OPTICAL pH SENSING MATERIAL PREPARED FROM DOPED SOL-GEL FILM FOR USE IN ACID-BASE TITRATION

Musa Ahmad and T.W. Tan

School of Chemical Science and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia

ABSTRACT

An optical pH sensing material has been prepared in this study by using sol-gel technique. Bromothymol blue, bromophenol blue and thymol blue were chosen in this study as acid-base indicators for strong acid-strong base, strong acid-weak base and weak acid-strong base titration, respectively. The results show that these indicators could be successfully entrapped inside the sol-gel film and still maintain its chemical behaviour as in solution. The entrapped acid-base indicators respond well to any pH changes and could be used to determine the end-point of the acid-base titration.

1. INTRODUCTION

Chemical sensors are small devices capable of continuously and reversibly monitoring the concentration of a chemical species[1]. The important characteristics that a sensor should have are high selectivity and specific interaction between a receptor and the analyte. The basic concept and the advantages of chemical sensors based on optical fibres have been previously discussed by many authors[1-8].

The work on the immobilised pH indicators for optical pH sensing has been reported by many workers[9-27]. The use of immobilised indicators will require the indicators to be immobilised to a solid support such as by entrapment in sol-gel film[12,16,18,27] or membrane[23] or simple absorption on a polymeric support[9,13,15]. Immobilising the acid-base indicators by using the doping method in thin film and membrane is much easier compared to covalent binding of a reagent to a solid support.

This paper, describes the preparation of an optical pH sensing material by entraping acid-base indicators in a sol-gel film. The sensing materials were later coupled to the low-cost portable optical fibre and used to monitor acid-base titration. Doped sol-gel glasses are preferred for their thermal, chemical and photochemical stability. They are also transparent well into the ultraviolet, making possible a whole array of photochemical, photophysical and optical applications.

2. EXPERIMENTAL

Figure 1 illustrates the design of the optrode used in this study. A perspex block of 5x18x20 mm was used to secure the position of the feed and return optical fibres. Both fibres were inserted in the respective hole on the perspex block and the distant between the two fibres was fixed at 3 mm. A trench measures 3x5 mm was made in between the two fibres to slot in the sensing materials when the optrode was used to monitor acid-base titration.

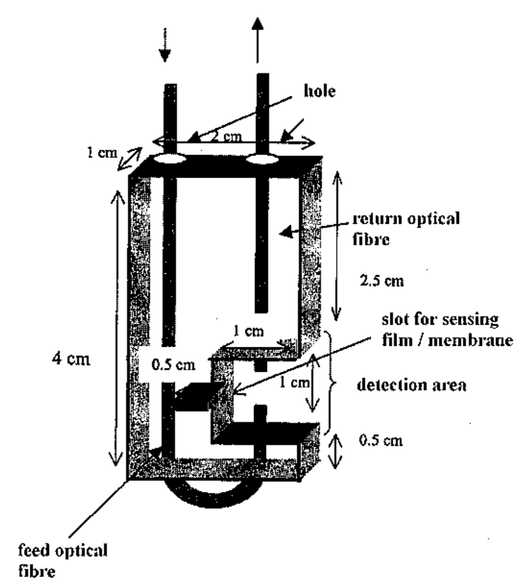


Figure 1: The design of the optical fibre pH probe.

The chemicals used to prepare a sol-gel matrix include tetraethylorthosilicate, TEOS (Fluka, 99 %), ethanol (BDH), distilled deionised water, hydrochloric acid (Merck, 37%) and triton x-100 (Fluka). Microscope slide glass is used to provide a support to a sol-gel film. Sol-gel solution was prepared by mixing 30 ml TEOS, 30 ml distilled deionised water, 31 ml ethanol, 0.50 ml hydrochloric acid and an appropriate amount of triton x-100 in a 100 ml beaker. The sol-gel solution was stirred for 1.5 hours before deposited on the microscope slide by dip coating. Dip-coating technique was used in this study because it is less expensive than conventional thin film forming processes such as sputtering and evaporation. The microscope slide glasses (3.0 cm x 1.5 cm) were mechanically dipped into the sol-gel mixture and recovered slowly and steadily to ensure even coating. The film was allowed to dry for 24 hours in ambient temperature. After the drying process, the film was washed under flowing water to remove any molecule absorbed on the surface of the film.

A home-made low-cost portable optical fibre sensor instrumentation was used in this study. It consisted of signal generator, laser diode light source, photodiode detector, pre-amplifier, sample-hold circuit, amplifier and a display unit.

