

## Highly Selective Iodide–Membrane Electrode Based On [CoL] SO<sub>4</sub>

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**Abstract:** A novel potentiometric membrane sensor has been developed and optimized based on 3,5,13,15-tetramethyl-4,14-diethyl-2,6,12,16,21,22-hexaazatricyclo [15.3.1<sup>1-17</sup>.1<sup>7-11</sup>] dicosal-1,(21),2,5,7,19,11(22),12,15,17,19-decaene Cobalt Sulphate ionophore in poly vinyl chloride matrix membrane (PVC) plasticized with dibutyl phthalate (DBP), for high selective determination of iodide ion. The sensor works well in a linear range:  $1.0 \times 10^{-2} - 1.0 \times 10^{-6}$  M with a Nernstian slope of  $-58.6 \pm 0.4$  mV/decade and its detection limit is  $8.0 \times 10^{-7}$  M. The sensor shows working range over the pH 3.0-9.5 and stable for a period of 2 months with response time <15 s. The selectivity coefficient values as determined by fixed interference method indicate a good selectivity for ions over a wide variety of other tested anions.

### I. Introduction

Iodine is an indispensable microelement to human. Iodine is toxic and its vapours irritate the eyes and lungs. The maximum allowable concentration<sup>1</sup> in air when working with iodine is just  $1.0 \text{ mg m}^{-3}$ . Iodine plays a key role in many biological activities such as, brain functions, cell growth, neurological activities, metabolism and thyroid functions. Iodide ions are also present in the composition of various drugs. Due to vital importance of iodide in environment, medicines and industry, determination of iodide is very important in clinical and chemical analysis<sup>2,4</sup>.

The first iodide selective electrode was prepared by **Pungor and Hollos**<sup>5,6</sup> in 1961 using silver iodide and Paraffin as the membrane. They used this electrode for the determination of sulfur dioxide, by passing SO<sub>2</sub> gas through iodide solution, and the iodide formed was determined with this electrode. In recent decade some PVC membrane electrodes with complex carriers have been developed<sup>7-10</sup> with Nernstian slope. In this work, we describe [Co(L)]SO<sub>4</sub> [Figure 1] as a novel ionophore used in PVC polymeric iodide selective electrode.

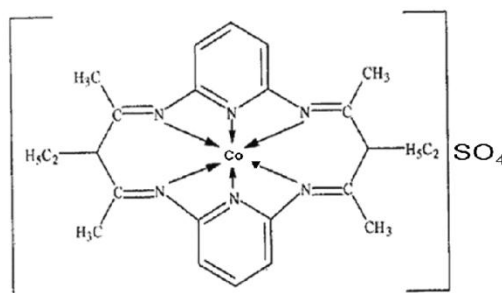


Figure 1 Ionophore [Co(L)]SO<sub>4</sub>

### II. Experimental

#### 2.1 Reagents and Instruments

Reagent-grade dibutyl phthalate (DBP), AP, BA, TBP and hexadecyltrimethyl ammonium chloride (HTAC), tetrahydrofuran (THF), and high relative molecular weight (PVC) were purchased from Aldrich and used as received. Sodium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification. All the solutions were prepared in doubly distilled water.

Potentials were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V, India). The pH measurements were carried out on digital pH meter (LabIndia pH Conmmeter, India). Auto ranging Conductivity meter/TDS meter TCM-15 (Toshniwal Instruments Mfg. Pvt. Ltd Ajmer).

#### 2.2 Emf measurements

All emf measurements were carried out with the following assembly:  
Ag/AgCl/internal solution ( $1.0 \times 10^{-2}$  mol L<sup>-1</sup> NaI) /PVC membrane / test solution / KCl (satd.) /AgCl /Ag.  
Activities were calculated according to the Debye-Huckel procedure.

### 2.3 Electrode preparation

Different compositions of membrane ingredients, including ionophore, the plasticizers DBP, BA, AP, NB, TBP, the additive HTAC and PVC [Table 1], were thoroughly dissolved in 10 ml THF. The resulting solution was carefully cast in to a glass dish of 2 cm diameter for slow evaporation at room temperature to obtain membrane of about 0.3 mm thickness with optimum composition and behavior<sup>11-18</sup>. The membrane was cut and pasted to the one end of pyrex tube with the help of araldite. The electrode was then filled with an internal solution of  $1.0 \times 10^{-2}$  M NaI. The prepared electrodes were finally conditioned by soaking in a  $1.0 \times 10^{-2}$  M NaI solution for 24 h.

