Electroanalytical Applications of Some Mixed Complex Combinations with Schiff Base

MARIA PLENICEANU, MARIAN ISVORANU and CEZAR SPINU*

Department of Inorganic Chemistry, Faculty of Chemistry
University of Craiova, A.I. Cuza 13, 1100-Craiova, Romania
E-mail: spinu_cezar@yahoo.com

Four electrodes with liquid membrane, Cu^{2+}-selective and Ni^{2+}-selective were prepared and characterized. Electrodes 1 and 2 are based on mixed complexes of Cu(II) and Ni(II) with N-[2-thyenilmethylidene]-2-aminopyridine as ligand and electrodes 3 and 4 are based on the mixed complexes with N,N'-[2,2'-bis-thyenilmethylidene]tolylene. Cu^{2+}-selective and Ni^{2+}-selective electrodes have been used to determine the copper and nickel ions in aqueous solutions, by both direct potentiometric and potentiometric titration with EDTA. They have also been used for determining the Cu^{2+} and Ni^{2+} ions in industrial waters by direct potentiometry. The analytical results obtained have been checked by the standard addition method and by comparison with determinations through atomic absorption spectrometry.

Key Words: Copper, Nickel, Liquid-membrane electrodes, Potentiometry.

INTRODUCTION

Literature[1–6] has highlighted the achievement of new ion-selective electrodes for a large series of cations and anions and their use in solving various analytical problems, in industrial processes, the automated control of environmental pollution, biochemistry, etc.

The present study is a continuation of our previous work described in earlier papers[7–12] and presents the possibility of obtaining Cu^{2+} and Ni^{2+}-selective electrodes with liquid membrane. These electrodes are based on complex combinations of Cu(II) and Ni(II), extractable in water non-miscible organic solvent.

The response of these electrodes to the concentration of Cu^{2+} and Ni^{2+} in solution has been formally attributed to a process of exchange of Cu^{2+} and Ni^{2+} ions between the analyzed aqueous solution and the solution of membrane in nitrobenzene.

Considering this thermodynamic hypothesis, the expression of the membrane potential was derived:

$$E = E^{o} + RT/2F \ln a_{M^{2+}} \tag{1}$$

where $a_{M^{2+}}$ is the activity of the $Cu^{2+}Ni^{2+}$ ions in aqueous solution. The possibility

of using mixed complexes of Cu(II) and Ni(II) for obtaining selective membranes for the copper and nickel ions has thus been proved.

EXPERIMENTAL

Analytical grade $CuSO_4$, $Ni(NO_3)_2$ and nitrobenzene were supplied by Merck with a purity higher than 99%. The water used was twice distilled and deionized. The mixed complexes used as ion selective membranes were synthesized according to a procedure previously described[13, 14] and characterized by elemental analysis, UV-Vis spectroscopy, IR spectroscopy, NMR and ESR. The electrode used for the determinations was made according to a procedure previously described by Pleniceanu *et al.*[12]

Construction of the electrode: The body of the electrode is made of a 75 mm long teflon tube (1) (Fig. 1) with an inside diameter of 6 mm at the lower end, where it is closed with a 15 mm long graphite rod (2). The latter is impregnated with the solution of the active substance 10^{-3} M in nitrobenzene. The internal reference solution (3) is made up of nitrobenzene in which the complex combination is dissolved. The graphite rod plays the roles of both mechanical support for the liquid membrane and electrical support, taking over the electrical potential of the membrane when this one is in contact with the aqueous phase.

The internal reference electrode has been eliminated by introducing a 115 mm long stainless-steel wire (4) having a diameter of 1.5 mm. The wire was introduced inside the graphite rod and makes contact with the connection terminal (6) of the measuring instrument.
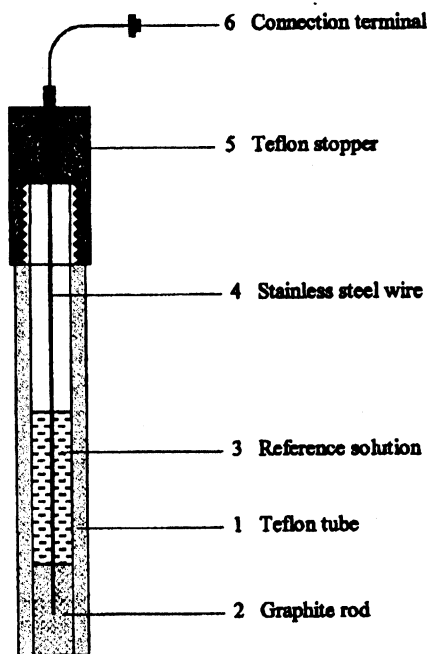

Fig. 1.   Schematic representation of the electrode

In order to prevent evaporation of the internal solution and as a consequence, any change of concentration in the membrane, the electrode is equipped with a screwed teflon stopper (5) at the top through which the stainless-steel wire penetrates, the system being perfectly airtight. The teflon stopper is detachable and allows the filling of the electrode with the organic solution (3).

