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Potentiometric determination of Copper (II) and Nickel (II) ions using Barium sulphate as an electro active material

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Abstract

A new Araldite matrix membrane electrode for Cu^{2+} and Ni^{2+} ion based on their Barium dichromate as membrane carrier as prepared. The Nernstian response for Cu^{2+} and Ni^{2+} ion over a wide concentration range of (1M-1x10^{-5} M) with detection limits of the order of 10^{-5} M. The response time of the sensor is 40 seconds for Cu^{2+} Ions and 52 seconds for Ni^{2+} ions and membrane can be used for more than six month without observing any deviation. The proposed membrane sensor shows excellent discriminating ability towards Cu^{2+} and Ni^{2+} ions in comparison to several alkali, alkaline earth, transition and heavy metal ions. The effect of pH and effect of medium, selectivity co-efficient values have been found to give better responses.

Key words: Copper (II), Nickel (II), Araldite-matrix, selective membrane sensors.

Introduction

Copper and Nickel is a trace element, which is the both essential and toxic for animals and humans. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthwarms. The decomposition of organic may seriously slow down because of the Nickel is released into the air by power plants and trash incinerators. It will then settle to the ground or fall down after reactions with raindrops. The larger part of all Nickel compounds that are released to the environment will adsorbed sediment of soil particles and become immobile as a result.

The field of ion-selective electrodes bridge fundamental host guest chemistry membrane science and specific application. Because of their simplicity low cost sufficiently reliable and respectable measurements[3-4].

The potentiometric titration becomes popular, as they not only established equivalence points of many reactions. But also provide information about concentration of one or more of the reactants during the titrations.

In the present study a simple[1-2] heterogeneous precipitate based membrane have been prepared along with the potentiometric performances of these sensors. Effect of pH, effect of medium, response time and selectivity co-efficient with respect to different interfering ions have also been studied.

Methodology :

Preparation of ionophore:

A White precipitate of $BaSO_4$ was prepared by adding 10 ml of Barium Chloride (1M) (LR Grade.Hi-Pure fine chem) solution was mixed with 10 ml of Sulphuric acid (1N). The White precipitate obtained was filtered, washed with doubly distilled water. It was dried in air for 12 h and then powdered.

Preparation of membranes:

A number of membranes were prepared using varying amount of powdered precipitate (0.2,0.3,0.4&0.5 g) Fixed amount of (2 drops) of araldite matrix was mixed thoroughly with finely powdered exchanger in varying amounts to make a homogeneous paste which was then applied on a whatmann filter paper No. 42. The pastes obtained for varying amount of precipitates were spread uniformly over the filter paper so that 0.9 mm thickness of the electro active membrane were obtained. The membrane were air dried for 48 h.

Preparation of Ion Selective electrodes:

A circular piece from each of the membrane were cut and fixed with resin at one end of hollow glass tubes of diameter 2 cm and length 10 cm. The tubes were filled with 1M solution of Barium chloride and reference copper metal wire of diameter 0.5 mm and length 12 cm was inserted through the other end of tube in such a way that it remained dipped in the 1 M solution of Barium Chloride. The electrodes were then kept in doubly distilled water for a week and later the EMF measurements were carried out using the following cell assembly

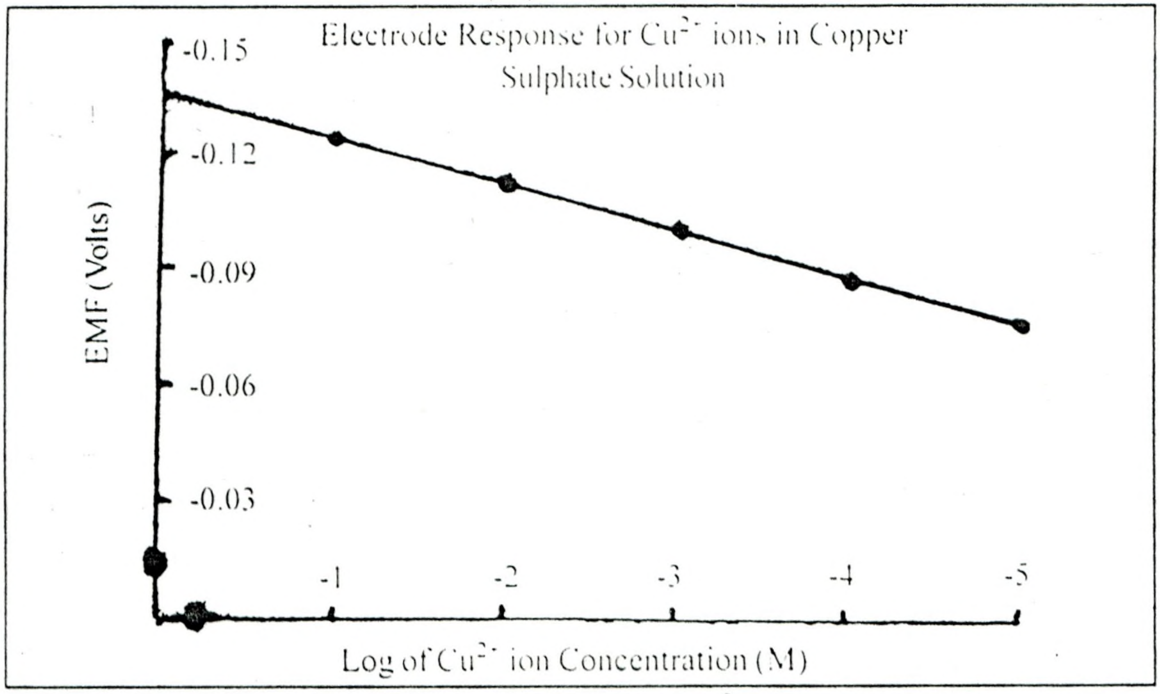
Internal reference Electrode (Cu wire)	Internal reference solution $BaCl_2$ solution	Electro active membrane	Sample solution	External reference electrode (SCE)