The optical fibre instrument was warmed-up for about 1 hour to provide better signal stability. A 150 mL beaker was used as a titration container in which the optrode, magnetic bar and the conventional pH meter were placed. The pH meter was calibrated using standard buffer solution of pH 4.0 and pH 9.0 before use.

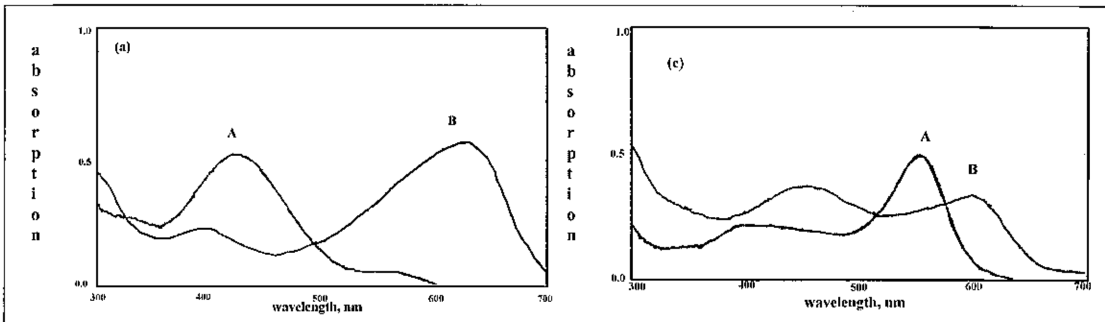
For titration between strong acid and weak base, 40 mL of 0.1 M HCl solution was placed in a beaker whereas NaOH 0.1 M solution, used as a titran, was placed in a burette. After adding 5 drops of bromothymol blue (Hopkins & Williams) in the acid solution, the mixture was stirred using a magnetic stirrer at a constant speed. The NaOH solution was then added gradually and both readings from the optrode and pH meter were recorded. The same titration process was repeated for titration between strong acid-weak base (0.1 M HCl and 0.1 M NH_4OH) and strong base-weak acid (0.1 M CH_3COOH and 0.1 M NaOH) by using bromophenol blue (Hopkins & Williams) and thymol blue (BDH) as an indicator, respectively. The strong acid or strong base was used as a titran in each titration.

3. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the entrapped bromothymol blue, bromophenol blue and thymol blue in sol-gel film both in acid and base solution. The maximum absorption of the entrapped indicators in both acid and base solution remains almost at the same wavelength of 434nm and 619nm; 435nm and 593nm; and 437nm and 598nm for the maximum absorption of the respective indicators of bromothymol blue, bromophenol blue and thymol blue in free solution. The same trend of results was also observed in our previous works [28-31]. These observations suggest that the entrapment of the reagent did not alter the chemical behaviour of the reagent and no chemical reaction took place.

The titration curves for all the acid-base titrations, using the entrapped indicators, were shown in Figure 3-5. The titration curves using the conventional pH glass electrode to measure the pH of the solution were also shown. Figure 3-5(A) show the voltmeter reading of the optical fibre pH sensor which was found to change steadily as the titran was gradually added to the analyte solution. When the end-point of the titration is reached, the change of the indicator's colour is completed and an abrupt change occurs in the volt reading as shown in Figure 3-5 (A). A similar shape of titration curves was also observed for acid-base titration between HCl and NaOH monitored by optical fibre pH sensor based on reflectance measurement[15]. These changes correspond with the changes observed in the pH reading as shown in Figure 3-5 (B) when conventional pH glass electrode was used.

Table 1 summarises the values of pH range as well as the titration end-point for all the sensing materials used in this study as measured by conventional pH meter and optical fibre pH sensor developed in this study. As shown, the pH range and the titration end-point data obtained from both methods are comparable.



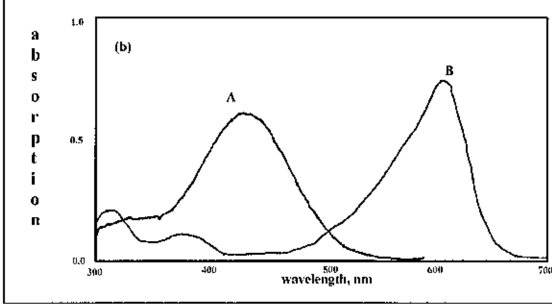


Figure 2: Absorption spectra of sol-gel film doped with bromothymol blue (a), bromo phenol blue (b) and thymol blue (c) in acidic (A) and basic solution (B).

