Sodium Ion Sensing by Cellulose Triacetate Plasticizer Membrane Containing Dibenzo-16-crown-5 Chromoionophore

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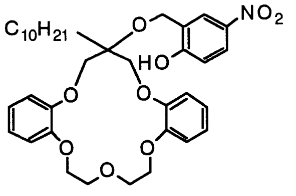
We have designed new optical membrane sensor which is composed of cellulose triacetate polymer as a membrane support, *o*-nitophenyloctyl ether as a membrane plasticizer and *sym*-(decyl)(2-hydroxy-5-nitrobenzyloxy)dibenzo-16-crown-5 (**1**) as a Na^+ ion selective chromoionophore. This type of membrane was found to selectively respond to Na^+ in the detection limit of 10^{-5} M (1 M = 1 mol dm^{-3}) with no significant interference from Li^+ and K^+ ions.

Recently we have shown that a polymeric plasticizer membrane which is composed of cellulose triacetate (CTA) as a membrane support, *o*-nitrophenyloctyl ether (NPOE) as a membrane plasticizer, and 1,5-bis[2-(2'-carboxyheptyloxy)-phenoxy]-3-oxapentane as a metal-ion carrier exhibited selective and effective uphill transport for Pb(II) ion based on the selective Pb(II) extraction ability of the dicarboxylic acid carrier.[1] The plasticizer (NPOE) in the membrane was found to effectively act as an organic solvent similar to the liquid-liquid extraction systems.[2] Compared with the poly(vinylchloride) plasticizer membrane which is widely used for ion-selective electrode, the CTA membrane can contain a larger amounts of plasticizer due to a high affinity between CTA and NPOE.[3] In addition, the CTA plasticizer membrane forms a stable and a transparent film. By replacing the dicarboxylic acid carrier with chromoionophores used for extraction photometry,[4] therefore, an effective optical membrane sensor as an optode device[5] may be feasible.



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In this study, a novel crown ether chromoionophore, *sym*-(decyl)(2-hydroxy-5-nitrobenzyloxy)dibenzo-16-crown-5 (**1**) prepared in our recent study[6] was utilized for Na^+ ion sensing. Based upon the results of earlier studies, attachment of a decyl group to the same polyether ring carbon that bears the chromophore side arm was anticipated to orient the phenolic group of the chromophore over the crown ether cavity.[7] Such preorganization should enhance selective interaction of the dibenzo-16-crown-5 binding site with Na^+ over other alkali metal cations in solution.[8] The chromoionophore **1** was dissolved into the CTA-NPOE membrane described above and investigated its photometric response to alkali metal ions in buffered aqueous sample solution.

The CTA-NPOE membrane containing chromoionophore **1** was prepared according to the reported procedure.[1] In 10 cm^3 of chloroform, 0.2 g of CTA (Eastman Kodak Co.), 0.4 g of NPOE (Dojindo Co.), and 2 cm^3 of 1,4-dioxane containing 5.7 $\times 10^{-3}$ M chromoionophore **1** were dissolved. Of this solution 4 cm^3 was poured into a glass culture dish (5.0 cm in diameter). After one day at room temperature, cold water was added and the membrane was peeled away from the dish. The membrane was attached into two compartment cell (membrane area, 2.8 cm^2), and the cell was fixed by two quartz galsses. The buffered sample solutions containing alkali metal cation were flowed through both side of the membrane with a peristaltic pump (flow rate, 5.8 cm^3 min^{-1}) and the color change of the membrane was measured with a UV-Vis spectrophotometer (Shimadzu UV-2100) through the quartz windows.

Figure 1 shows a spectral change of the membrane when the sample solution of 0.040 M alkali metal chloride (pH 10.6 adjusted by tetramethylammonium hydroxide, TMAOH) was flowed through the cell. Only in the presence of Na^+ ion in the sample solution, a significant spectral change of the membrane was noted at wavelength from 400 nm to 460 nm. This demonstrates that the chromoionophore **1** selectively extracts Na^+ from aqueous sample solution into the membrane phase at this pH condition.

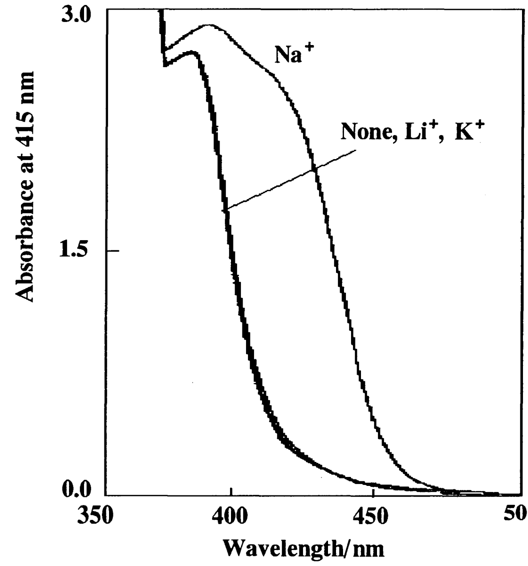

Figure 1. Absorption spectra obtained with membrane sensor containing DB16C5 chlomoionophore. Sample solution: 0.04 M Alkali metal chloride (pH=10.6 adjusted by TMAOH).