Electrodes employed: Four new Cu^{2+} and Ni^{2+}-selective electrodes with a liquid membrane have been obtained and characterized. Among these, the electrodes are based on mixed complex combinations of Cu(II) and Ni(II) with N-[2-thyenilmethylidene]-2-aminopyridine (TNAPY) and N,N'-[2,2'-bis-thyenil-methylidene]tolylene (TNATL) as ligands which have the formulas:

TNAPY

CH₃
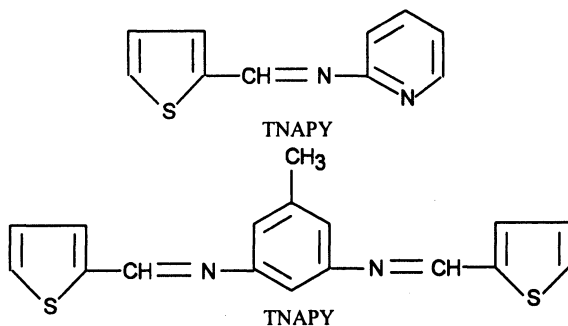
TNAPY

The formulation of the mixed complex combinations of Cu(II) and Ni(II) whose solutions in nitrobenzene constitute the membrane on a graphite rod for the realized electrodes is as follows;

Electrode 1: $[Cu(TNAPY)_2Cl_2]$;   Electrode 2: $[Ni(TNAPY)_2Cl_2]$;

Electrode 3: $[Cu(TNATL)Cl_2]$ Electrode 4: $[Ni(TNATL)Cl_2]$.

RESULTS AND DISCUSSION

Response of electrodes to the concentration of Cu^{2+} and Ni^{2+} ions: In Table-1 are illustrated the variations of electromotive force obtained with the four ion-selective electrodes at 25°C and ionic strength $\mu = 0.4$ (obtained with KNO_3 which does not influence the electrode potential), depending on the concentration of Cu^{2+} and Ni^{2+} ions.

TABLE-1
THE VALUES OF THE ELECTROMOTIVE FORCE OF THE
Cu^{2+} AND Ni^{2+}-SELECTIVE ELECTRODES *vs.* THE SATURATED
CALOMEL ELECTRODE (SCE) AT 25°C, $\mu = 0.4$ (KNO_3) AND pH = 4–4.2

Electrode 1		Electrode 2		Electrode 3		Electrode 4	
$[Cu^{2+}]$	E (mV)	$[Ni^{2+}]$	E (mV)	$[Cu^{2+}]$	E (mV)	$[Ni^{2+}]$	E (mV)
10^{-1}	425	10^{-1}	294	10^{-1}	444	10^{-1}	304
10^{-2}	396	10^{-2}	265	10^{-2}	415	10^{-2}	275
10^{-3}	367	10^{-3}	236	10^{-3}	386	10^{-3}	246
10^{-4}	338	10^{-4}	207	10^{-4}	357	10^{-4}	217
10^{-5}	309	10^{-5}	178	10^{-5}	328	10^{-5}	188
10^{-6}	281	10^{-6}	149	10^{-6}	300	10^{-6}	159
10^{-7}	268	10^{-7}	135	10^{-7}	286	10^{-7}	146

The influence of pH on the response of the Cu^{2+} and Ni^{2+}-selective electrodes was also studied. The pH of the aqueous solution of Cu^{2+} and Ni^{2+} was set at the desired value by means of Kolthoff and Vleeschhouwer[15] buffer solutions. The pH measurements were made with a Jenway 3305 pH-meter, using a glass electrode and a saturated calomel electrode. The variation of pH between 2.5 and