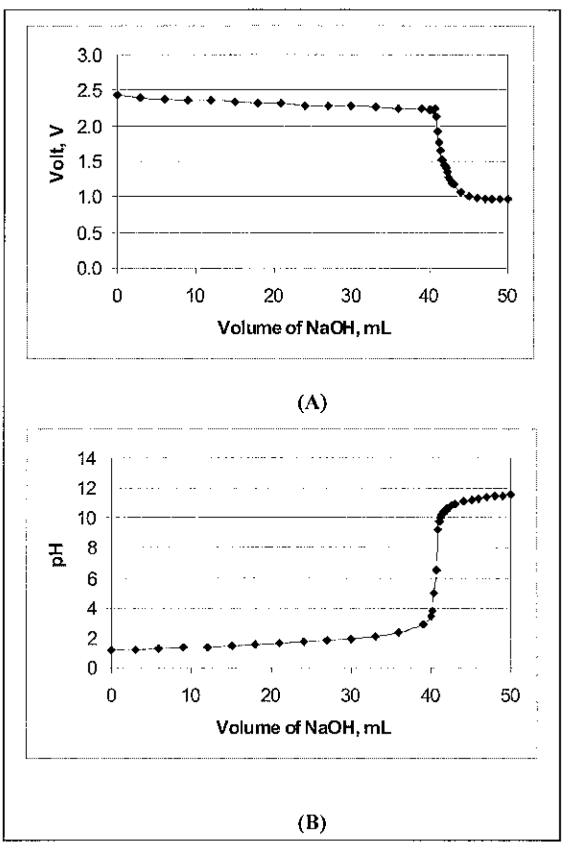


Figure 3: Titration curve for titration between 40 mL HCl, 0.1M and NaOH, 0.1M measured by optical fibre pH sensor based on bromothymol blue entrapped in sol-gel film (A) and conventional pH meter (B), when bromotymol blue was used as an indicator.

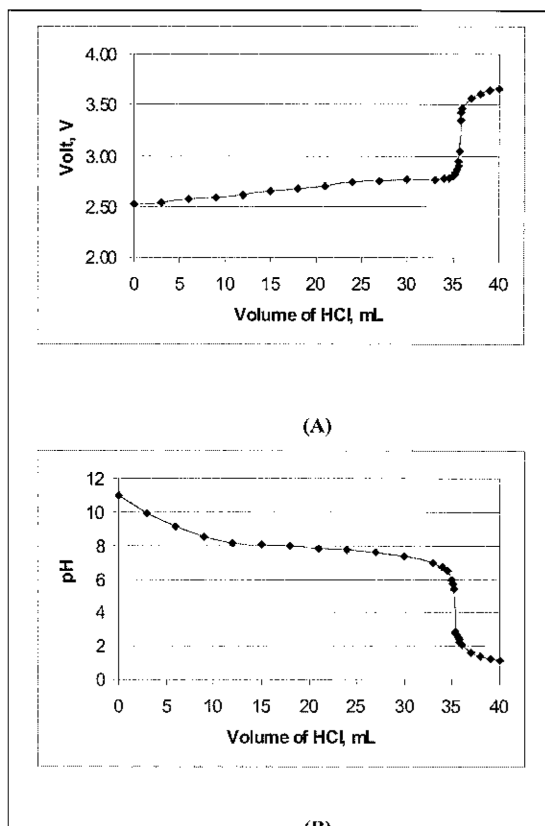


Figure 4: Titration curve for titration between 40 mL NH_3, 0.1M and HCl, 0.1M measured by optical fibre pH sensor based on bromophenol blue entrapped in sol gel film (A) and conventional pH meter (B), when bromophenol blue was used as an indicator.

