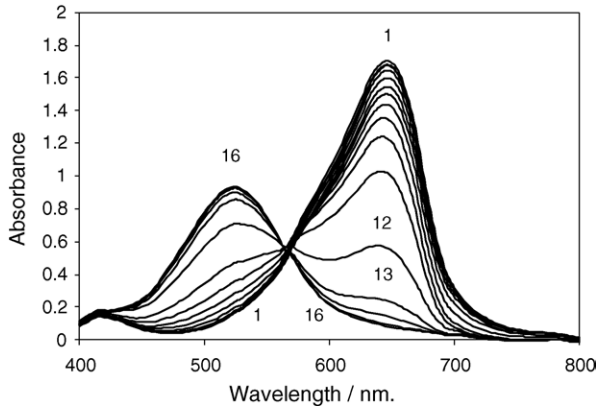

Fig. 1. Absorption spectra for NB optode in aqueous buffer solutions with pH values of: (1) 1.0, (2) 1.8, (3) 2.2, (4) 2.6, (5) 3.3, (6) 4.4, (7) 5.0, (8) 5.7, (9) 6.4, (10) 7.5, (11) 8.4, (12) 9.4, (13) 10.4, (14) 11.2, (15) 12.0 and (16) 12.7.

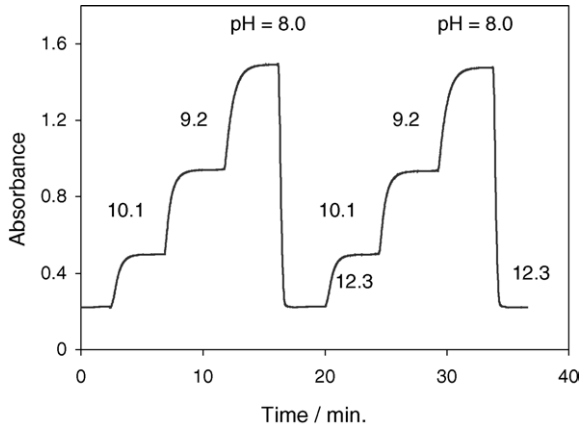

Fig. 2. The changes in the absorbance of the membrane at 645 nm for alternative changes of pH from 12.3 to three different pH values of 10.1, 9.2 and 8.0.

for slope calculation was performed by Table Curve Windows Software.

The response-repeatability of the membrane at 645 nm, for alternative changes of pH from 12.3 to three different pH values of 10.1, 9.2 and 8.0 (Fig. 2) were recorded. The relative standard deviation is less than 1% for seven measurements of the maximum changes at 645 nm from the acidic form of the indicator to its basic form. The average of response times (the time required for the output signal to reach a value that differs by less than 5% from the steady state signal) for six successive acidic to basic and basic to acidic forms of indicator transitions is 51 and 65 s, respectively. The optode produced by this method possesses good stability, short response time and good spectral characteristics.

3.2. Dynamic and flow studies

As mentioned previously, when the signal of pH optode is measured by conventional method (after equilibrium is reached), a measuring range of 7.3–10.8 was obtained. However, in order to obtain a wider dynamic range we tried to measure the responses of the same optode before equilibrium is reached. In this case, the process of proton diffusion across the membrane mainly governs the response. This proton diffusion can be determined using the well-known Fick's law. Fig. 3 shows the typical experimental time-pH-response profiles of the proposed optode. The membrane shows a slower absorbance response change to protons when the difference between initial and final pH values of membrane is decreased. Similar time response profile for a poly-HEMA/Nile blue pH optode has been reported previously (between pH 5 and 9) [2].

Fig. 3 also shows that with decreasing the time of optode exposure to the samples, pH-measuring range of optode shifts to acidic region so that an optode with conventional basic response region (7.3–10.8) can be used for measurement in high acidic region (0–2). With well-known efficiency and ability of flow methods, it was decided to use a flow system, in which the measurements are performed in the unfinished reaction mode. In flow measurements, the optode was treated with a high basic buffer washing solution (pH 11.98) for reducing its absorbance to base line. The flow rates of washing solution and acidic solutions were 14 and 7.3 ml min^{-1}, respectively.