6.35 for Cu^{2+} and 2 and 8.6 for Ni^{2+} does not affect the membrane potential. As a consequence the linear portion of the E-pH curves is a function of the Cu^{2+} and Ni^{2+} concentration in the aqueous phase (Fig. 2).
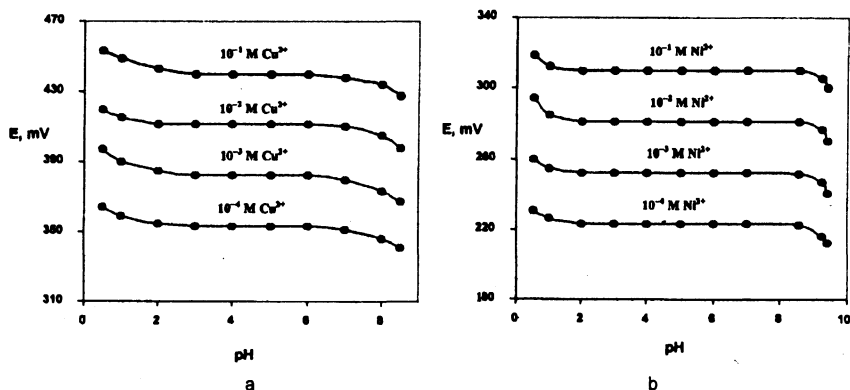

Fi.e 2.   The influence of pH on the reponse of the ion-selective electrodes: (a) [Cu(TNATL)Cl$_2$], (b) [Ni(TNATL)Cl$_2$]

All the direct measurements of the potential were carried out in solutions of $CuSO_4$ and $Ni(NO_3)_2$, respectively, at pH 4 and 4.2, achieved with a CH_3COOH 0.2 M + CH_3COONa (0.2 M) buffer solution (82 mL of CH_3COOH (0.2 M) + 18 mL of CH_3COONa (0.2 M) for pH = 4; 73.5 mL of CH_3COOH (0.2 M) + 26.5 mL of CH_3COONa 0.2 M for pH = 4.2).

Selectivity of the electrodes: The selectivity constants for the cations indicated in Table-2 were estimated by Srinivasan and Rechnitz's method[16] and checked by Eisenman's procedure[17].

TABLE-2

THE CHARACTERISTICS OF Cu^{2+} AND Ni^{2+}-SELECTIVE ELECTRODES
(BASED ON MIXED COMPLEXES) AT 25°C, A CONSTANT
IONIC STRENGTH $\mu = 0.4$ (KNO$_3$) AND pH = 4–4.2

Electrode M^{2+}- selective	$\Delta E/\Delta$ log c (mV)	Range of linear response (M)	Constants of selectivity to the cations: $(\times 10^{-4})$			
			Sn^{2+}	Pb^{2+}	Fe^{2+}	Co^{2+}
1	29	10^{-1}–10^{-6}	4.0	3.5	2.5	5.0
2	29	10^{-1}–10^{-6}	5.7	4.8	6.8	9.5
3	29	10^{-1}–10^{-6}	1.6	2.1	1.0	2.5
4	29	10^{-1}–10^{-6}	5.1	4.6	6.3	8.4

From Table-2 it can be observed that the achieved electrodes have a cationic response $\Delta E/\Delta$ log c of 29 mV at 25°C. This value corresponds to a Nernstian slope of RT/2F. The Nernstian response is obeyed in the concentration 10^{-1}–10^{-6} M for all electrodes based on the mixed complexes. By consequence the Cu^{2+} and Ni^{2+}-selective electrodes can be used within this concentration range for potentiometric determination of copper and nickel.

For Cu^{2+}-selective electrodes 1 and 3, the interference of Ni^{2+} ions is avoided by adding dimethylglioxime as masking agent, while for Ni^{2+}-selective electrodes 2 and 4, α-nitrozo-β-naphthole reagent can be used to avoid the interference of Cu^{2+} ions, in analyzed aqueous solutions.

According to the experimental data given in Table-2, the Cu^{2+} and Ni^{2+} selective electrodes based on mixed complexes have a wider range of linear response and a better selectivity for the interfering ions.

Dynamic response and reproducibility of electrodes: The response characteristics of the Cu^{2+} and Ni^{2+}-selective electrodes were estimated using solutions of $CuSO_4$ and $Ni(NO_3)_2$ with different concentrations (usually 10 times higher) and by recording the values of the potentials as a function of time.

The response times of the electrodes in dilute solutions (10^{-4}–10^{-6} M) were of about 2 min, whereas for more concentrated solutions (10^{-1}–10^{-3} M), the electrode potential reached an equilibrium value in about 20 s.

