

Thermodynamic study of Cu(II) ion-selective membrane electrode based on bis (N-salicylidene-3,3'-diamino diphenyl) sulfone

E. Baghdar¹, F. Fekri Lari¹, M. Giasi², S. Farhadi³ and M. Aghaie^{4,*}

¹ Ph.D. Student, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

² Department of Chemistry, Faculty of Science, Lahijan Branch, Islamic Azad University, Lahijan, Iran

³ Department of Chemistry, Lorestan University, Khorramabad, Iran

⁴ Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

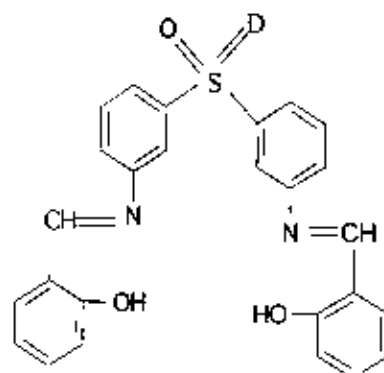
The effect of temperature on the behavior of Cu(II) ion electrode based on bis(N-salicylidene-3,3'-diamino diphenyl) sulfone (BSDDS) was studied. This electrode showed a good Nernstian response in the temperature range of 20-50 °C. Also, the behavior of the synthesized electrode was investigated in the mixed solvents "ethanol+water" and "dioxane+water".

Keywords: Temperature coefficient; Mixed solvent; Nernstian response

INTRODUCTION

The development of selective membrane electrodes based on neutral carriers is one of the most promising trends in ionometry [1]. 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 [2,3] and their use in the medical area, environmental, agricultural and industrial field is developing day to day [2-6]. Copper is one of the most important elements. It distributes in the environment of industrialized countries. It, almost, contributes in all organisms, land and marine. Copper is an essential element for many biological processes, e.g. blood formation and the functions of many important enzymes [7-11].

In our previous work, we published some behaviors of Cu(II)-ion selective electrode based on bis (N-Salicylidene-3,3'-diamino diphenyl) Sulfone (BSDDS) which we abbreviate it as B Cu(II)ISE [12]. But in this work we have tried to study the effect of temperature and mixed solvents on the behavior of this electrode.



Scheme 1. Structure of bis[N-Salicylidene-3,3'-diamino diphenyl] Sulfone (BSDDS) as ionophore.

EXPERIMENTAL

Apparatus

A metrohm pH/mV meter, an Ag-AgCl/KCl (satd) electrode in conjunction with the respective indicator electrode, SCE, and a Haeke model FK2 circulation water bath at considered temperature were used.

*Corresponding author. marmin20042000@yahoo.com
m-aghahae@iau-tb.ac.ir

Reagents

All reagents except BSDDS were of analytical reagent grade but BSDDS was synthesized and purified in the laboratory of Lorestan university. Reagent grade, oleic acid (OA), tetrahydrofuran (THF), dibutyl phthalate (DBP) and high relative molecular weight PVC (all from Merck) were used as received. Nitrate salt of copper used (from Merck) and was of the highest purity available and used without further purification. Double distilled deionized water was used throughout of this work.

Electrode preparation

The optimized electrode for each case of our works was prepared by mixing of 60% DBP in the presence of 30% PVC, 5% innophore and 5% oleic acid [12].

It should be noted that the presence of lipophilic and immobilized ionic additive [13, 14] or salt of two lipophilic ions [15] could diminish the membrane resistance and eliminate the diffusion potential [16,17].

The changes of E^0_{cell} with temperature can be fitted as eq.(1)

$$E^0_{cell}(t^0C) = E^0_{cell}(25^0C) + (dE^0/dt)_{cell}(t-25) \quad (1)$$

where t represent temperature in selsius and dE^0/dt is temperature coefficient of the cell [18-20].