## III. Results and discussion

### 3.1 Potential Responses of the Sensor

In preliminary experiments, [Co(L)]SO<sub>4</sub> complex was used as an ion carrier in construction of ion-selective electrodes for some common anions [Figure 2(a) and (b)]. The membrane sensor displayed remarkable selectivity for iodide ions over other anions. The preferential response toward iodide is believed to be associated with the coordination of iodide with the central metal of the carrier.

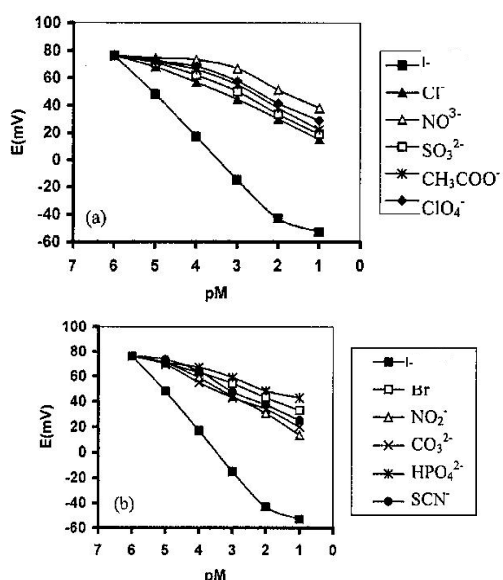


Figure 2 Potential responses of various ion-selective electrodes.

### 3.2 UV-Vis. spectra

To obtain a clue about the interaction mechanism of [Co(L)]SO<sub>4</sub> with iodide, the UV-Vis. spectra of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> [Co(L)]SO<sub>4</sub> in DMSO were obtained with and without the presence of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> iodide and the results are shown in [Figure 3]. A comparison between the two spectra in [Figure 3] reveals that the addition of I<sup>-</sup> to a [Co(L)]SO<sub>4</sub> solution in DMSO considerably increases the absorbance maxima of ionophore located at 364 nm and upon interaction with iodide ion, the peak of [Co(L)]SO<sub>4</sub> located at 473 nm shift to lower wavelengths. The results suggested that the anti-Hofmeister behavior of the sensor can be explained by the observed specific interaction of iodide with the ionophore used and revealed that [Co(L)]SO<sub>4</sub> could be used as a highly selective ionophore for the preparation of an iodide ion-selective electrode.

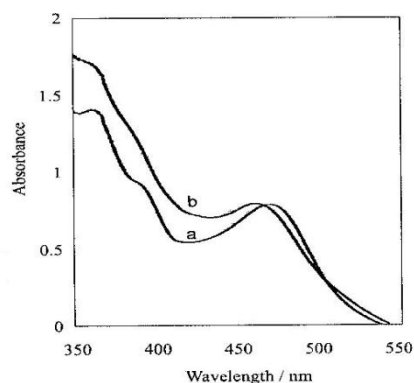


Figure 3. UV-Vis. spectra of  $1.0 \times 10^{-4} \text{ mol L}^{-1} [\text{Co(L)}]\text{SO}_4$  in DMSO solution in the absence (a) and presence (b) of iodide.

### 3.3 Effect of Membrane Composition

It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives<sup>22-24</sup>. Thus the influence of the membrane composition, nature, and amount of plasticizer, and lipophilic additives on the potential response of the membrane was investigated, and the results are shown in **Table 1**. As it is seen, the best response was obtained with the membrane composed of the following ingredients: PVC 31%, DBP 62%, complex 4% and HTAC additive 3%.

