



SELECTIVE SENSORS FOR POTENTIOMETRIC ASSESSMENT OF IODIDE BASED ON ANION RECOGNITION THROUGH COPPER (II) [DIPEPTIDE DERIVATIVE] COMPLEX

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New selective sensors based on potentiometric transduction for iodide assessment are described. The sensors based on the use of a newly synthesized copper (II) [N,N-bis-(1-carboxy-2-(p-hydroxybenzyl))-2,6-di(aminocarbonyl)pyridine] complex (CuL) as neutral ionophore in plasticized poly(vinyl chloride) (PVC) membranes. The influence of lipophilic cationic and anionic additives on the response properties of the sensors was evaluated. The fabricated sensors exhibited enhanced response towards iodide ions over the concentration range 6.3×10^{-6} to 1.0×10^{-2} mol L⁻¹ with a detection limit of $0.33 \mu\text{g mL}^{-1}$ and a slope of -63.6 ± 0.2 mV per decade. These sensors showed a fast and stable response, good reproducibility, and long-term stability. The sensors showed a stable potential over a wide pH range (4.5–9) and exhibited high selectivity for I⁻ ion in the presence of many common anions. The sensors were applied for direct potentiometric measurements of iodide ions over the concentration range 0.8 – $1270 \mu\text{g mL}^{-1}$ and also for the titration of some metal ions (e.g. Ag⁺, Hg²⁺) and MnO₄⁻ through sequential monitoring. The sequential binding of these ions with I⁻ ensured share stepwise titration curves with consecutive end point breaks at the equivalent points.

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Introduction

Anions play an important role in biology, medicine, and environmental chemistry, so there is a constantly increasing need for their online monitoring. Among them, iodide is of particular interest because of its presence in food, drug compounds and in drinking water. Moreover, it is often added to table salt for preventing iodine deficiency disorders.¹ It is also used as a catalyst and stabilizer in the production of polymers and as a disinfectant. Iodine is an essential micronutrient that are required for the biosynthesis of the thyroid hormones thyroxine and triiodothyronine by the thyroid gland. Iodine deficiency is widely known as a global problem because 30% of the world's population lives in an environment where the soil has low iodine content. Also, its deficiency in human causes hypothyroidism and formation of goiter in adults or cretinism in children.² An excess of iodine or iodide ingestion can produce goiter and hypothyroidism as well as hyperthyroidism.^{3,4} Therefore, determination of iodide and other iodine species is an important analytical task in a variety of fields such as food, clinical, biological and environmental samples. Numerous analytical methods have been reported in the literature for iodide determination at trace levels. These include gas chromatography (GC-MS),⁵ neutron activation analysis,⁶ polarography,⁷ spectrophotometry,⁸ chemiluminescence,⁹ pulse stripping analysis,¹⁰ inductively coupled plasma-atomic emission spectrometry¹¹ and capillary electrophoresis.^{12,13} These approaches, although sensitive,

suffer from the need for expensive instrumentation, well controlled experimental conditions, frequent maintenance and sample pretreatment. Therefore, development of analytical techniques for iodide assessment that do not require expensive or complicated equipment has become increasingly important.

On the other hand, potentiometric sensors offer an inexpensive and convenient method for fast analysis with high sensitivity and selectivity.¹⁴⁻¹⁷ They can be considered as one of the promising tools used for direct determination of various species in the biological and industrial analysis.¹⁸⁻²²

Ion selective electrodes (ISEs) for anions, based on ion exchangers such as lipophilic quaternary ammonium or phosphonium salts, displayed classical Hofmeister selectivity behavior in which membrane selectivity is controlled by the free energy of hydration of ions involved.²³ The anti-Hofmeister anion selectivity is obtained in the case of membrane electrodes incorporated with an organometallic complex,²⁴ metalloporphyrins,²⁵ metal phthalocyanines²⁶ and Schiff base metallic complexes.²⁷ This deviation arises from the steric effects coming from the structure of the ionophore and from the binding affinity of the central atom in the ionophore with the anion. Therefore, the focus of this research is on the anion-sensitive materials with anti-Hofmeister behavior.

