Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 4 (1)
(2007)
Science and Research Campus
ISSN: 1735-2126

Cu(II) Ion- Selective Membrane Electrode Based on bis(N-salicylidene-3,3'-diamino diphenyl) sulfone

M. Aghaie[1*], M. H. Fekri[2], M.Giahi[3], E. Baghdar[1] and S. Farhadi[4]

1. Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran
2. Department of Chemistry, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran
3. Department of Chemistry,Faculty of Science,Lahijan Branch, Islamic Azad University, Lahijan, Iran
4. Department of Chemistry, Lorestan University, Khorramabad, Iran

ABSTRACT

In order to study the Cu(II) ion selective electrode, an optimized membrane was prepared by mixing of 30 mg of PVC powdered, 5 mg of considered ionophore, 60 mg of plasticizer and 5 mg of additive. The sensor showed a near Nernstian response for Cu(II) ions over a concentration range from 1.0×0^{-6} –1.0×0^{-2} M with a slope of 28.9 ± 0.5 mV per concentration decade with a working pH range of 3.5-6.3. The limit of detection was 1.0×10^{-6} M. The response time of the electrode is about 15s and can be used for more than 2 month without any divergence in potential.

The proposed sensor showed fairly a good discriminating ability towards Cu(II) ion in comparison to other ions. The practical application of the electrode was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Cu(II) with EDTA solution.

Keywords: Ion selective electrode; PVC membrane; Cu(II) determination; potentiometry

---

∗ . Corresponding author

INTRODUCTION

In recent years, there has been a growing need for constructing chemical sensors for the fast and economical monitoring of pharmaceutical compounds. Ion-Selective Electrodes are part of a group of relatively inexpensive analytical tools which are commonly referred to as sensor [14, 15] and their use in the medical arena, environmental, agricultural and industrial fields is developing day to day [1-6].

Copper is one of the most widely distributed elements in the environment of industrialized countries. It is present in all organisms, land and marine. It has been shown that copper is an essential element for many biological processes, e.g. blood formation and the function of many important enzymes [7-11]. The purpose of this work was the development of a copper(II)-selective electrode based on a plasticized poly(vinyl chloride) (PVC) membrane, containing bis(N-salicylidene-3,3'-diamino diphenyl) sulfone (Fig.1.) as the membrane active phase. The electrochemical selectivity for a variety ions and the effect of membrane matrix, ionophore concentration, additives, and pH on the potentiometric response properties of the electrode were investigated. The electrode was also used as an indicator electrode for titration of Cu^{2+} ion with EDTA and for determination of copper in spiked sample.

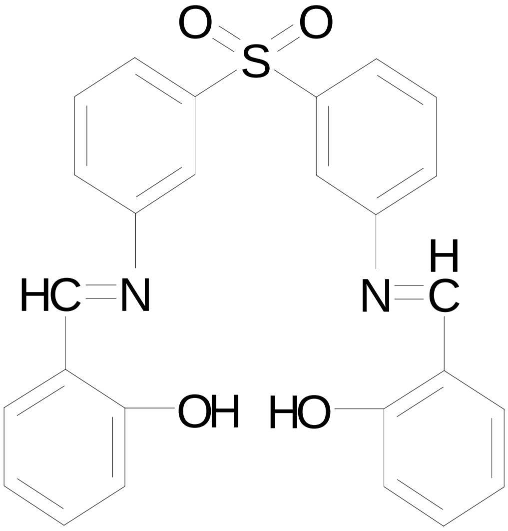

Figure 1. Structure of bis(N-salicylidene-3,3'-diamino diphenyl) sulfone (BSDDS) as ionophore.

EXPERIMENTAL

1. Apparatus

A metrohm pH/mV meter, an Ag-AgCl /KCl (sat) electrode (Azar electrode Company,urmia,Iran) in conjunction with the respective indicator electrode (SCE) and a Haoke model FK2 circulation water bath at 25.0 ± 0.2 °C were used to carry out the respective experiments.

2. Reagents

All reagents except bis(N-salicylidene-3,3'-diamino diphenyl) sulfone (BSDDS) were of analytical reagent grade. BSDDS was synthesized and purified in the laboratory of Lorestan University.