Based on the above discussion, the level of the output signals at different times depends on the difference between initial and final pH values, the flow rate of the flowing solutions, and the inherent response time of the sensor. In other words, the pH determination range of the sensor can be tuned via controlling

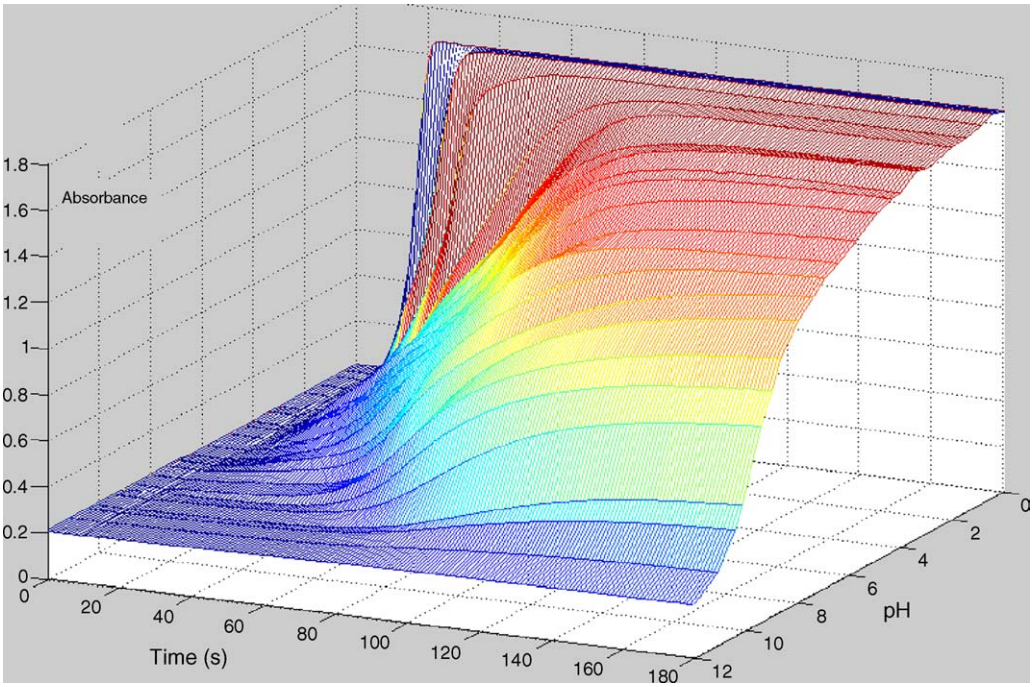

Fig. 3. The time response profiles of the NB pH optode when the proposed optode with initial pH value of 13.3 is treated with 22 different universal pH buffer solutions with pH values between 0 (curve 1) and 12.07 (curve 22).

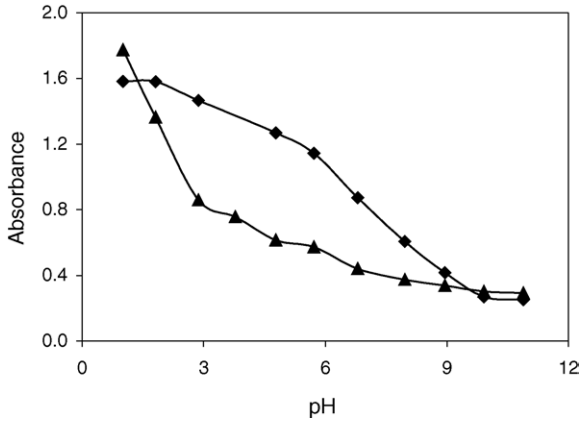

Fig. 4. Typical flow analysis results at 30 (▲) and 45 s (♦) for different pH values.

the exposure time of the optode to the solution. As an example, Fig. 4 shows that at two different exposure times of 30 and 45 s, different calibration curves, and thus different determination ranges are obtained.

The relative standard deviation for seven measurements is less than 1% for transitions between pH values of 7.5 and 11.98 with 45 s exposure time (Fig. 5).

3.2.1. Modeling of diffusion-controlled results

Although by simply using the dynamic approach it was possible to use a single optode within 10 units of pH, we tried to seek the applicability of the use of chemometrics in order to extend the measurable range of the present optode.

Simulation, modeling, curve fitting, statistical and numerical analysis are often a major and inevitable part of chemical experimentations. With modeling the diffusion-controlled response of the proposed optode, the pH-measuring range was extended to more than 11 units.

3.2.2. Data description

For each pH, a series of 25 absorbance signals that lie among 10 and 130 s were chosen from time response profile (Fig. 4). The data were randomly split into calibration and validation sets consisting of 12 series and 10 series for model definition and evaluation, respectively.