Several iodide sensors based on a variety of ion carriers have also been reported in the literature.²⁸⁻⁵⁰ Some of these sensors showed narrow linear range^{28,30,31,41,43,44,49,50} narrow pH range,^{31-33,36,43} high detection limit,^{31,49,50} long response time.^{28,49} Others showed a serious interference from some anions such as SCN⁻,^{30,33,34,36,41-43,46,49,50} NO₂⁻,^{39,43,48} Br⁻,^{36,49} CN⁻,^{42,46} and Sal⁻.^{29,30,49,50}

In this study, we have synthesized copper(II) [N,N-bis-(1-carboxy-2-(p-hydroxybenzyl))-2,6-di(aminocarbonyl)pyri-

dine] complex (CuL) as a new ionophore in the fabrication of polymeric membrane sensors for iodide ion assessment. The performance characteristics of the sensors were evaluated and satisfactorily used for accurate determination of μg quantities of iodide. Sequential monitoring of Ag^+ , Hg^{2+} , Bi^{3+} and MnO_4^- in single or binary mixtures via the titration with iodide was also performed. The sequential binding of these ions with I^- shared stepwise titration curves with consecutive breaks at the equivalent points.

Experimental

Reagents and solutions

All chemicals were of analytical-reagent grade. Twice-distilled water was used to prepare all solution and in all experiments. Dioctyl phthalate (DOP), *p*-chlorotetrakis-tetraphenyl borate (*p*CITPB) and high molecular weight polyvinylchloride (PVC) were obtained from Sigma-Aldrich (Steinheim, Germany). Tridodecylmethylammonium chloride (TDMAC) and THF were purchased from Fluka (S.A.G. Buchs, Switzerland). All anions used were in their sodium salts and purchased from Merck [Dermasdat, Germany]. The ligand [N,N-bis-(1-carboxy-2-(*p*-hydroxybenzyl))-2,6-di(aminocarbonyl)pyridine] (Figure 1) was synthesized as described before.⁵¹ Standard iodide solution, 0.1 mol L^{-1} , was prepared by dissolving accurately weighed NaI in 100 mL twice-distilled water. Iodide solutions used for the sensor characterization (1×10^{-6} – $1 \times 10^{-2} \text{ mol L}^{-1}$) were prepared daily from the stock solution. The ionic strength (IS) was adjusted to 0.01 mol L^{-1} by means of a $3.5 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution. The pH adjustment was carried out with 0.01 mol L^{-1} phosphate buffer solutions of pH 6 in addition to 0.01 mol L^{-1} IS.

Equipment

All potentiometric measurements were made at $25 \pm 0.1^\circ\text{C}$ with a Cole-Parmer pH/mV meter (USA model 59003-05) and iodide-PVC membrane sensors in conjunction with a Sentek, Ag/AgCl double junction reference electrode (UK model R2/2MM) filled with $1.0 \text{ mol L}^{-1} \text{ KNO}_3$ in the outer compartment. A combination glass pH electrode (Schott blue line 25, Germany) was used for all pH measurements. The IR spectra were measured on Prestige-21 FT-IR instrument (SHIMADZU, Japan). The thermal studies were carried out using DTG 60 AH (SHIMADZU, Japan) under the following conditions: temperature ranges 25 – 1000°C , heating rate $25^\circ\text{C min}^{-1}$ and sample weight 6.0 mg . Elemental analyzes were carried out on Elementar Vario EL cube, Germany. Cu-content was determined by Perkin Elmer Atomic Absorption Spectrometer (Model 3100 USA). The molar conductivity of the complex was measured by using OAKTON (Model CON510 USA) conductivity meter.

Syntheses of the complexes

A 20 mL of a methanolic solution containing 2.77 g (10 mmol) of $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was added to a hot 20 mL methanolic solution containing 10 mmol of the ligand. After stirring for 1 h , the formed green precipitate complex was filtered, collected and then washed for several times with

hot methanol until the filtrate became colorless. The complex was dried in a desiccator over anhydrous CaCl_2 under vacuum. The dried ligands and complex were subjected to IR, elemental and thermal gravimetric analysis. The complex is air-stable, nonhygroscopic, insoluble in H_2O , slightly soluble in ethanol. The elemental analysis of the free ligand [L] ($\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_8$) was found: C, 60.84; H, 4.69; N, 8.51. Characteristics of the complex were as follows: $[\text{CuL} \cdot \text{H}_2\text{O}]$ ($\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_9\text{Cu}$): Yield 85%. Color: green. M.P. $>300^\circ\text{C}$. $\Lambda_m(\Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1})$ 4.2. Elemental analysis: Found (%): C 52.358; H 4.014; N 7.3302; Cu 11.082. Calcd: C 52.21; H 4.35; N 7.31; Cu 11.05.