A plot of E^0_{cell} versus (t-25) produced a straight line, as shown in Fig. 2. The slope of this line was taken as the temperature coefficient of the cell. It amounts near to 0.001 V/ 0C . The standard potentials of the SCE at different temperatures may be calculated using the following equation $E^0_{SCE} = 0.241 - 0.00066(t-25)$ (2)

The values of the standard potential of BCu(II)-ISE, $E^0_{electrode}$, at different temperatures, can be obtained from the following equation

$$E^0_{cell} + E^0_{SCE} = E^0_{electrode} \quad (3)$$

A plot of $E^0_{electrode}$ versus (t-25) gave also a straight line as shown in Fig 3. The slope of this line was taken as the temperature coefficient of BCu(II) ISE. It amounts to 0.004 V/ 0C .

Table 1. Some BCu(II) ISE characteristics at different temperature

Temperature / 0C	Slope/mV/decade	E^0_{cell} /mV	E^0_{ele} / mV	Linear range/M
20	27.2	184.57	428.86	1.0×10^{-6} to 1.0×10^{-2}
25	27.7	192.53	433.55	"
30	27.8	196.87	434.57	"
35	28.0	201.33	435.73	"
40	28.1	206.98	438.08	"
45	28.2	212.42	440.22	"
50	28.4	217.78	442.28	"

RESULTS AND DISCUSSION

Effect of temperature

The synthesized electrode showed a good Nernstian response in the concentration range of $1 \times 10^{-6} - 1.0 \times 10^{-2}$ M at 25^0C . We tested this behavior at some other temperatures, 20, 30, 35, 40, 45 and 50^0C and we observed that this behavior is almostly continuing at every mentioned temperature.

The E^0_{cell} at every mentioned temperature was obtained as intercept of the plot of E_{cell} versus $p^{Cu^{2+}}$. The results are gathered in Tab 1

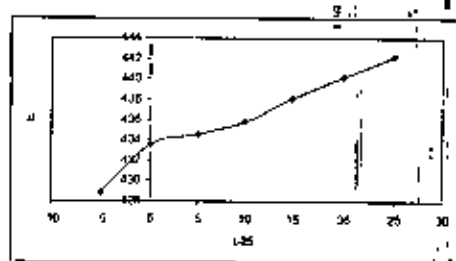


Fig. 2. Variation of standard potential of the cell with temperature.

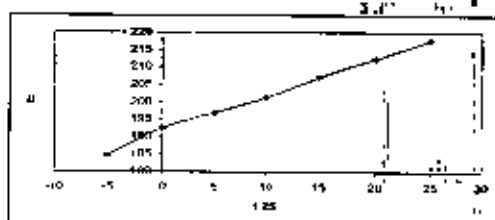


Fig. 3. Variation of standard potential of the electrode with temperature

In addition, the behaviour of electrode was studied in the mixed solvent "ethanol +water" (volume percents of ethanol 0-25%) "and "dioxane+water" (volume percents of dioxane 0-10%) at 25°C respectively. The results are reported in Tab 2.

As it is clear from the Table 2, the electrode gives a fairly good Nernstian response in the mixed solvents (E+W) and (D+W) in the studied range of concentration at 25°C.

CONCLUSION

The synthesized electrode gave a fairly good Nernstian response in the temperature range of 25 to 50°C in aqueous solution and in the concentration range of 1.0×10^{-6} – 1.0×10^{-2} M. This behavior was also observed in the studied

mixed solvents "ethanol+water" and "dioxane+water" at 25°C.

Table 2. The behaviour of BCu(II)-ISE in the mixed solvents

Percentages of compound by volume, V/V	Slope (mV/decade)	Linear range/M
Ethanol 0	29.22	1.0×10^{-6} to
5	31.97	1.0×10^{-2}
10	28.68	"
15	28.22	"
20	26.19	"
25	22.95	"
Dioxane 0	28.86	"
5	28.15	"
10	10.85	"

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