Reagent grade acetophenone (AP), oleic acid (OA), tetrahydrofuran (THF), dibutyl phthalate (DBP) and high relative molecular weight PVC (all from Merck) were used as received. Chloride and nitrate salts of all other cations and detergent used (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

3. Electrode Preparing

The common procedure was used to prepare the PVC membrane. It was to mix thoroughly 30 mg of PVC powdered, 5 mg of ionophore, 60 mg of plasticizer (DBP) and 5 mg of additive oleic acid. Then the mixture was dissolved in 3 ml of dry freshly distilled THF. The resulting mixture was transferred in to a glass dish of 2 cm diameter .The solvent was evaporated slowly until an oily concentrated mixture obtained. A pyrex tube (5 mm o.d) was dipped into the mixture for about 10 s. So that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 2 h. The tube was then filled with internal solution 1.0×10^{-3} M Cu^{2+} ion with pH = 5. The electrode was finally conditioned for 8 h by soaking in a 1.0×10^{-2} M Cu^{2+} solution with pH = 5 [16].

RESULTS AND DISCUSSION

1. Electrods response

Solutions of each considered cation with the concentration range of 1.0×10^{-1}M to 1.0×10^{-7} M was prepared. Then corresponding electrode to each cation was immersed in own solution and its emf was measured. The potential responses of various ion-selective electrodes based on bis(N-salicylidene-3,3'-diamino diphenyl) sulfone(BSDDS) are shown in Fig. 2. It is seen that, the corresponding slope of potential-pM, plot for Cu (II) ion selective electrode is very near to the nernstian slope; while for the other studied ions are much lower than expected nernstian slope.

The slope of the calibration curve was 28.9 ± 0.5 mV/decade of Cu(II) concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 1.0×10^{-6} M. The standard deviation of 6 replicate measurements is ± 0.5 mV. The membrane sensors prepared could be used for more than 2 months without any measurable change in potential.

Emf measurements of Cu (II) ion selective electrode were carried out with the following assembly:

Ag–AgCl |internal solution (1.0×10^{-3} M Cu^{2+} +1.0×10^{-5} M HNO_3) |PVC membrane| test solution| KCl (satd) |Hg_2Cl_2|Hg.

2. The optimization of the Cu (II) ion selective electrode

The sensitivity and selectivity of an ion selective electrode depends significantly on the membrane composition and the nature of solvent mediator and the additive [8]. Thus, the influences of the membrane composition, nature and amount of plasticizer and amount and kind of additive and amount of ionophore on the Cu(II) sensor were investigated, and the results are summarized in Table1. It is seen that, the use of 60 % DBP in the presence of 30 % PVC, 5 % ionophore and 5 % oleic acid (No. 6, Table 1) results a good electrode performance. It should be noted that the presence of lipophilic and immobilized ionic additives [17, 18] or salt of two lipophilic ions [20] could diminish the membrane resistance and eliminate the diffusion potential [9]. Additionally, in some cases, they change the selective pattern of the ion-selective PVC performance membrane and resulting in a good working.

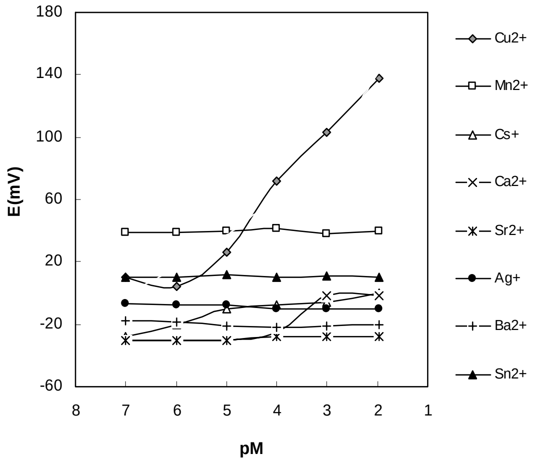

Figure.2. Potential response at pH 5 against different cations for ion-selective electrodes containing BSDDS as ionophore.

Table 1. Optimization of the membrane ingredients

No.	Composition(%)				Slope (mV/decade)	Linear range [M]
	Ionophore	PVC	Plasticizer	Additive		
1	-	29.4	64.7(AP)	5.9(OA)	3.3	-
2	1.6	31.1	62.2(AP)	5.1(OA)	18.3	1.0×10^{-6}-1.0×10^{-2}
3	1.5	39.4	49.3(AP)	9.8(OA)	22.2	1.0×10^{-6}-1.0×10^{-2}
4	3.1	30.6	61.2(AP)	5.1(OA)	18.5	1.0×10^{-6}-1.0×10^{-2}
5	5	30	60(AP)	5(OA)	12.4	1.0×10^{-6}-1.0×10^{-2}
6	5	30	60(DBP)	5(OA)	28.9	1.0×10^{-6}-1.0×10^{-2}
7	5.3	42.1	42.1(DBP)	10.5(OA)	12.2	1.0×10^{-6}-1.0×10^{-2}
8	6.6	32.7	56.1(AP)	4.6(OA)	18.1	1.0×10^{-6}-1.0×10^{-2}
9	9.5	28.6	57.2(AP)	4.7(OA)	18.5	1.0×10^{-6}-1.0×10^{-2}
10	8.7	34.8	52.1(AP)	4.4(OA)	19.1	1.0×10^{-6}-1.0×10^{-2}

3. The Effect of pH

The pH dependence of Cu(II) ion selective electrode potential (while the cupper ion concentration was1.0×10^{-3}M) was tested over a pH range of 1-8 and the results are summarized in Fig.3. The potential response remained almost constant over the pH ranges of 3.5-6.3.

