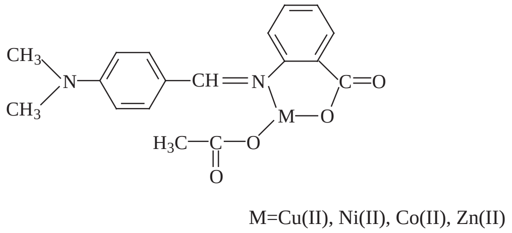
Thiocyanate-selective PVC Membrane Electrode Based on Tricoordinate Schiff Base Copper(II) Complex

Jian-Yuan Dai, Ya-Qin Chai, Ruo Yuan,* Yi-Sen Zhang, Yan Liu, Xia Zhong, and Dian-Ping Tang
Chongqing Key Laboratory of Analytical Chemistry, Southwest China Normal University,
Chongqing 400715, P. R. China

(Received October 28, 2004; CL-041277)

A new thiocyanate selective PVC membrane electrode was prepared by using a tricoordinate dimethylaminobenzaldehyde Schiff base copper(II) complex as neutral carrier, which demonstrates highly selectivity response to thiocyanate with substantially improved performance such as long lifetime, wide potentiometric response range, and low detection limit.

Ion-selective electrodes (ISEs) have grown substantially over recent years and were widely used to direct and rapid analytical detection of inorganic and organic ions due to their potentiometric response characteristics such as relatively fast response, wide linear response range, low detection limit, reasonable selectivity, and low cost.[1] Recently some new anion-selective PVC membrane electrodes based on lipophilic organometallic compounds,[2,3] metalloporphyrins,[4–6] metallophthalocyanines,[7–9] and Schiff base metallic complexes[10–16] have been reported. Unfortunately, most of these electrodes have one, two, or in some cases, all of the following problems: a) narrow linear ranges, b) high detection limit, c) long response time, d) instability and/or, e) serious interfering effect of such anions as ClO_4^-, NO_3^-, Br^-, and Cl^-. In addition, as most of the central metals of the membrane active components are square planar coordinated, up to date, there is no literature reports on electrodes based on the carriers which are triangular planar coordinated. In the present work, we report on the anion-selective properties of a tricoordinate Schiff base dimethylaminobenzaldehyde-(*o*-aminobenzoic acid) metallic complexes involving Cu(II), Ni(II), Co(II), and Zn(II) (Scheme 1).



Scheme 1. Dimethylaminobenzaldehyde-(*o*-aminobenzoic acid) metallic complexes [M-DMABABA].

The dimethylaminobenzaldehyde-(*o*-aminobenzoic acid) metallic complexes of Cu(II), Ni(II), Co(II), and Zn(II) were synthesized by modification of the reported procedures as described in the literatures.[17,18] The membrane composition was 3.0 wt % ionophore, 67.2 wt % 2-nitrophenyl octyl ether (*o*-NPOE) and 29.8 wt % PVC. The PVC membrane electrodes were fabricated from various carriers and assembled according to Thomas and his co-works.[19] The electrode cells for potential measurements were of the following cell assemblies:

$Hg–Hg_2Cl_2$/KCl (sat)/sample solution/membrane/0.1 M KCl/AgCl–Ag.

Potentiometric response characteristics of the electrodes containing the different carriers are shown in Figure 1. The electrode incorporating [Cu(II)-DMABABA] displayed a near-Nernstian potentiometric response to thiocyanate ion ranging from 9.0×10^{-7}–1.0×10^{-1} M with a detection limit of 7.0×10^{-7} M and a slope of −57.4 mV/decade in pH 4.0 of phosphate buffer solution at 25 °C. The response time ($t_{95\%}$) is 6–10 s in the linear response range, which implies that the reversible anion exchange is rapid. From Figure 1, one can see that under the same experimental conditions, the potentiometric response characteristics of the electrodes based on [Ni(II)-DMABABA], [Co(II)-DMABABA], and [Zn(II)-DMABABA] are poor, These different potentiometric response characteristics implied that the chemical environment, especially a certain substituent, has important influence on the performance of the electrodes. The [Cu(II)-DMABABA]-based electrode could be used continually for more than two months without detectable loss of performance characteristic.

