

# Highly Selective Perchlorate Membrane Electrode Based on Synthesized Schiff Base Complex

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**ABSTRACT:** In this work we introduce a practical use of synthesized Schiff base metal complex in sensing application. A new perchlorate-selective electrode based on the complex *N, N'*-4-nitro-phenylmethanebis-(salicylaldiminato) copper (II) [CuL] as the membrane carrier was developed. The electrode exhibits a good Nernstian slope of  $-55.0 \pm 1.0$  mV/decade and a linear range of  $7.0 \times 10^{-7}$  -  $1.0 \times 10^{-1}$  M for perchlorate. The limit of detection is  $3.0 \times 10^{-7}$  M. It has a fast response time <15s and can be used for more than three months. The selective coefficients of Perchlorate-selective electrode were determined by the Fixed Interference Method (FIM) and Fixed Primary ion Method (FPM), and could be used in the pH range 4.0-9.0. It was employed as an indicator electrode for direct determination of perchlorate in real samples.

**KEY WORDS:** Schiff base, Perchlorate-selective electrode, Potentiometry.

## INTRODUCTION

The various salts of perchlorate-including potassium, ammonium, and sodium are used as oxidizers where explosive or combustive reactions are required to occur under low oxygen conditions. Ammonium perchlorate is present in commercially available products such as road

flares, fireworks, airbags, and some fertilizers [1, 2]. Perchlorate originates as a contaminant in the environment from the use of solid salts in the manufacture of solid rocket furls and munitions [3]. Perchlorate is quite soluble, extremely mobile in aqueous systems, and rather

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1021-9986/10/3/127

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nonreactive with other constituents in water. Environmental contamination of water sources primarily occurs near military and industrial installations where perchlorate is handled. In contrast to the health effects data on humans and rodents [4, 5], little data exist on potential ecological effects of environmental perchlorate contamination. There has been much debate over what level of perchlorate is safe for humans to consume daily. After considering the recommendations of the National Academy of Science National Research Council [6], the Environmental Protection Agency set a perchlorate reference dose for adult humans of  $0.7 \mu\text{g} / \text{kg} / \text{day}$  which translates to a Drinking Water Equivalent Level (DWEL) of  $24.5 \mu\text{g} / \text{L}$  [7].

Aromatic Schiff bases, especially those derived from reaction of salicylic aldehydes with aromatic amines (salen-type Schiff bases), form complexes with a variety of metal ions [8-10]. Among the various possible applications of these complexes, their high selectivity towards especial cations and anions is used for the design of ion selective electrodes in biochemical analysis and medical diagnostics [11-14].

Most of the reported  $\text{ClO}_4^-$  ion-selective electrodes are ion exchanger based liquid membranes, where the electroactive species including perchlorate ion-association complexes with cations and metal chelates [15, 16], long chain quaternary ammonium ions [17] and organic dyes [18] have been dissolved in various organic solvents. Moreover many of these electrodes are not sensitive enough to permit measurement of low levels of perchlorate, and/or are susceptible to interference from such common contaminants as  $\text{NO}_3^-$ ,  $\text{OH}^-$ , and  $\text{SCN}^-$  ions.

Recently, we have used ionophores in the construction of ISEs for  $\text{NO}_3^-$  [19, 20] and  $\text{SCN}^-$  [21]. The aim of this work is to assess the performances of this Schiff base (N,N'-4-nitro-phenylmethanebis-(salicylaldiminato)copper(II)) as an excellent ionophore for the preparation of a high selective ISE for the potentiometric determination of perchlorate ion over a wide concentration range. The potentiometric response properties, reproducibility and selectivity of ISE were evaluated by the response potentials and selectivity coefficients.

## EXPERIMENTAL SECTION

### Reagents

PVC, Tri Octylmethyl Ammonium Chloride (TOMAC)

and dibutyl phthalate (DBP) were used as received from Aldrich. Potassium or sodium salts of all anions, Tetra Hydro Furan (THF) and all other chemicals were of highest purity available from Merck, and were used without further purification, except THF, which was distilled before use. The ionophore of N, N'-4-nitro-phenylmethanebis-(salicylaldiminato) copper (II) [CuL] (Fig. 1) was synthesized and used after purification. Working solutions were prepared by successive dilutions with water. Both standard stock and working solutions of the anions tested were prepared in carbonate free doubly distilled water.