Sensors preparation and EMF measurement

The procedure to prepare the PVC membrane was based on mixing 190 mg of powdered PVC, 10 mg of the ionophore, 2 mg of cationic additive TMDAC and 350 mg of plasticizer DOP. The mixture was dissolved in 3 mL of dry THF. The membrane solutions were cast into conductive supports of tubular shapes and left overnight for drying. The sensors were then conditioned before use by soaking in $0.01 \text{ mol L}^{-1} \text{ NaI}$ solution (for at least 24 h) and stored in the same solution when not in use. Calibration was made by immersing the membrane sensor in conjunction with a double junction Ag/AgCl reference electrode in 25 mL beakers containing 10 mL aliquots of standard 1.0×10^{-6} – $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ NaI}$ solution. The pH of the solutions was adjusted to 6 using 0.01 mol L^{-1} phosphate buffer. Potential readings were carried out for iodide until stabilization occurred. The calibration plot was constructed by plotting the measured potential as a function of the logarithm of iodide concentrations. This calibration plot was used for subsequent measurements of unknown iodide samples.

Direct potentiometric determination of iodide

Iodide / iodine in pharmaceutical samples was analyzed using $[\text{CuL} + \text{TDMAC}]$ membrane sensor. Vaginal douche and mouthwash (1 – 10% w/v), collected from the local market, were diluted with de-ionized water. For total iodide + iodine measurement, the iodide sensor and a Sentek Ag/AgCl double junction reference electrode were immersed in a 25 mL beaker containing 10 mL of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ phosphate buffer of pH 6 and ascorbic acid 0.1 mol L^{-1} for reduction of iodine into iodide. Aliquots ($200 \mu\text{L}$) of the diluted samples were successively added and the potential response of each sample was measured after potential stabilization. Other aliquots ($200 \mu\text{L}$) of the diluted samples were successively added to a 25 mL beaker containing 10 mL of a 0.1 mol L^{-1} resorcinol of pH 8.0. The potential response is equivalent to $\frac{1}{2} \text{I}_2$ and I^- .

The calibration plot was constructed by plotting the potential change against the logarithm of the I^- concentration. The plot was then used for subsequent determination of unknown I^- samples.

Potentiometric titration of metal ions

A series of potentiometric precipitation titrations was performed in which the sensor was used as an indicator electrode to locate the equivalence point. Sample solutions