Table 1 Optimization of membrane ingredients

Electrode Number	Composition of the membrane (wt. %)				Slope (mV/decade)	
	PVC	Plasticizer	Ionophore	HTAC		
1	31	66, TBP	3	0	-45.4±1.2	
2	31	66, DBP	3	0	-52.5±0.5	
3	31	66, AP		3	0	-46.5±0.6
4	31	66, BA		3	0	-44.8±0.6
5	31	65, DBP	4	0	-53.4±0.5	
6	31	64, DBP	4	1	-54.5±0.5	
7	31	63, DBP	4	2	-56.8±0.4	
8	31	62, DBP	4	3	-58.6±0.4	
9	31	61, DBP	4	4	-54.8±0.6	
10	31	62, DBP		3	4	-52.7±0.6

The potentiometric response of the membranes was greatly improved in the presence of lipophilic cationic additives. It is known that, lipophilic salt, not only reduce the membrane resistance, but also enhance the response behavior and selectivity, and reduce interferences<sup>25-26</sup>. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion selective electrodes<sup>27-28</sup>. The response of the blank membranes containing additives but no carrier at all was far from Nernstian.

### 3.4 Electrode potential response

The electrode potential response was linear over the concentration range of  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-6} \text{ mol L}^{-1}$  of iodide. The calibration curve slope was  $-58.6 \pm 0.4 \text{ mV decade}^{-1}$  and the detection limit, calculated as recommended by the IUPAC, was  $8.0 \times 10^{-7} \text{ mol L}^{-1}$ . The calibration plot is shown in [Figure 4].

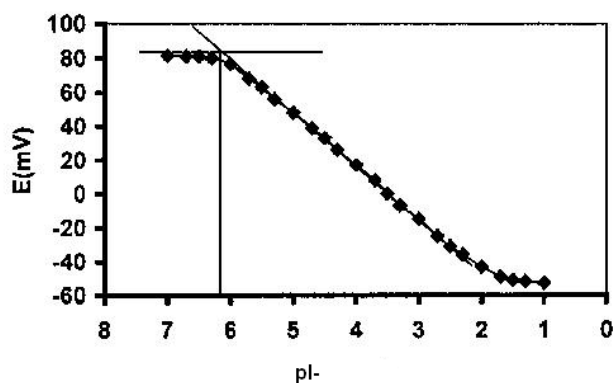


Figure 4 Calibration graph of I<sup>-</sup> ion-selective electrode.

### 3.5 Effect of the concentration of the internal solution

The concentration of the internal solution (NaI) in the electrode was changed from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> and the emf versus I<sup>-</sup> concentration plots were obtained [Figure 5]. It was found that the variation of the concentration of the initial NaI solution has a negligible effect on the potential response of the electrode, except for an expected change in the intercept of the resulting plots. However, a  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> concentration of internal reference solution showed a smooth Nernstian function of the polymeric membrane system and therefore, selected as concentration of internal solution.

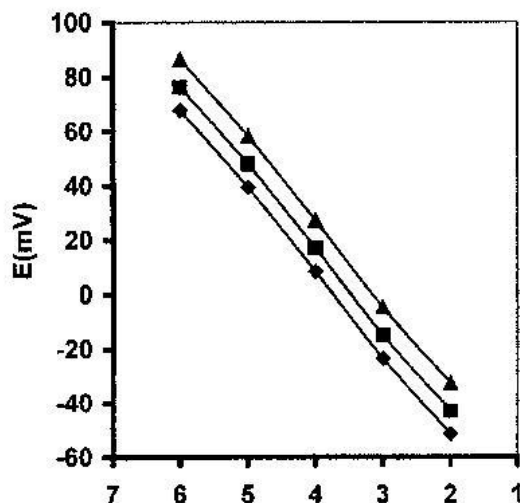


Figure 5 Effect of the concentration of the internal solution on the potential response of the electrode (◆  $10^{-2}$  M), (■  $10^{-3}$  M), (▲  $10^{-4}$  M).

### 3.6 Effect of pH

The influence of the pH of the test solution  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of I<sup>-</sup> on the potential responses of the membrane sensor was tested in the pH range 2.0 to 12 (by using concentrated HNO<sub>3</sub> or NaOH). [Figure 6]. The potential remains constant in the pH range 3.0 to 9.5. At higher alkaline media, pH > 10.0, the potential changed sharply, most probably due to hydroxide-coordinated central metal interference. In acidic media (pH < 3.0), the drift in the potential may be due to the instability of the ionophore (complex of the Co(II) with the ligand).