### Electrode preparation

The membrane ion-selective electrodes were prepared according to a previously reported method [22]. A mixture of PVC, plasticizer (DBP), and the membrane additive (TOMAC), total mass 100 mg was dissolved in approximately 10 mL freshly distilled THF. To this mixture was added the electroactive material [CuL] and solution was mixed well. The resulting mixture was poured into a small flat bottom dish of 2 cm diameter, covered with a filter paper and the solvent was allowed to evaporate at room temperature. The resulting membrane (ca. 0.2 mm thick) was then sectioned with a cork borer and mounted across the opening of a PVC tube of about 7 mm i.d. and 1.5 cm length using a glue of PVC in THF. The PVC tube with the membrane was then filled with an internal solution of in  $1.0 \times 10^{-2} \text{ M NaClO}_4$ . The filled electrode was conditioned by soaking in  $1.0 \times 10^{-2} \text{ M}$  analyt solution. The first conditioning time was approximately 4h, until a stable potential value was obtained and then 30-40min for successive uses. A silver/silver chloride electrode was used as an internal reference electrode.

### General procedure for synthesis of N, N'-bis (salicylidene)-4-nitro phenylmethane- diamin

To a solution of salicylaldehyde (0.38 g, 3 mmol) and 4-nitro-benzaldehyde (0.16 g, 1.5 mmol) in methanol (5 mL) was added  $\text{NH}_4\text{O}_2\text{CPh}$  (0.25 g, 3.27 mmol) in the presence of the  $\text{NEt}_3$  (0.6 mL) as a base by stirring in one portion. The mixture stirring was continued to 2 hours. The progress of the reaction was monitored by TLC. After the completion of the reaction, pail yellow substance was obtained. The solid product was filtered off and washed

with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N, N'-bis (salicylidene)-phenylmethane-diamine was obtained in 95% yield. The Schiff base products were identified by physical and spectroscopic data.

*N,N'*-bis(salicylidene)-4-nitro-phenylmethanediamine; yellow solid; mp 116-118 °C IR (KBr)/  $\nu$  (cm<sup>-1</sup>) 3400-3600 (br, OH), 1622 (s, C=N), 1480, 1570 (Ar), 1350, 1530 (N=O); <sup>1</sup>H NMR/ DMSO /  $\delta$  p.p.m: 6.4 (s, 1 H, NCHN), 6.5-7.6 (m, 12 H), 8.9 (s, 2 H, HC=N), 12.64 (s, 2 OH); <sup>13</sup>C NMR/DMSO/  $\delta$  p.p.m: 89.9, 117.30, 119.6, 120, 124.9, 132.94, 134.2 148, 148.9, 160.9, 167; UV (CHCl<sub>3</sub>)/  $\lambda_{\max}$  (nm) 323 (w), 262 (s); 262 (s); MS: m/z=376 (M<sup>+</sup>+1, 6), 375 (M<sup>+</sup>, 10), 255 (65), 254 (80), 134 (85).

#### General procedure for preparation of N, N' -4- nitro-phenylmethanebis-(salicyl-aldiminato) copper (II)

To a solution of N, N'-bis (salicylidene)-phenylmethanediamine in MeOH (1 mmol) was added Cu (O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (1 mmol) drop wise under mild condition at room temperature. The reaction mixture was stirred for 1 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, solid substance was obtained. The solid product was filtered off and washed with MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base complex, N, N'-4-nitro-phenylmethanebis-(salicylaldiminato) copper (II) was obtained in 95 % yield.

*N,N'*-4- nitro- phenylmethanebis- (salicylaldiminato) copper(II); green solid mp >300 °C IR (KBr)/  $\nu$  (cm<sup>-1</sup>) 1613 (s, C=N), 1470, 15650 (Ar), 1350, 1530 (N=O); <sup>1</sup>H NMR/ DMSO /  $\delta$  p.p.m: 6.8 (s, 1 H, NCHN), 6.9-7.8 (m, 12 H), 9.1 (s, 2 H, HC=N); <sup>13</sup>C NMR/DMSO/  $\delta$  p.p.m: 96.1, 117.30, 119.6, 120, 124.9, 132.94, 134.2 148, 148.9, 166.9, 174; MS: m/z=376 (M<sup>+</sup>+1, 12), 375 (M<sup>+</sup>, 20), 255 (70), 254 (80), 134(100), 91 (30); Anal. Calcd. For C. H. N: 57.66 (C), 3.43 (H), 9.61 (N); Found: 57.68 (C), 3.45 (H), 9.62 (N).