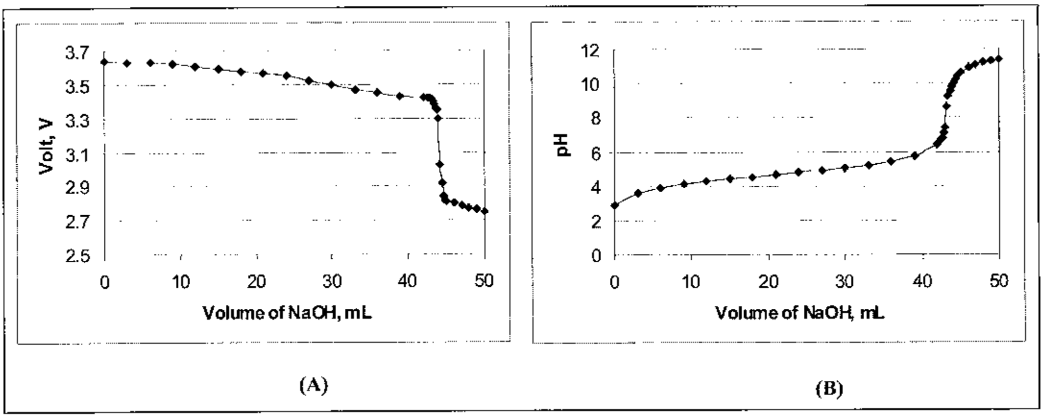


Figure 5: Titration curve for titration between 40 mL CH_3COOH, 0.1M and NaOH, 0.1M measured by optical fibre pH sensor based on thymol blue entrapped in sol-gel film (A) and conventional pH meter (B), when tymol blue was used as an indicator.

Table 1 : The pH range and titration data for bromothymol blue, bromophenol blue and thymol blue doped in sol-gel film as measured by optrode and pH meter.

pH indicator	Titration End-Point, mL			pH Range		
	meter pH	optrode	difference	reference[32]	meter pH	optrode
bromothymol blue	40.80	41.80	1.00	6.0 - 7.6	4.5 - 9.0	4.2 - 8.5
bromophenol blue	35.30	35.90	0.60	2.8 - 5.0	3.5 - 6.0	3.6 - 5.8
thymol blue	44.20	43.20	1.00	7.0 - 9.6	7.4 - 9.3	7.2 - 9.0

4. CONCLUSION

Bromothymol blue, bromophenol blue and thymol blue have been successfully immobilised inside the sol-gel film. Most of these sensing materials managed to retain the properties of the indicator like in homogeneous solution, and could be used to monitor the end-point of the acid-base titration.

5. ACKNOWLEDGEMENT

The researchers would like to acknowledge the Malaysian Government for the financial support of this research under IRPA 03-02-02-0044 research grant.

6. REFERENCES

1. Narayanaswamy, R. 1985. Optical Fibre Sensors In Chemical Analysis: Fibre Optics For Chemical Sensing. *Anal. Proc.* 22 : 204-206.
2. Seitz, W.R. 1984. Chemical Sensors Based On Fiber Optics, *Anal. Chem.* 56(1): 16A-34A.
3. Alder J.F., 1986, Optical fibre Chemical Sensors, Fresenius *Z. Anal. Chem,* 324, 372.
4. Narayanaswamy R and F. Sevilla III, 1988, Optical Fibre Sensors for Chemical Species, *J. Phys. E. Sci. Instrum.,* 21, 10.
5. Wolfbeis O.S., 1986, Analytical Chemistry with Optical Sensors, Fresenius Z. *Anal.Chem.,* 325, 387.
6. Norris J.O.W., 1989, Current status and Prospects for the Use of Optical Fibres in Chemical Analysis, *Analyst,* 114, 1359.
7. Narayanaswamy R., 1993, Chemical Transducers Based on Fiber Optics for Environmental Monitoring, *The Science of the Total Environment,* 135, 103.
8. Saari L.A., 1987, Trends in Fiber Optic Sensor Development, *Trends in Analytical Chemistry,* 6(4), 85.
9. Alabbas, S.H, Ashworth, D.C & Narayanaswamy, R. 1989. Design and Performance Features of an Optical-fibre Reflectance pH Sensor. *Anal. Proc* 26:373.
10. Otto S. Wolfbeis, Rodriguez N.V. and T. Werner, 1992, LED-Compatible Fluorosensor for Measurement of Near-Neutral pH Values, *Mikrochim. Acta,* 108, 113.
11. Munkholm C., Walt D.R., Milanovich F.P. and S.M. Klainer, 1986, Polymer Modification of Fiber Optic Chemical Sensors as a Method of Enhancing Fluorescence Signal for pH Measurement, *Anal. Chem.,* 58, 1427.
12. Ding J.Y., Shahriari M.R. and Sigel G.H., 1991, Fibre Optic pH Sensors Prepared by Sol-Gel Immobilisation Technique, *Electronics Letters,* 27 (17), 1560.
13. Kirkbright G.K., R. Narayanaswamy and N.A. Welti, 1984, Fibre Optic pH Probe Based on the Use of an Immobilised Colorimetric Indicator, *Analyst,* 109, 1025.
14. Peterson J.I., S.R. Goldstein and R.V. Fitzgerald, 1980, Fiber optic pH Probe for Physiological Use, *Anal. Chem.,* 52, 864.
15. Moreno M.C., Jimenez M., Conde C.P. and Camara C., 1990, Analytical Performance of an Optical pH Sensor for Acid-Base Titration, *Anal. Chim. Acta,* 230, 35.
16. Gupta B. D. and S. Sharma, 1998, A long-range fiber optic pH sensor prepared by dye doped sol-gel immobilization technique, *Optics Communications,* 154 (5-6), 282.
17. Xu Z., R. Andrew, A. Ricardo and M. Roger, 1998, Novel fiber-optic pH sensor incorporating carboxy SNAFL-2 and fluorescent wavelength-ratiometric detection, *Journal of Biomedical Materials Research,* 39, (1), 9-15.
18. Grant S.A. and R. S. Glass, 1997, A sol-gel based fiber optic sensor for local blood pH measurements, Sensors and Actuators B: Chemical, 45(1), 35-42.
19. Pilar M.D., T. Sotomayor, M. A. De Paoli and W. A.Oliveira, 1997, Fiber-optic pH sensor based on Poly(o-methoxyaniline), *Analytica Chimica Acta,* 353 (2-3), 275-280.