The reproducibility of the potential measurements was checked during a period of 3–5 weeks for the concentration range 10^{-1}–10^{-6} M $CuSO_4$ and $Ni(NO_3)_2$ for all four electrodes ($\mu = 0.4$).

Analytical applications

The Cu^{2+} and Ni^{2+}-selective electrodes have been used to determine the Cu^{2+} and Ni^{2+} ions in aqueous solution both by direct potentiometry and by potentiometric titration with EDTA.

For the direct potentiometric determination, a calibration curve is used. This has been obtained by the variation of the electrode potential of the Cu^{2+} and Ni^{2+}-selective electrodes 1, 2, 3, 4, as a function of $-\log [M^{2+}]$ vs. the saturated calomel electrode (SCE) as external reference electrode. The experimental data are shown in Table-1, and are obtained at 25°C, $\mu = 0.4$ (KNO_3) and pH 4 (4.2). The lower M^{2+} concentration limit, which can be determined by direct potentiometry, is of 10^{-6} M with electrodes 1, 2, 3 and 4.

The electrodes were also tested for potentiometric titration with EDTA by using 10^{-3} M titrated solutions of $CuSO_4$ and $Ni(NO_3)_2$. This titration was based on well-defined titration curves and a potential change of 194 and 160 mV for electrodes 1 and 2 was observed (Fig. 3). In the case of electrodes 3 and 4 much larger changes of 209 and 162 mV were obtained (Fig. 4).

Determination of copper and nickel by direct potentiometry in industrial waters: Samples of water originating from a water cleaning station were analyzed; the concentration of copper and nickel has been determined for every sample by atomic absorption spectrometry. The content of copper was determined by direct potentiometry using the Cu^{2+}-selective electrode No. 3, based on $[Cu(TNATL)Cl_2]$. In the same way, the content of nickel was determined by using the Ni^{2+}-selective electrode No. 4, based on $[Ni(TNATL)Cl_2]$.

The results of the experimental determinations are given in Table-3, representing the average values of the 10 measurements. It can be observed that the results obtained with the Cu^{2+}-selective electrode No. 3 and the Ni^{2+}-selective electrode No. 4 are in agreement with those obtained by AAS. To certify the advantages of using the potentiometric method with the mentioned Cu^{2+} and Ni^{2+}-selective electrodes, using the method of standard additions, the experimental data were checked.

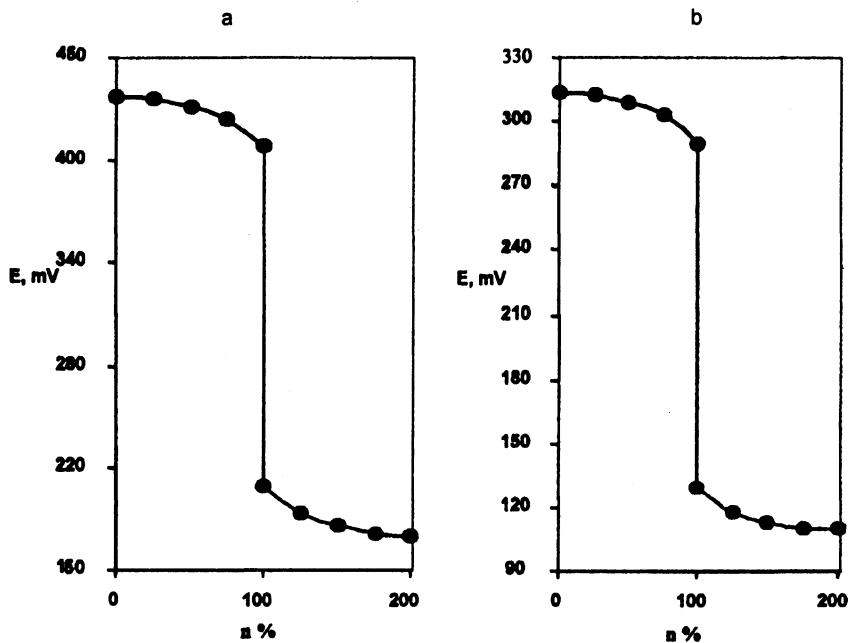Fig. 3.   The potentiometric titration curves of Cu^{2+} (a) and Ni^{2+} (b) ions with EDTA, obtained by using the ion-selective electrodes based on mixed complex with TNAPY
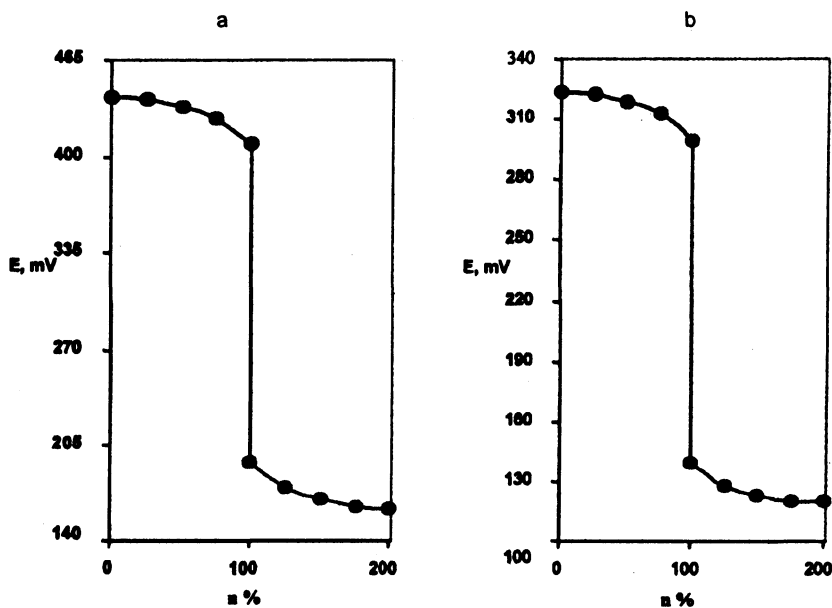