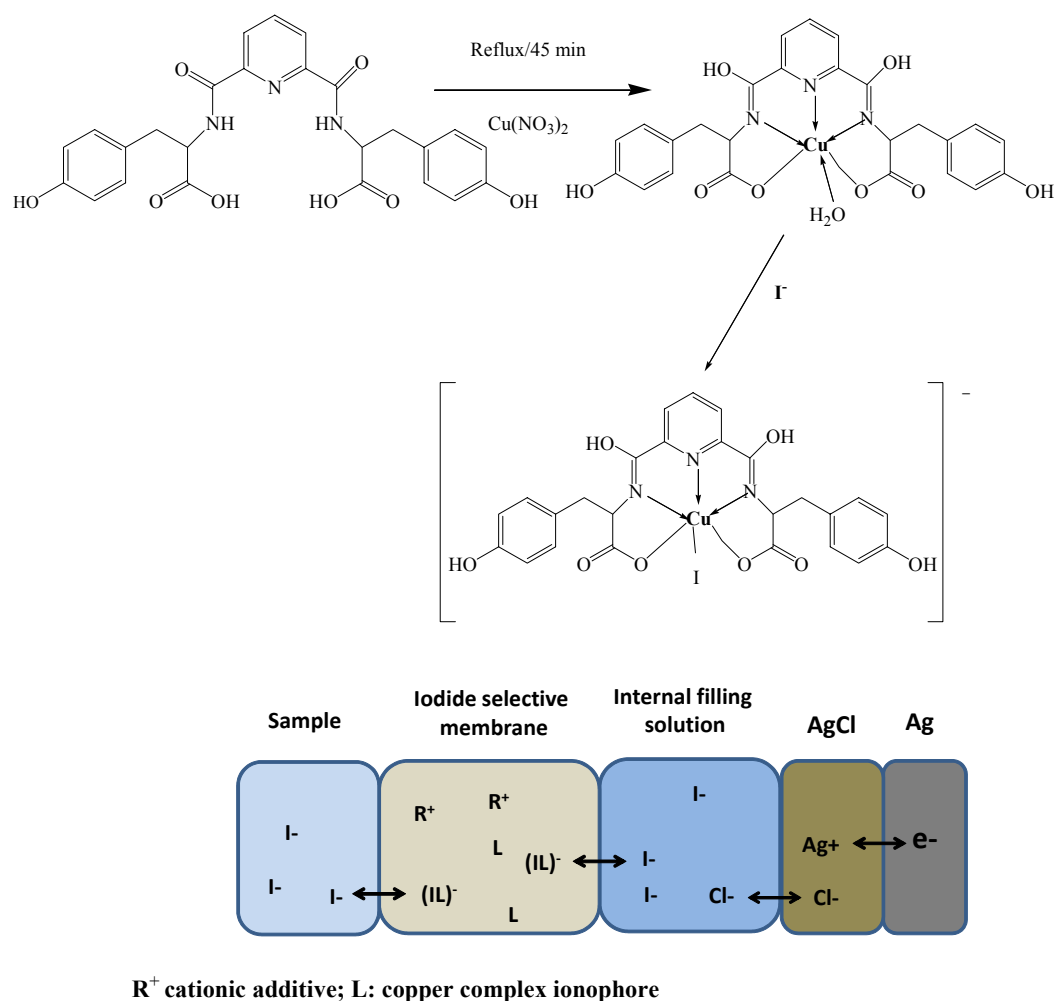


Figure 1. Chemical structure of the ionophore and an illustrative scheme describing the measuring instrument.

containing a single ion (e.g. Ag^+ , Hg^{2+} , MnO_4^-) were then titrated with $0.01 \text{ mol L}^{-1} \text{I}^-$. The equivalence points at each inflection break were determined and the concentration of each ion was assessed ($1 \text{ mol I}^- = 0.5 \text{ mol Hg}^{2+} = 1 \text{ mol Ag}^+ = 0.33 \text{ mol MnO}_4^-$).

Results and discussion

All applied ionophore in the ISE field must be able to bind the target ion via a selective (pattern) reversible reaction in order to generate a stable response in a short time.⁵² The potentiometric sensor containing the CuL ionophore significantly responded to iodide ion according to Nernstian response over other common anions. Therefore, the detailed characteristic performance of the membrane sensor based on the application of this carrier has been evaluated. In a preliminary experiment, membranes with/without the ionophore were constructed. Blank membranes showed poor selectivity toward iodide and their response was not reliable. However, the addition of the proposed ionophore to the membrane leads to the generation of a Nernstian response and remarkable response to iodide ions over several common anions. The preferential response toward iodide anion is believed to be associated with its selective coordination as a carrier to the copper center in the complex.

Structural properties

Pyridine carboxamides can be considered as a burgeoning class of multidentate ligands containing carboxamide [-CONH-] linkage. It can be prepared from condensation reactions between pyridyl-bearing amine or carboxylic acid precursors, promoted by coupling agents such as 1,1'-carbonyldiimidazole, diphenoxy phosphoryl azide or triphenyl phosphite.⁵³⁻⁵⁵ The behavior of pyridine carboxamides towards biologically relevant d-block metals has been widely investigated. These ligands support a range of coordination numbers, geometries, and nuclearities for copper (II).⁵⁶⁻⁶⁰

Elemental analysis and magnetic susceptibility data of the ligand and complex indicated the formation of 1:1 $[\text{Cu:L}]$. The molar conductance values of the synthesized complex determined using $1 \times 10^{-3} \text{ mol L}^{-1}$ DMF solution were in the range of $4.5\text{--}6.8 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$. These results suggested the presence of a non-electrolytic nature in the same solvent.⁶¹ These values also indicated that there were no anions in the outer coordination sphere.

The IR spectrum of the complex, in comparison with that of the free ligand, displayed significant changes that could be indicative of the type of coordination (Figure 2). The FTIR spectrum of free ligand showed characteristic bands at

3600 – 2617 (broadband, OH, and NH), 1728.2 (C=O, acid), 1662.6, 1516, 1230.5 (amide I, II and III) cm^{-1} . In the IR spectra of metal complexes, characteristic bands at 3600 – 2750 (broadband, OH phenolic, and OH iminol), 1627 (C=N, iminol), and 1384.8 (C=N, bending). The peaks at 1732, 1657, 1533 and 1225 were completely disappeared. In addition to these bands, the complex also showed weak bands at 837.1, 759.9 and 660-640 cm^{-1} due to coordinated water. On the basis of the physical and spectral data of the free ligand and the complex discussed above, one can assume that the two imide groups coordinate to copper ion forming iminol groups in addition to (nitrogen) from pyridine and the two carboxylic groups present in the free ligand as illustrated in Figure 1.