Results and Discussion

1) Optimization of membrane composition:

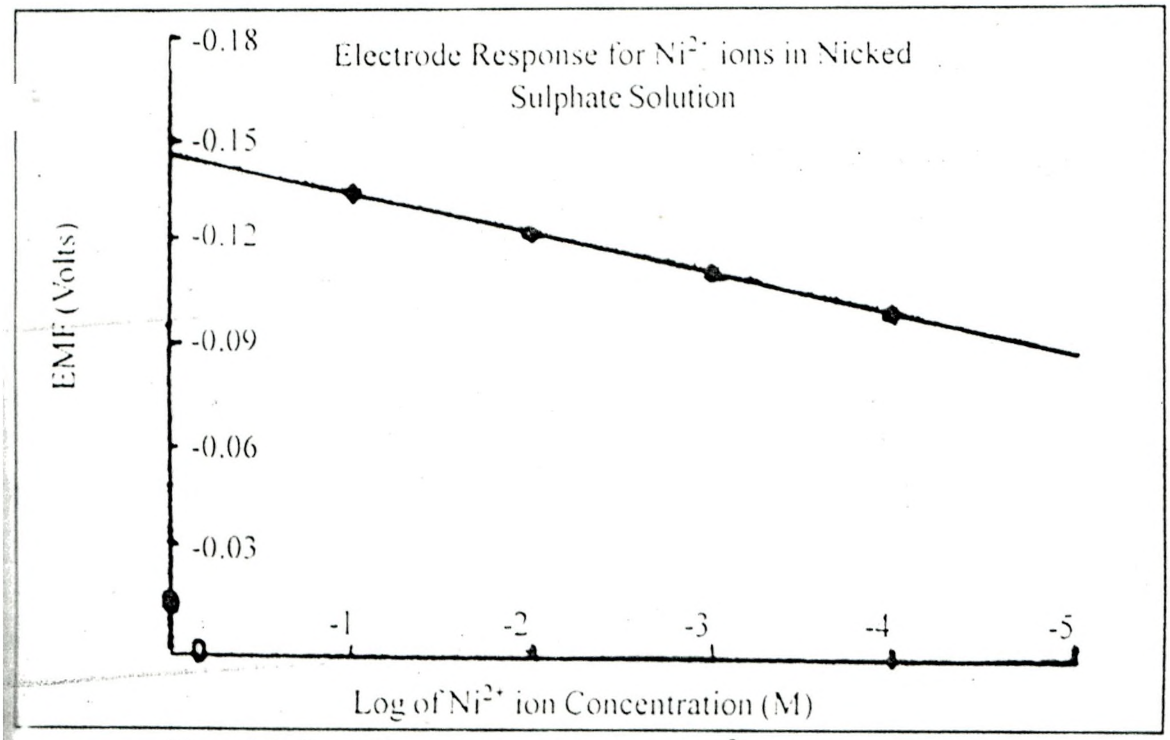
Potential measurements were determined for concentrations of Cu^{2+} as well as Ni^{2+} ion solutions to find the effect of membrane composition on the response of the electrodes. The electrode give linear response to Cu^{2+} &Ni^{2+} ion concentration in the range of 1M-$1x10^{-5}$M (Table 1 & 2). These Cu^{2+}-ISE and Ni^{2+}-ISE revealed near Nernstian slopes 30mv/decade (Graph-1).