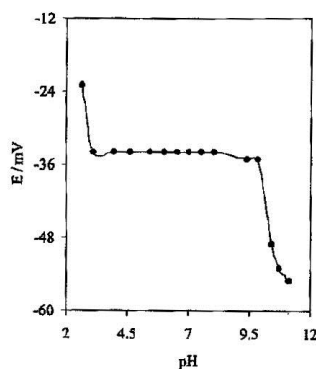


Figure 6 Effect of pH of the test solution ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup> of I<sup>-</sup>) on the potential responses of the I<sup>-</sup> ion-selective electrode.

### 3.7 Dynamic response

Dynamic response time is an important factor for any ion selective electrode<sup>29-36</sup>. In this study, the practical response time was recorded by changing solution with low to high iodide concentrations ( $1.0 \times 10^{-6}$  mol L<sup>-1</sup> to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>) [Figure 7]. In whole the concentration range, the electrode reaches the equilibrium response in a very short time (< 15 s). To evaluate the reversibility of the electrode, a similar procedure at the opposite direction was adopted. This time measurements were performed in the sequence of high-to-low ( $1.0 \times 10^{-1}$  mol L<sup>-1</sup> to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) sample concentration and results showed that the potentiometric response of the sensor was reversible, although the time needed to reach equilibrium values were some what longer than that of the low-to-high order of sample concentration.

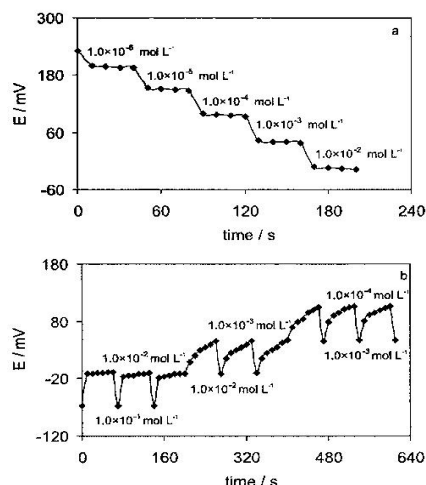


Figure 7. Potentiometric dynamic response of [Co(L)]SO<sub>4</sub> membrane electrode for step changes of from (a) low-to-high and (b) high-to-low iodide concentrations.

Table 2. Characteristics of optimized iodide-ISE

<b>Linear range / M</b>	<b><math>1.0 \times 10^{-2} \text{ M} - 1.0 \times 10^{-6} \text{ M}</math></b>
<b>Slope / <math>\text{mVdecade}^{-1}</math></b>	<b><math>-58.6 \pm 0.4 \text{ mV decade}^{-1}</math></b>
<b>pH range</b>	<b>3.0-9.5</b>
<b>Detection limit/M</b>	<b><math>8.0 \times 10^{-7} \text{ mol L}^{-1}</math></b>
<b>Life time/month</b>	<b>&gt; 2</b>
<b>Response time/s</b>	<b>&lt;15s</b>

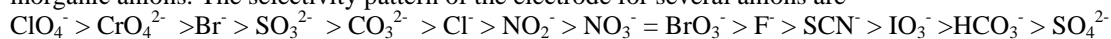
### 3.8 Determination of the potentiometric selectivity coefficients

One of the most important characteristics of any ion-selective sensors is its response to the primary ion in the presence of other ions in the solution, which is expressed in terms of the potentiometric selectivity coefficients ( $K_{I^-,A^n}$ ), describing the preference by the membrane for an interfering ion ( $A^n$ ) relative to  $I^-$ , were determined by the fixed interference method (FIM)<sup>19-21</sup>. The selectivity coefficient for an anion was evaluated by the mixed solution method with a fixed concentration of interference, and varying amounts of  $I^-$  concentrations. Potentiometric selectivity coefficient data of the sensor for several anions relative  $I^-$  are shown in Table 3.