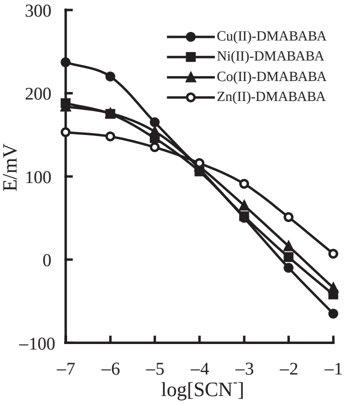


Figure 1. Potentiometric response characteristics of PVC membranes with various carriers.

Different buffers, 0.01 M H_3PO_4 solutions adjusted with NaOH at pH 3.0, 4.0, 5.0, 6.0, were used to study the effect of the pH on the response of the electrodes doped with [Cu(II)-DMABABA] to thiocyanate-sensitive. Figure 2 shows the results obtained when the electrode was immersed into buffer solutions with different pH values. SCN^- and OH^- ions seem to coordinate competitively with the central metal of [Cu(II)-DMABABA]. The coordination ability of SCN^- is stronger than that of OH^-. In the higher concentration section of SCN^- (1.0×10^{-1}–1.0×10^{-4} M), thiocyanate ion is the primary analyte ion and OH^- does not cause any obvious interference for the SCN^- response; while at a lower concentration level of SCN^-

(1.0×10^{-4}–1.0×10^{-7} M) with an increase in the OH^- concentration, the OH^- ion becomes the primary analyte ion and the potentiometric response characteristics of the electrode for SCN^- deviates from linear one, especially at high pH values. The same phenomenon was observed previously with metalloporphyrin derivatives.[4] The experimental results show that at pH 4.0, the analytical signal of the electrode presented better slope and detection limits for SCN^-. In subsequent experiments, such a buffer solution was selected.

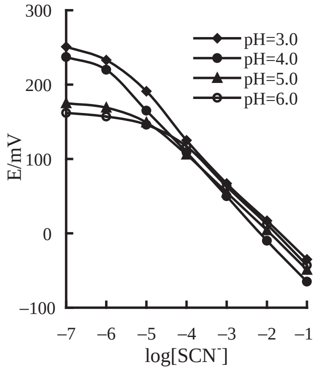
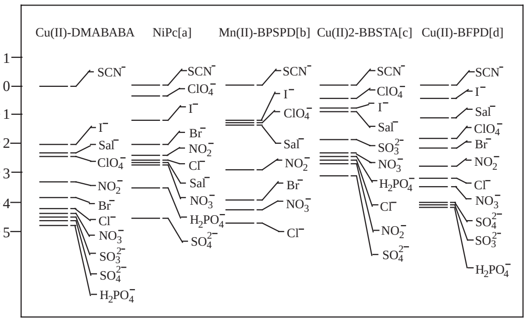


Figure 2. pH effect on potentiometric response characteristics of the electrode incorporating [Cu(II)-DMABABA] carrier.

The selectivity coefficients of the electrode were determined by the separate solution method according to IUPAC recommendations[20] and compared with those of the electrodes reported by the literature.[8,12,15,16] The results in Figure 3 show that the electrode based on [Cu(II)-DMABABA] demonstrate high selectivity towards SCN^- and exhibit an anti-Hofmeister selectivity sequence of anions in the following order: $SCN^- > I^- > Sal^- > ClO_4^- > NO_2^- > Br^- > Cl^- > NO_3^- > SO_3^{2-} > SO_4^{2-} > H_2PO_4^-$.



a–d refer to references 8,12, and 15–16, respectively

Figure 3. Selectivity coefficients of different SCN^- ion-selective electrodes.