To investigate a response time and a reproducibility of the membrane, the time course study was carried out (Figure 2). The aqueous buffered solution of 0.04 M NaCl (pH 10.6) was first flowed through the cell. It is seen that the response time of 10 min was required to reach the absorption equilibrium. By flowing the solution of 0.1 M HCl through the cell, the membrane absorbance was recovered to the initial condition. A good reproducibility was observed in this system.

To attain a rapid analysis, the response time of 3.0 min was selected for the detection of Na^+ ion in aqueous sample solution. Thus the buffered sample solution (pH 10.6) was flowed through the cell for 3.0 min and subsequently the sample solution was changed to 0.1 M HCl solution. The resultant response signals as a function of recording time are shown in Figure 3. The Na^+ ion concentration was varied from 0.03 mM to 10 mM. A good correlation between the Na^+ ion concentration and the absorption intensity at 415 nm was observed. It must be noted that a sensitivity of the system can be enhanced by elongating the response time to be measured. The membrane was found to respond to Na^+ with a detection limit of 10^{-5} M. No interference from Li^+ and K^+ up to 0.10 M was observed for the detection of 1.0 mM Na^+ in aqueous sample solution. Thus the polymeric plasticizer membrane containing chromoionophore **1** is shown to be quite effective for Na^+ ion sensing. Since this type of membrane is physically stable and easily handled, it would also be useful as a metal ion-test paper by which metal ion species and concentration can be visually determined like a pH-test paper.

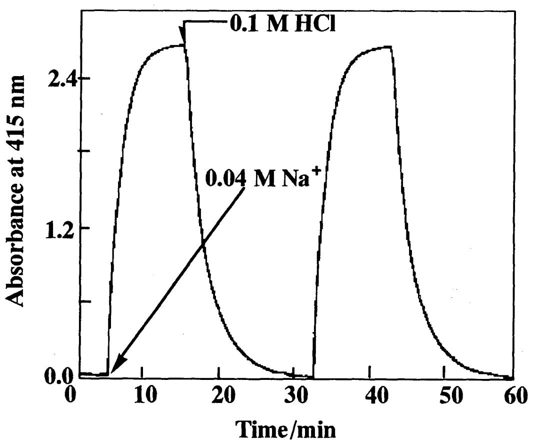

Figure 2. Time response and reproducibility for membrane sensor containing DB16C5 chromoionophore. Sample solution: 0.04 M NaCl (pH=10.5 adjusted by TMAOH). Stripping solution: 0.1 M HCl.

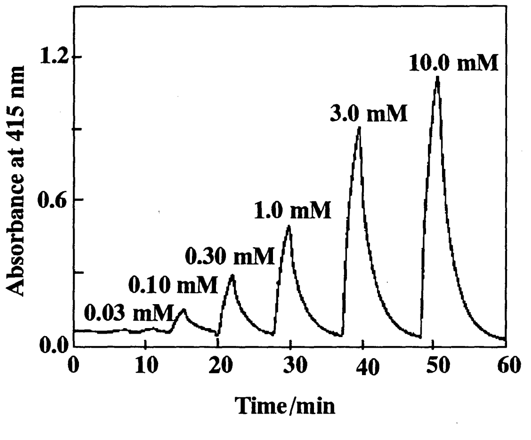

Figure 3. Calibration for sodium ion with membrane sensor containing DB16C5 chromoionophore. Sample solution: NaCl (pH=10.5 adjusted by TMAOH). Stripping solution: 0.1 M HCl; response time: 3.0 min.

Several factors such as chromoionophore concentration, membrane thickness, and mass transfer of ions on the surface of the membrane must affect the kinetics of membrane extraction. The detailed comparison between the solvent extraction and the membrane extraction by chromoionphore **1** are underway in our laboratory.

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References and Notes

1 T. Hayashita, T. Fujimoto, Y. Morita, and R. A. Bartsch, *Chem. Lett.*, **1994**, 2385.
2 M. Sugiura, M. Kikkawa, and S. Urita, *J. Membr. Sci.*, **42**, 47 (1989); *Sepn. Sci. Techn*, **22**, 2263 (1987).
3 When the PVC-NPOE membrane was prepared under the same composition with the CTA-NPOE membrane (0.80 g NPOE/ 0.20 g polymer), the PVC-NPOE membrane became very sticky whereas the CTA-NPOE membrane formed a stable film.
4 M. Takagi and K. Ueno, *"Host Guest Complex Chemistry, Topics in Current Chemistry"*, ed by F.L. Boschke, Springer, Berlin (1984); M. Takagi, *" Cation Binding by Macrocycles"*, ed. by Y. Inoue and G. W. Gokel, Marcel Dekker, New York (1990).
5 D. W. Lubbers and N. Opitz, *Z. Naturforsch.*, **30c**, 532 (1975); K. Watanabe, E. Nakagawa, H. Yamada, H. Hisamoto, and K. Suzuki, *Anal. Chem.*, **65**, 2704 (1993).
6 T. Hayashita, K. Kunogi, M. Takagi, J. C. Lee, and R. A. Bartsch, *Chem. Lett.*, **1995** (July issue) in press.
7 T. Hayashita, M. J. Goo, J. C. Lee, J. S. Kim, J. Krzykawski, and R. A. Bartsch, *Anal. Chem.* , **62**, 2283 (1990); R. A. Bartsch, T. Hayashita, J. H. Lee, J. S. Kim and M. G. Hankins, *Supramol. Chem.*, **1**, 305 (1993).
8 R. A. Bartsch, *Solvent Extr. Ion Exch.*, **7**, 829, (1989).