Table 3 Logarithm of the Selectivity coefficients of various interfering ions

Anion	$\log(K_{I^-,A^n})$	Anion	$\log(K_{I^-,A^n})$
SO <sub>3</sub> <sup>2-</sup>	-2.80	CrO <sub>4</sub> <sup>2-</sup>	-2.64
SCN <sup>-</sup>	-3.58	HCO <sub>3</sub> <sup>-</sup>	-3.75
CO <sub>3</sub> <sup>2-</sup>	-3.14	SO <sub>4</sub> <sup>2-</sup>	-4.11
NO <sub>2</sub> <sup>-</sup>	-3.54	IO <sub>3</sub> <sup>-</sup>	-3.67
F <sup>-</sup>	-3.65	ClO <sub>4</sub> <sup>-</sup>	-2.47
BrO <sub>3</sub> <sup>-</sup>	-3.50	Cl <sup>-</sup>	-3.40
NO <sub>3</sub> <sup>-</sup>	-3.50	Br <sup>-</sup>	-2.88

The selectivity coefficients clearly show that the electrode is selective to iodide over a number of other inorganic anions. The selectivity pattern of the electrode for several anions are



The electrode demonstrates a significant deviation in selectivity from the Hofmeister series<sup>37-39</sup>. The reason that the selectivity coefficients do not comply with the Hofmeister series can be due to specific interaction of the anions with the metal center in the carrier [Co(II)L]SO<sub>4</sub> used in this study, i.e. chemical recognition of the anions, and specially of iodide, by the complex.

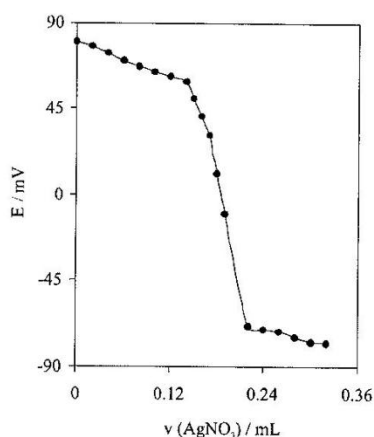
### 3.9 Practical application

The proposed iodide membrane electrode was found to work well under laboratory conditions. It was applied successfully as an indicator electrode in the potentiometric titration of 20 mL of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  KI with  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  AgNO<sub>3</sub> and the resulting titration curve are shown in Figure 8. As can be seen, the

amount of iodide can be determined with electrode. To assess the applicability of the proposed electrode to real sample, an attempt was made to recovery of iodide in edible salt solutions<sup>40-47</sup>. For this purpose, a new calibration graph has been prepared in a solution containing 3.5 mol L<sup>-1</sup> NaCl which is the concentration of edible salt when 20 g of it dissolved in 100 mL water. This has to be done because of the very high concentration of chloride in edible salt. Then, 20 g of edible salt was dissolved in 100 mL of water and the potential measurements were made using the proposed electrode. The resulting data are shown in **Table 4**. Satisfactory recovery of the iodide ion added to edible salt samples was achieved without any prior treatment of the samples.

**Table 4. Determination of iodide ion in edible salt samples.**

I <sup>-</sup> added (mol L <sup>-1</sup> )	I <sup>-</sup> found <sup>a</sup> (mol L <sup>-1</sup> )	% Recovery
0.0	(6.83±0.26)×10 <sup>-5</sup>	-
6.80×10 <sup>-5</sup>	(1.33±0.05)×10 <sup>-4</sup>	97.80
1.36×10 <sup>-4</sup>	(2.10±0.08)×10 <sup>-4</sup>	102.94



**Figure 8. Application of the iodide membrane electrode for the potentiometric titration of 20.0 mL of 1.0×10<sup>-4</sup> mol L<sup>-1</sup> KI with 1.0×10<sup>-2</sup> mol L<sup>-1</sup> AgNO<sub>3</sub>.**

#### IV. Conclusion

A highly selective membrane electrode for iodide ions based on [Co(L)]SO<sub>4</sub> as ionophore was investigated. The optimized formulation of the membrane (*i.e.* 59% BEHP, 30% PVC, 5% CoSPPClO<sub>4</sub>, 6% HTAB) shows a linear concentration range of 5.0×10<sup>-7</sup> to 1.0×10<sup>-1</sup> mol L<sup>-1</sup> with a slope of -58.9 mV per decade and limit of detection of 3.0×10<sup>-7</sup> mol L<sup>-1</sup>. The selectivity coefficient data for iodide ion relative to most of interfering ions are negligibly small. The electrode has a fast response time and good reproducibility. The analytical applications of the proposed electrode were successfully checked.

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