Some lipophilic organometallic compounds were reported as anion ionophores exhibiting specific anion-selective behavior which deviated from the so-called Hofmeister anion response pattern. Their anion selectivities were mainly controlled by geometric configuration of the carriers and specific interactions between the central metals in organometallic complexes and anions, rather than by the lipophilicity of anions or simple electrostatic interactions with anions. The [Cu(II)-DMABABA]-based electrode exhibited high selectivity and high sensitivity to SCN^-, which can be explained as follows: in [Cu(II)-DMABABA] molecule, Cu(II) is triangular planar coordinated, it is relatively easy for [Cu(II)-DMABABA] to coordinate SCN^- and form a stable quadricoordinate complex.

In order to investigate the interaction mechanism of [Cu(II)-DMABABA] with SCN^-, UV-spectra of the sensing material with and without interacting with SCN^- were obtained. It is possible to distinguish the interaction between the central metal and thiocyanate. Comparing the spectra of [Cu(II)-DMABABA] and [Cu(II)-DMABABA]-SCN^-, one notices that the Soret bands of 234 and 328 nm red shift to 244 and 338 nm with increased intensity, respectively. It suggested that the absorbing species had increased in size and planar coordination was thought to take place.

In this paper, we have described a new highly thiocyanate-selective electrode based on [Cu(II)-DMABABA]. This electrode is very easy to prepare, has high selectivity and sensitivity, a wide range, fast response time, fair stability and reproducibility, and low detection limit.

The support of this work by the National Natural Science Foundation of China (29705001), the Chinese Education Ministry Foundation for excellent young teacher and the Natural Science Foundation of Chongqing city, China is gratefully acknowledged.

References

1 P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, **98**, 1593 (1998).
2 Z. Q. Li, R. Yuan, and R. Q. Yu, *Talanta*, **46**, 943 (1998).
3 T. Moriuchi-Kawakami, H. Aoto, K. Fujimori, and Y. Shibutani, *Chem. Lett.*, **2001**, 1298.
4 D. Gao, J. Z. Li, and R. Q. Yu, *Anal. Chem.*, **66**, 2245 (1994).
5 E. Malinowska and M. E. Meyerhoff, *Anal. Chim. Acta*, **300**, 33 (1995).
6 S. Shahrokhian, A. Hamzehloei, and M. Bagherzadeh, *Anal. Chem.*, **74**, 3312 (2002).
7 J. Z. Li, R. Yuan, and R. Q. Yu, *Analyst*, **119**, 1363 (1994).
8 M. K. Amini, S. Shahrokhian, and S. Tangestaninejad, *Anal. Chim. Acta*, **402**, 137 (1999).
9 S. Shahrokhian, *Anal. Chem.*, **73**, 5972 (2001).
10 R. Yuan, Y. Q. Chai, and R. Q. Yu, *Anal. Chem.*, **65**, 2572 (1993).
11 R. Yuan, Y. Q. Song, and Y. Q. Chai, *Talanta*, **48**, 649 (1999).
12 Z. Q. Li, Z. Y. Wu, R. Yuan, M. Ying, G. L. Shen, and R. Q. Yu, *Electrochim. Acta*, **44**, 2543 (1999).
13 S. Shahrokhian, M. K. Amini, R. Kia, and S. Tangestaninejad, *Anal. Chem.*, **72**, 956 (2000).
14 M. Shamsipur, M. Yousefi, M. Hosseini, M. R. Ganjali, H. Sharghi, and H. Naeimi, *Anal. Chem.*, **73**, 2869 (2001).
15 R. Yuan, X. L. Wang, and Y. Q. Chai, *Electrochem. Commun.*, **5**, 717 (2003).
16 Z. Y. Sun, R. Yuan, Y. Q. Chai, and L. Xu, *Anal. Bioanal. Chem.*, **378**, 490 (2004).
17 Z. Wang, Z. S. Wu, and Z. H. Yen, *Synth. React. Inorg. Met-Org. Chem.*, **24**, 1453 (1994).
18 X. C. Li and R. A. He, *Nat. Prod. R & D*, **11**, 33 (1999).
19 A. Craggs, G. J. Moody, and J. D. R. Thomas, *J. Chem. Educ.*, **51**, 541 (1974).
20 R. P. Buck and E. Lindner, *Pure Appl. Chem.*, **66**, 2527 (1994).