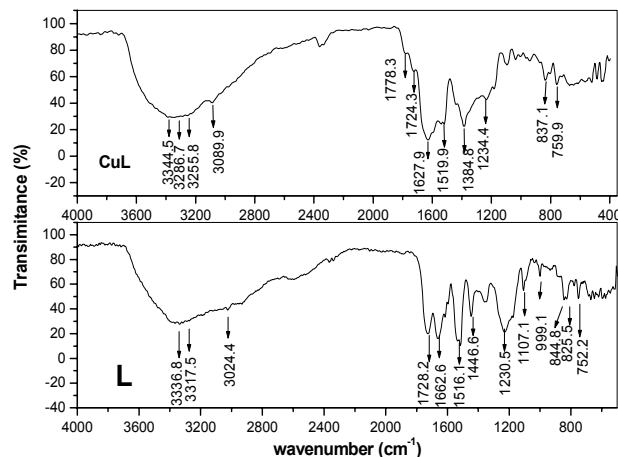


Figure 2. FTIR spectrum for the free ligand and its copper complex.

The thermal gravimetric analysis of the complex was shown in figure 3. The dehydration step in the complex occurred in the 60-120 $^{\circ}\text{C}$ range. The weight losses correspond to the loss of one water molecule and the complex decomposed in three steps via the formation of unstable intermediates. The decomposition started at 173-445 $^{\circ}\text{C}$ and ended at 450-1000 $^{\circ}\text{C}$ (oxides formation). The metal percentages of the complex were calculated from the residual metal oxide % formed in the final step and were in good agreement with data obtained by the elemental analysis. On the basis of the above observations, the following general scheme for thermal decomposition may be proposed for the metal complex.

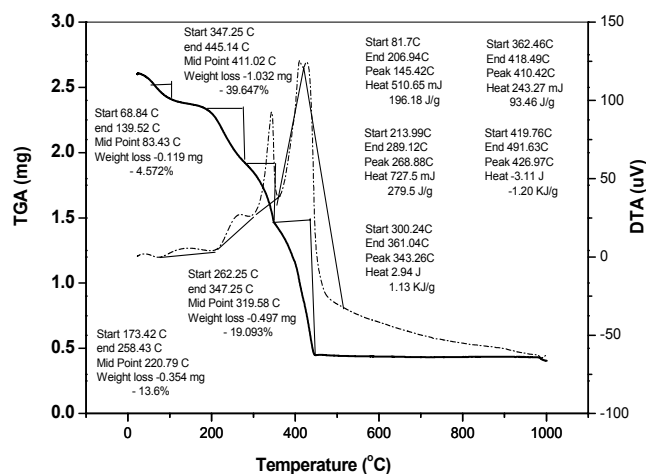


Figure 3. TG and DTG-plots of the Cu (1:1) complex.

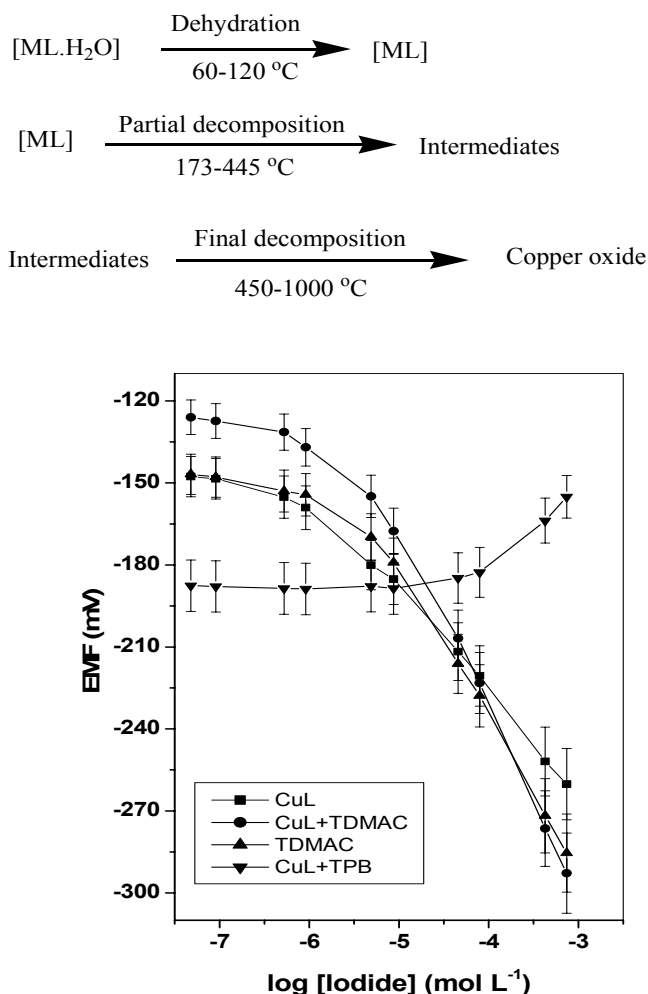


Figure 4. Potentiometric plot of iodide membrane sensors in 0.01 mol L^{-1} phosphate buffer (pH 6.0).