20. Wallace P.A., M. Campbell, Y.Yang, A.S.Holmes-Smith and M.Uttamlal, 1997, A distributed optical fibre fluorosensor for pH measurement, *Journal of Luminescence,* 72-74, 1017-1019.
21. McCulloch, S. and Uttamchandani D., 1997, Development of a fibre optic micro-optrode for intracellular pH measurements, *IEE Proceedings Optoelectronics,* 144 (3), 162-167
22. Bromberg A., J. Zilberstein, G. Frishman, S. Riesemberg, E. Benori, E. Silberstein, J. Zimnavoda and A. Kritzman, 1996, Optical-fibre sensors for blood gases and pH, based on porous glass tips, Sensors and Actuators B: *Chemical,* 31(3), 181-191.
23. Zhang S. F. , Y. A. B. D. Wickramasinghe and P. Rolfe, 1996, Investigation of an optical fibre pH sensor with the membrane based on phospholipid copolymer, *Biosensors and Bioelectronics,* 11(1-2), 11-16.
24. Netto E. J. , J. I. Peterson, M. McShane and V. Hampshire, 1995, A fiber-optic broad-range pH sensor system for gastric measurements, *Sensors and Actuators B:Chemical,* 29 (1-3), 157-163.
25. Motellier S. , M. H. NoirÇ, B. DurÇault and H. Pitsch, 1995, pH determination of clay interstitial water using a fiber-optic sensor, *Sensors and Actuators B:Chemical,* 29(1-3).
26. Zhang S., Tanaka S., Wickramasinghe Y.A.B.D. and Rolfe P., 1995, Fibre-optical sensor based on fluorescent indicator for monitoring physiological pH values, *Medical & Biological Engineering & Computing,* 33(2), 152-156.
27. Ding, J.Y. , Shahriari, M.R , Sigel, G.H. 1991. Fiber Optic pH Sensors Prepared By Sol Gel Immobilisation Technique. *Electronic Letters.* 27 : 1560-1562.
28. Musa A. and Q. A. Ling, 1997, Sol-Gel Film Doped with Phenolpthalien: Potential Use for CO2 Sensor, *Pertanika J. Sci. And Techn.,* 5(2), 157-167.
29. Musa A. and L. M. Shu, 1997, Doping of Bromotymol Blue onto Glass Matrices Prepared by Sol-Gel Technique Using Silica Oxide, Aluminium Oxide and Magnesium Oxide as Starting Materials, *The Malaysian Journal of Analytical Science,* 3(2), 281-288.
30. Musa, A. and R. Narayanaswamy. 1995. The use of sol-gel film as a matrix for immobilisation of some fluorimetric reagents. In *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities* ed. P.N. Prasad, E. Mark and T.J. Fai, p. 727-737. New York: Plenum Press.
31. Musa, A. and R. Narayanaswamy. 1995. Entrapment of Some Aluminium(III)-Sensitive Reagents in Sol-Gel Films. *Bull. Singapore Nat. Inst. Chem.,* 23, 55-60.
32. Christian, G.D. 1994. *Analytical Chemistry.* Ed. Ke-5. New York : John Wiley & Sons, Inc. 172-177 , 220-232.