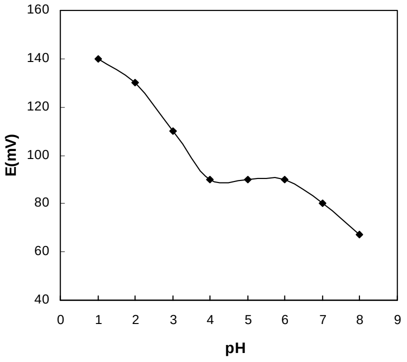

Fig. 3. Effect of pH of test solutions (1.0×10^{-3} M) on the potential response of the Cu(II)-ISE based on BSDDS.

4. Response time

The response time of an ion selective electrode is one of the important factors especially in connection to the analytical applications [16].

The response time, i.e. the time taken by the electrode to achieve stable and low noise potentials. The average time required for the membrane electrode to reach a potential within ±1 mV of the final equilibrium value after successive immersion of Cu(II) ion solutions, each having a 10-fold difference in concentration, was investigated. A potential-time plot for the electrode is given in Fig. 4. The static response time of the PVC membrane thus obtained was 15 s for concentration 1.0×10^{-3} M. It should be noted that the equilibrium potentials essentially remained constant for more than 5 min, after which only a very slow divergence within the resolution of the potentiometer (±1 mV) was recorded.

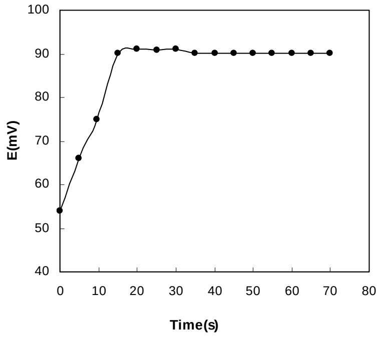

Fig. 4. Static response time of proposed electrode by changing the Cu^{2+} concentration from1.0×10^{-4} to1.0×10^{-3}.

5. Potentiometric Selectivity

The membrane sensors have many characteristics but the most important of them is the relative response respect to the selected cation over other cations present in the solution [21, 22]. This characteristic is expressed in terms of potentiometric selectivity coefficient (K^{SSM}).

This was evaluated by the separate solution method (SSM) [23] at the 1.0×10^{-3} M concentration of Cu(II) according to the following equation:

$$\log K^{SSM} = [(E_B - E_A)\, Z_A\, F/2.303\,RT] + \left(1-\frac{Z_A}{Z_B}\right)\log a$$

where E_A is the electrode potential for the solution of Cu(II) ions and E_B is the electrode potential for the solution of other cations in the same activities. As seen from Table 2, with the exception of Mg^{2+} ion, the selectivity coefficients obtained for all other cations were in the order of 10^{-2} or smaller, indicating that they do not disturb the functioning of the Cu(II) ion selective electrode significantly.

Table 2. Potentiometric selectivity coefficient of various interfering cations (X^{n+})

Ag^{+}	1.8×10^{-2}	Mg^{2+}	2.8×10^{-1}
M^{n+}	$K^{SSM}_{Cu^{2+}}$	M^{n+}	$K^{SSM}_{Cu^{2+}}$
Ca^{2+}	1.4×10^{-2}	Sr^{2+}	5.1×10^{-2}
Na^{+}	5.7×10^{-3}	Mn^{2+}	1.6×10^{-2}
Zn^{2+}	2.1×10^{-2}	Hg^{2+}	3.1×10^{-2}
K^{+}	4.9×10^{-3}	Ba^{2+}	2.7×10^{-2}

6. Analytical Application

One of the most important properties of EDTA as a titrant is its reaction with some metal ions by the ratio of 1:1 .This reaction takes place in low acidic condition [12].The formation constant of CuY^{-2} is $K_f = 6.3\times 10^{18}$[12]. The practical application of the electrode was tested by using it as an indicator electrode to determine the end point in the potentiometric titration of Cu(II) with EDTA solution. Fig.5 shows the titration of 20 ml of 1.0×10^{-4} M solution of Cu(II) with 1.0×10^{-3}M solution of EDTA. As seen, the amount of Cu^{2+} ions in solution can be accurately determined with the sensor. The electrode was successfully applied to the direct determination of Copper in different spiked sample.