Response characteristics of iodide sensors

The potentiometric response characteristics of the sensors assembled with the different membranes were shown in Figure 4. The sensor based on [copper complex] showed a linear response towards iodide over the concentration range of 4.1×10^{-6} – 1.0×10^{-3} mol L^{-1} in a 0.01 mol L^{-1} phosphate buffer solution of pH 6 with a slope of -35.5 ± 2.3 mV decade $^{-1}$ and a detection limit of 0.13 $\mu\text{g mL}^{-1}$. On the other hand, the addition of 5 mg of TDMAC relative to the ionophore to the membranes showed an enhancement of the potentiometric response characteristics. These membrane electrodes exhibited a slope of -63.6 ± 0.2 mV decade $^{-1}$ over the concentration range of 6.3×10^{-6} – 1.0×10^{-3} mol L^{-1} and detection limit of 0.32 mol L^{-1} . However, the sensor based on cationic additive alone showed a linear response towards iodide over the concentration range of 6.1×10^{-6} – 1.0×10^{-3} mol L^{-1} with a slope of -53.6 ± 0.3 mV decade $^{-1}$ and detection limit 8.9 $\mu\text{g mL}^{-1}$ (Table 1). This is in accordance with the results reported previously that the cationic sites in neutral carrier-based electrodes can stabilize the formation of the negatively charged product (iodide copper complex) in the membrane phase as well as lowering the electrical membrane resistance and improving the potentiometric response characteristics of the membrane electrodes.⁶²⁻⁶⁴

Table 1. Response characteristics of [CuL] membrane based sensors at pH 6.

Parameter	CuL	CuL+TDMAC	TDMAC
Slope, mV decade ⁻¹	-35.5±2.3	-63.6±0.2	-53.6±0.3
coefficient, r	-0.996	-0.997	0.999
Detection limit, µg mL ⁻¹	1.0 × 10 ⁻⁶	2.5 × 10 ⁻⁶	6.1 × 10 ⁻⁶
Linear range, mol L ⁻¹	4.1 × 10 ⁻⁶ - 1.0 × 10 ⁻³	6.3 × 10 ⁻⁶ - 1.0 × 10 ⁻³	7.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²
Response time, s	10 - 20	10 - 20	10 - 20
Working pH range	4.5 - 9	4.5 - 9	4 - 10
SD (%)	1.3	1.5	1.5
Accuracy (%)	99.3	98.8	98.7
Precision, C _v w(%)	0.9	0.7	1.1
Between-day variability, C _v b(%)	1.1	0.9	0.9

The robustness of the method was also evaluated via testing the effect of pH and the measuring time on the potentiometric response. The influence of the pH was tested using 10⁻⁴ and 10⁻³ mol L⁻¹ iodide solutions over the pH range 2–10. Adjustment of pH values was carried out using NaOH and/or HCl. From pH-potential profiles, it was apparent that there is no change in potential response within the pH range 4.5–9 for all sensors. At high pH values (> 9), the sensor response increased, probably due to the ability of hydroxide ions to be coordinated on the axial coordination site of the central metal. At pH < 3, the response towards iodide decreased probably due to the oxidation of iodide into iodine by molecular oxygen which was stabilized in acidic medium.

The response time of the electrodes was obtained by measuring the time required to achieve a steady state potential (within ± 1mV) after successive immersion of the electrodes in a series of iodide ions solutions, each having a 10-fold increase in concentration from 1.0 × 10⁻⁶ to 1.0 × 10⁻³ mol L⁻¹. The actual potential versus time trace showed, all concentrations ranges, that the sensors reach the equilibrium response in a very short time (<10 s). These results indicate that all sensors were amenable to be used with the automated system.