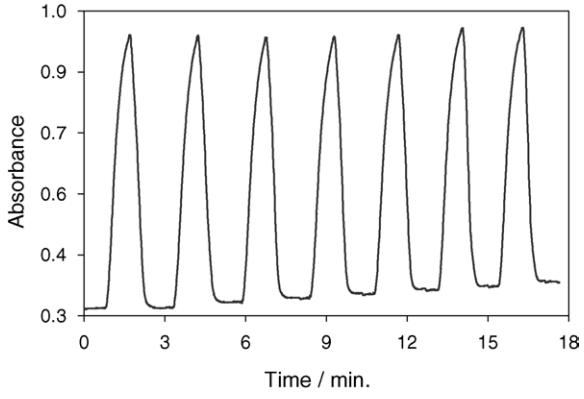

Fig. 5. The response-repeatability of the membrane at 645 nm, for alternative change of pH between 7.5 and 11.98 in flow system.

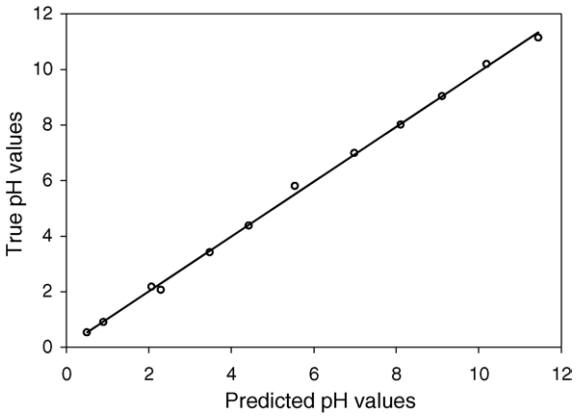

Fig. 6. The correlation between true and predicted pH values.

3.2.3. Calibration procedures

For the data set described above, the calibration set was used as the input for artificial neural network. A prediction mean square error (MSE) was calculated for the proposed method by:

$$\mathrm{MSE} = \sum_{i=1}^{n} \frac{(t_i - o_i)^2}{n}$$

where t_i is the actual pH of the ith sample, o_i the predicted pH for the ith sample and n is the total number of samples.

A multilayer feed-forward artificial neural network with the back-propagation of errors learning algorithm was used to model the input–output data of the proposed optical pH sensor. A minimum in the error of prediction (with average error of 0.11, MSE value of 0.02 and correlation value of 0.999 that is illustrated in Fig. 6) occurred when four nodes were taken in the hidden layer with a sigmoidal transfer function. The learning rate (η) and momentum (α) were 0.6 and 0.2, respectively, at continued training up to 7000. Fig. 6 shows very good agreement between true pH values and predicted ones.

4. Conclusion

The presented dynamic method for pH measurements with optodes has several important characteristics compared with batch measurements; wide determination range, which is simply controllable via selection of appropriate exposure time of the optode, higher sampling rate, enhanced response time and improved precision. These advantages make it feasible and economical to apply automated measurements to a relatively large number of samples of a non-routine kind.

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References

[1] O.S. Wolfbeis, Fiber Optic Chemical Sensors and Biosensors, vol. 1, CRC Press Inc., Boca Raton, 1991, and references cited therein.
[2] H. Hisamoto, M. Tsubuku, T. Enomoto, K. Watanabe, H. Kawaguchi, Y. Koike, K. Suzuki, Anal. Chem. 68 (1996) 3871.
[3] A. Safavi, M. Bagheri, Sens. Actuators B 99 (2004) 608.
[4] A. Safavi, M. Pakniat, Anal. Chim. Acta 335 (1996) 227.
[5] A. Safavi, H. Abdollahi, Anal. Chim. Acta 367 (1998) 167.
[6] D.R. Walt, G. Gabor, Anal. Chim. Acta 274 (1993) 47.
[7] M.N. Taib, R. Andres, R. Narayanaswamy, Anal. Chim. Acta 330 (1996) 31.
[8] M.N. Taib, R. Narayanaswamy, Sens. Actuators B39 (1997) 365.
[9] Y.A. Safavi, M. Bagheri, Sens. Actuators B 90 (2003) 143.
[10] Y. Kostov, S. Tzonkov, L. Yotova, Analyst 118 (1993) 987.
[11] E. Bakker, M. Lerchi, T. Rosatzin, B. Rusterholz, W. Simon, Anal. Chim. Acta 278 (1993) 211.
[12] M.M. Davis, H.B. Hetzer, Anal. Chem. 38 (1966) 451.
[13] T.P. Jones, M.D. Porter, Anal. Chem. 60 (1988) 404.