Fig. 4.   The potentiometric titration curves of Cu^{2+} (a) and Ni^{2+} (b) ions with EDTA, obtained by using the ion-selective electrodes based on mixed complex with TNATL

TABLE-3

RESULTS OF Cu^{2+} AND Ni^{2+} IONS DETERMINATION IN INDUSTRIAL WATERS

Sample No.	Cu^{2+} (mg L^{-1})		Ni^{2+} (mg L^{-1})	
	Potentiometrically, with the Cu^{2+}-selective electrode No. 3	By AAS	Potentiometrically, with the Ni^{2+}-selective electrode No. 4	By AAS
1	1.03	1.08	0.17	0.19
2	1.81	1.80	0.23	0.26
3	0.82	0.80	0.10	0.13
4	1.04	1.10	0.21	0.20
5	1.61	1.75	0.23	0.28
6	3.60	3.75	0.13	0.16
7	3.20	3.27	0.28	0.30
8	2.86	2.95	0.35	0.36
9	2.03	2.10	0.44	0.48
10	1.30	1.35	0.24	0.22

The results given in Table-4 and 5 indicate a good agreement of the AAS and direct potentiometric methods. Also, they suggest a proper use of the Cu^{2+} and Ni^{2+}-selective electrodes based on mixed complexes for the determination of copper and nickel ions from industrial waters.

TABLE-4

RESULTS OF Cu^{2+} IONS DETERMINATION IN INDUSTRIAL WATERS USING THE METHOD OF STANDARD ADDITIONS

Sample No.	Cu^{2+} (mg L^{-1})			
	Initial Cu^{2+} (AAS method)	Cu^{2+} added	Theoretical total of Cu^{2+}	Experimental Cu^{2+}, with electrode No. 3
1	0.80	1.00	1.80	1.76
2	1.08	1.00	2.08	2.02
3	1.75	1.00	2.75	2.70
4	2.95	0.50	3.45	3.40
5	3.75	0.50	4.25	4.22

TABLE-5

RESULTS OF Ni^{2+} IONS DETERMINATION IN INDUSTRIAL WATERS USING THE METHOD OF STANDARD ADDITIONS

Sample No.	Ni^{2+} (mg L^{-1})			
	Initial Ni^{2+} (AAS method)	Ni^{2+} added	Theoretical total of Ni^{2+}	Experimetnal Ni^{2+}, with electrode No. 4
1	0.22	2.00	2.22	2.19
2	0.26	1.50	1.76	1.70
3	0.30	1.50	1.80	1.76
4	0.36	1.75	2.11	2.07
5	0.48	1.50	1.98	1.94

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Contact:
Dr. Philippe Bühlmann
Dept. of Chemistry, University of Minnesota
207 Pleasant St. SE
Minneapolis, MN 55455, USA
E-mail: matrafured@org.chem.ethz.ch
Website: http://www.matrafured-05.ethz.ch