Electrode Response for Cu^{2+} ions



Plot of Cell EMF (Volts) Versus Log of Cu^{2+} ion Concentration

Electrode Response for Ni^{2+} ions



Plot of Cell EMF (Volts) Versus Log of Ni^{2+} ion Concentration

Table1. Comparison of electrode potentials for four electrodes in Copper sulphate solution with varying composition of membranes

Electrode number	$BaCr_2O_7$ (gram)	Binder	Slope (mv/decade)	Measurement Range	Response time (seconds)
1	0.2	Araldite	22	$1x10^{-5}$-1M	80
2	0.3	Araldite	24	$1x10^{-5}$-1M	70
3	0.4	Araldite	23	$1x10^{-5}$-1M	55
4	0.5	Araldite	30	$1x10^{-5}$-1M	40

Table 2. Comparison of electrode potentials for four electrodes in Nickel sulphate solution with varying composition of membranes

Electrode number	$BaCr_2O_7$ (gram)	Binder	Slope (mv/decade)	Measurement Range	Response time (seconds)
1	0.2	Araldite	28	$1x10^{-5}$-1M	85
2	0.3	Araldite	29	$1x10^{-5}$-1M	74
3	0.4	Araldite	28	$1x10^{-5}$-1M	65
4	0.5	Araldite	30	$1x10^{-5}$-1M	52

Electrode response:

A series of aqueous solution of $CuSO_4$ of different concentration ranging from 1M to $1x10^{-5}$ M were prepared. A linear response was observed from 1M to $1x10^{-5}$ M of $CuSO_4$ and $NiSO_4$ solution the values are tabulated in Table 3 and 4.

Table 3. Electrode response for Cu^{2+} ions

S. No.	Concentration of $CuSO_4$ solution (1M)	EMF (Volts)
1	1	-0.136
2	$1x10^{-1}$	-0.124
3	$1x10^{-2}$	-0.112
4	$1x10^{-3}$	-0.100
5	$1x10^{-4}$	-0.088
6	$1x10^{-5}$	-0.076

Standard Electrode potential (E^0) determined by extrapolation method was found to be -0.151 V. The slope value was found to be 28mv/decade. This shows that the electrode behaves according to Nernst equation.

Table 4. Electrode response for Ni^{2+} ions

S. No.	Concentration of $CuSO_4$ solution (1M)	EMF (Volts)
1	1	-0.148
2	$1x10^{-1}$	-0.136
3	$1x10^{-2}$	-0.125
4	$1x10^{-3}$	-0.113
5	$1x10^{-4}$	-0.101
6	$1x10^{-5}$	-0.089

Standard Electrode potential (E^0) determined by extrapolation method was found to be -0.156 V. The slope value was found to be 29 mv/decade. This shows that the electrode behaves according to Nernst equation.

Effect of pH and effect of medium:

To study the effect of pH, a standard solution containing 1M Cu(II) and 1M Ni(II) ion were prepared in which a series of buffer solution 2-4 was added. It was found that the potential remained unchanged with in the pH range of 2 to 4 which is found to be the working pH range for the electrode.

To study the effect of medium, a standard solution containing 1M Cu (II) & 1M Ni (II) ion in a series of 25%, 50%, 75% Acetone, ethanol and propanol medium was studied. It was found that the Cu (II) electrode was good in 25% partially non-aqueous solvent and for Ni (II) electrode was good in 25%. 50%, 75% partially non-aqueous solvent.

Selectivity:

The selectivity which is an important characteristic of a membrane sensor is measured in terms of the potentiometric selectivity K. it measures the response of the sensor towards the primary ion in the presence of secondary ions present in the sample solution. The selectivity co-efficient have been determined using fixed interference methods (FTM) based on semi empirical Nicolskii-Eisenman equation. In this method, the concentration of primary ion, Cu(II) ion & Ni(II) ion is varied where as the concentration of secondary interfering ions is kept constant in the test solution which is $1x10^{-1}$ M. concentration of interfering ion present case.

Table 5.

S. No.	Cation (Interfering ion)	Electrode $K^{pot}_{Ni^{2+},M}$	Anion (Interfering ion)	Electrode $K^{pot}_{Ni^{2+},M}$
1	NH_4^+	-0.145	Br	-0.145
2	Zn^{2+}	-0.144	So_4^{2-}	-0.144
3	Na^+	-0.145	NO^{3-}	-0.145
4	Mg^{2+}	-0.146	$Cr_2O_7^{2-}$	-0.146
5	Li^+	-0.145	Cl^-	-0.145
6	K^+	-0.145	F^-	-0.145
7	Co^{2+}	-0.143	$S_2O_3^{2-}$	-0.143

Table 6.

S. No.	Cation (Interfering ion)	Electrode $K^{pot}_{Ni^{2+},M}$	Anion (Interfering ion)	Electrode $K^{pot}_{Ni^{2+},}$
1	NH_4^+	-0.137	Br	-0.137
2	Zn^{2+}	-0.136	So_4^{2-}	-0.136
3	Na^+	-0.134	NO^{3-}	-0.134
4	Mg^{2+}	-0.135	$Cr_2O_7^{2-}$	-0.135
5	Li^+	-0.137	Cl^-	-0.137
6	K^+	-0.133	F^-	-0.133
7	Co^{2+}	-0.132	$S_2O_3^{2-}$	-0.132

To assess the applicability of the sensor to real samples an attempt was made to determine Cu and Ni ion in soil analysis, water analysis and in alloy analysis. The recovery of Cu (II) and Ni (II) from different analysis was found to be almost quantitative with in the maximum recovery of 99%.

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