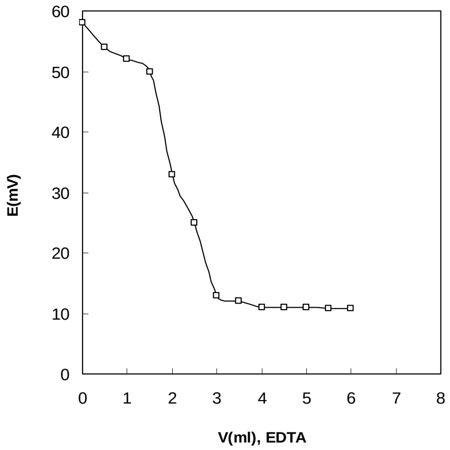

Fig. 5. Potentiometric titration curve of 20 ml of 1.0×10^{-4}M Cu^{2+} solution with 1.0×10^{-3}M EDTA using proposed electrode as an indicator electrode.

CONCLUSION

The made membrane sensor can be used to determine Cu (II) in the wide concentration range. The sensor exhibited good reproducibility over a useful lifetime about 2 months.

This electrode is supervior to the existing electrodes with regard to the slope, pH range, response time and selectivity over a number of cation (Table 2). The present electrode permits the direct measurement of Cu(II) in real samples without prior separation steps, thus considerabiy simplifying the determination procedure with respect to the other analytical methods used.

REFERENCES

1. Buhlmann, P., Pretsh, E., Bakker, E., Chem.Rev. 1998, 98, 1593 .
2. Zanjanchi, M.A., Arvand, M., Akbari, M., Tabatabaeian, K., Zaraei, G., Sensors and Actuators B 2006,11, 3304-309.
3. Aghaie, H., Giahi, M., Monajjemi, M., Arvand, M., Naffisi, G.H., Aghaie, M., Sensors and Actuators B 2005, 107, 156-161.
4. Arvand , M., Moghimi, A. M., Afshari, A., Mahmoodi, M., Anal.Chim.Acta. 2006, 579, 102-108
5. Aghaie, H., Fekri, M.H., Arvand, M., Zare, K., Aghaie, M., Iranian J. Phys. & Theo. Chem. I. A.U. 2006, 3, 145-150.
6. Aghaie, M., Zare, K., Giahi, M., Iranian J. Phys. & Theo. Chem. I. A. U. 2006 ,3, 151-158.
7. Venugopal, B., Luckey, T. D., Metal toxicity in mammals 1978, Vol 2. Plenum Press, New York.
8. Linder, M.C., Moor, J.R., Wright, K., J Nat Cancer Inst.1981, 67, 263.
9. Tyrala, E.E., Brodsky, N.L., Auerbach, V., Am J Clin Nutr. 1982, 35, 542.
10. Berman, E., Toxic metals and their analysis. 1980, Heyden and Sons, London
11. Castillo Duran, C., Fisberg, M., Uauy, R., Rev Chil Pediatr, 1982, 53, 262.
12. Dauglas, A. S., Donald, M. W., Fundamental of Analytical Chemistry, Third Edition 1976, 13.
13. Tavakoli, N., Shamsipur, M., Anal.Lett. 1996, 29, 2269.
14. Mousavi, M. F., Shamsipur, S., Alizadeh, N., Shamsipur, M., Anal. Chim. Acta. 2000, 414, 89.
15. Sing, A. K., Ponwar, A., Kumar, S., Baniwol, S., Analyst 1999, 124, 521.
16. Kamata, S., Bhale, A., Fukunaga, Y., Murata, A., Anal. Chem. 1988, 60, 2464.
17. Bakker, E., Buhlmann, P., Pretsh, E., Chem. Rev. 1997, 97, 3083.
18. Huser, M., Gehrig, P. M., Morf, W. E., Simon, W., Lindner, E., Jeney, J., Tokh, K.,Pangor, E., Anal. Chim. Acta. 1991, 63, 1380.
19. Mikhelson, K. N., Lewenstan, A., Ddina, S. E., Electroanalysis, 1999, 11, 793.
20. Ammann, D., Presch, E., Simon, W., Lindner, E., Bezegh, A., Pungor, E., Anal.Chim.Acta.1985, 101, 119.
21. Umezawa,Y., CRC Hand book of Ion-selective Electrodes, Boca Raton (Fl) CRC Press,1990.
22. Baliley, P.L., Analysis with Ion – selective Electrodes, London, Heyden, 1996.
23. Badavy, S. S., Shoukry, A. F., Assa, Y. M., Analyst, 1986, 111, 1363.