Selectivity

Potentiometric selectivity coefficients ($K^{pot}_{I,B}$) were evaluated according to IUPAC guidelines using the separate solutions method^{65,66} in which the potential of a cell comprising the membrane electrode and a reference electrode is measured with two separate solutions, one containing the iodide ion *A* at the activity a_A (but no *B*), the other containing the interfering ion *B* at the same activity $a_A = a_B$ (but no *A*) and E_A and E_B are the measured values, respectively. Different interfering anions at a concentration of 1 × 10⁻³ mol L⁻¹ at pH 6 were utilized and the results were obtained using the equation:

$$\log K^{pot}_{A,B} = (E_B - E_A)/S + (1 - Z_A/Z_B) \log a_A \quad (1)$$

where

$K^{pot}_{A,B}$ is the potentiometric selectivity coefficient,
 S the slope of the calibration plot,
 a_A the activity of iodide and
 Z_A and Z_B are the charges on I⁻ and the interfering anion, respectively.

The selectivity coefficient values were shown in Table 2. The selectivity coefficients of [CuL] membrane sensor without membrane additive were in the order: I⁻ > SCN⁻ > ClO₄⁻ > IO₄⁻ > IO₃⁻ > Asco⁻ > Cl⁻ > Br⁻ > NO₂⁻ > NO₃⁻ > F⁻ > SO₄²⁻ > CH₃COO⁻ > PO₄³⁻. For [CuL] based membrane sensor doped with TDMAC as a cationic additive, the selectivity behavior of the sensor was in the order: I⁻ > ClO₄⁻ > IO₄⁻ ~ SCN⁻ > NO₃⁻ > Br⁻ > IO₃⁻ > NO₂⁻ ~ Cl⁻ > Asco⁻ > SO₄²⁻ > F⁻ > PO₄³⁻ > CH₃COO⁻ which is almost identical with the Hofmeister pattern. Membrane sensors incorporating [CuL] without additives exhibited enhanced selectivity towards iodide ions but the selectivity pattern was anti-Hofmeister. This selectivity order clarified that the response mechanism is a neutral carrier mechanism that showed a non-Hofmeister selectivity pattern. This explanation is based on the strong coordination affinity between the metal center in the ionophore and the iodide ion.

Table 2. Selectivity coefficients ($K^{pot}_{I,j}$) of iodide PVC membrane sensors.

Ion	[CuL]	[CuL]+TDMAC	TDMAC
I ⁻	0	0	0
IO ₄ ⁻	-2.60	-0.8	+1.1
IO ₃ ⁻	-3.12	-2.21	-2.85
SCN ⁻	-1.80	-0.88	+1.0
Ascorbate	-3.40	-3.27	-3.21
ClO ₄ ⁻	-2.10	-0.75	+1.7
NO ₃ ⁻	-3.81	-1.41	-1.2
NO ₂ ⁻	-3.73	-2.66	-2.3
Cl ⁻	-3.42	-2.70	-2.5
Br ⁻	-3.51	-2.06	-2.1
F ⁻	-4.22	-3.61	-3.5
SO ₄ ²⁻	-4.30	-3.42	-3.3
PO ₄ ³⁻	-4.32	-3.92	-4.1
CH ₃ COO ⁻	-4.31	-4.01	-3.9

Determination of iodide and iodine in pharmaceutical formulations

Vaginal douche and mouthwash and vaginal douche collected from local market containing iodide/iodine in pharmaceutical samples were analyzed using [CuL+TDMAC] membrane sensor. Determination of iodine in the presence of iodide ions required two potentiometric measurements. The first involved measurement of total iodine and iodide (I₂ & I⁻) after treatment with a suitable reducing agent such as 0.1 mol L⁻¹ ascorbic acid. The second measurement is done by measuring the remained iodide ions (1/2 I₂ & I⁻) after reaction with resorcinol at pH 8.0 via iodination.⁶⁷ The results obtained for determining iodide and iodine in povidone iodine was in good agreement with data obtained using the titrimetric method recommended by British Pharmacopoeia⁶⁷ (Table 3).

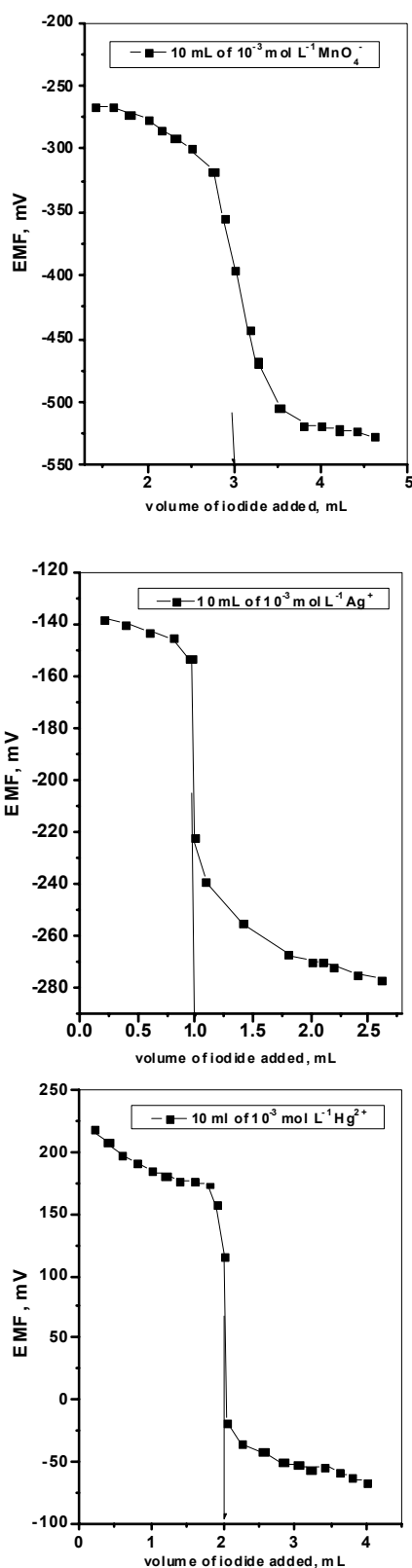


Figure 5. Potentiometric titration plot of Ag^+ , Hg^{2+} and MnO_4^- with $0.01 \text{ mol L}^{-1} \text{I}^-$ using an iodide membrane sensor.

Table 3. Potentiometric determination of povidone iodine using $[\text{CuL}+\text{TDMAC}]$ PVC membrane based sensor.

Sample*	This work	BP ⁶⁶	Recovery, %
Betadine mouth wash	1.87 ± 0.5 $\text{mg I}_2 \text{ mL}^{-1}$	1.91 ± 0.7 $\text{mg I}_2 \text{ mL}^{-1}$	97.9
Betadine vaginal douch	10.23 ± 0.6 $\text{mg I}_2 \text{ mL}^{-1}$	10.12 ± 0.2 $\text{mg I}_2 \text{ mL}^{-1}$	101.1

*Obtained from the Nile pharm. chem., Egypt

Potentiometric titration of metal ions

The iodide membrane sensor based on ionophore (I) was also used for monitoring some ions (e.g. Ag^+ , Hg^{2+} , and MnO_4^-), single or in binary mixtures, with a standardized iodide solution. The titration curves obtained showed sharp inflection breaks ($\sim 80 \text{ mV}$) at 1:1 for I^-/Ag^+ and (~ 200 & 180 mV) at 1:2 and 1:3 reactions for $\text{I}^-/\text{Hg}^{2+}$ and $\text{I}^-/\text{MnO}_4^-$, respectively. Typical potentiometric titration curves were shown in figure 5.

Conclusion

Novel potentiometric iodide sensors based on copper complex of $[\text{N,N- bis-(1carboxy-2-(p-hydroxy benzyl))-2,6-(diaminocarbonyl)-pyridine}]$ were constructed and evaluated. The performance characteristics of the sensors showed stable and selective potential responses towards iodide ions over the concentration range of 6.3×10^{-6} – $1.0 \times 10^{-2} \text{ mol L}^{-1}$ with a limit of detection $2.5 \times 10^{-6} \text{ mol L}^{-1}$ and a slope of $-63.6 \pm 0.3 \text{ mV decade}^{-1}$. The addition of a cationic additive to the membranes showed a slope of $-63.6 \pm 0.2 \text{ mV decade}^{-1}$ over the concentration range of 6.3×10^{-6} – $1.0 \times 10^{-3} \text{ mol L}^{-1}$ and detection limit of 0.32 mol L^{-1} . The iodide PVC-based membrane sensor was satisfactorily used for potentiometric determination of iodide under the static mode of operation in pharmaceutical formulations. Sequential monitoring via potentiometric titration of some ions (e.g. Hg^{2+} , Ag^+ and MnO_4^-) was determined using the iodide sensor to locate the equivalent points. The sequential binding of these ions with I^- ensured share stepwise titration curves with consecutive end point breaks at their equivalent points. It is interesting to note that a comparison of the selectivity and working of the proposed iodide electrode along with those reported before clearly indicate a good enhancement in the behavior of the proposed iodide sensors.

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