#### Potential measurement and calibration

The potential build up across the membrane electrode was measured using the galvanic cell of the following type:

Ag | AgCl | KCl (3M) internal solution (1.0×10<sup>-2</sup> M NaClO<sub>4</sub>) | PVC membrane | test solution || SCE

All potentials were measured at 25 ± 1°C using a digital pH/ mV meter, model 781 Metrohm. A saturated

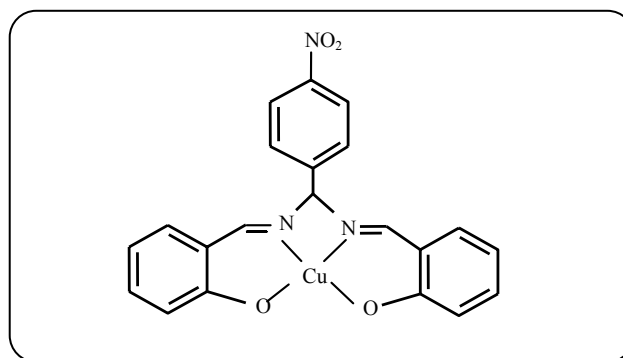


Fig. 1: Structural representation of the compound of [N,N'-4-nitro-phenylmethanebis-(salicylaldiminato) copper (II)] used as ionophore for perchlorate ion selective electrode.

calomel electrode (SCE, Metrohm) with a fiber junction was used as the external reference electrode. Activities were calculated according to the Debye-Hückle procedure [23] for the calibration curve, concentration instead of activity was used. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm).

The performance of the electrode was investigated by measuring its potential in sodium perchlorate solutions prepared in the concentration range 1.0×10<sup>-7</sup>–1.0 M by serial dilution. All solutions were freshly prepared by dilution from the stock standard solution, 1.0 M, with doubly distilled water. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential vs. the logarithm of the ClO<sub>4</sub><sup>-</sup> concentration.

#### RESULTS AND DISCUSSION

In this work, the ability of N, N'-4-nitro-phenylmethanebis-(salicylaldiminato) copper (II) to serve as ionophore in polymeric membrane ion selective electrodes (ISEs) is investigated. The membrane without the ionophore displayed insignificant selectivity toward perchlorate whereas, in the presence of the ionophore, the membrane shows remarkable selectivity for perchlorate over most common inorganic and organic anions. We therefore studied in detail the performance of the electrode for perchlorate ion. In order to test the performance of the membrane characteristics, various operation parameters viz. selectivity, response time, sensitivity, lifetime, working range of the electrode at different concentrations of the anion, pH and the effect of the membrane composition were investigated.

**Table 1: Optimized membrane compositions and their potentiometric response properties in  $\text{ClO}_4^-$  - ISE**  
(Values in table are mass ratio in percent).

No	%PVC	%Plasticizer	%Ionophore	%Additive	Slope mV/decade	Linear dynamic range, M
1	30	63	5	2	-55.0	$7.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$
2	30	63	6	1	-50.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
3	30	63	3	4	-53.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
4	30	63	4	3	-51.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
5	27	66	5	2	-48.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
6	25	68	5	2	-50.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
7	25	67	6	1	-45.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$
8	22	71	5	2	-51.0	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$

**Table 2: Characteristics of optimized  $\text{ClO}_4^-$ -ISE.**

Linear range (M)	$7.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$
Slope ( $\text{mVdecade}^{-1}$ )	-55.0
pH range	4.0-9.0
Precision	At concentrations of $1.0 \times 10^{-2}$ , $1.0 \times 10^{-3}$ , $1.0 \times 10^{-4}$ and $1.0 \times 10^{-5}$ M $\text{ClO}_4^-$ standard deviations were of $\pm 0.6$ , $\pm 0.7$ , $\pm 0.8$ and $\pm 1.0$ mV respectively.
Detection limit (M)	$3.0 \times 10^{-7}$
Life time (month)	>2
Response time (s)	5-20

### Potentiometric measurements

Initially, we examined solvent polymeric membranes at various incorporating compositions with different percents of ionophore, cationic additive, plasticizer and poly (vinyl) chloride (PVC). Studies were carried out with N, N'-4-nitro-phenylmethanebis-(salicylaldehyde-iminato) copper (II) in a membrane matrix of DBP / PVC. The compositions and corresponding potentiometric response properties of the various membrane formulations examined are summarized in Table 1. Previous studies showed that besides the critical role of the nature of the ionophore in preparing PVC membrane-selective electrodes, some other important features of the PVC membrane are known to significantly influence the selectivity, linear range and sensitivity of ion-selective electrodes [24-26]. Thus,

the effect of membrane composition, the content and kind of lipophilic salts, membrane solvent, and the ionophore concentration on the potential response of  $\text{ClO}_4^-$  sensor were investigated. The optimized membrane composition was obtained with a membrane incorporating 30% PVC, 63% DBP, 2% TOMAC, and 5% of the membrane active compound. This composition was, therefore, used to study the performance characteristics of the electrode, viz. selectivity, lifetime, the effect of pH, response time, and the working concentration range. The characteristics properties of the optimized membrane are summarized in Table 2. The sensitivity of electrode response increases with increasing ionophore content from 3 to 5%. Further addition of ionophore to 6%, show diminished response of the electrode. It is most probably due to some inhomogenetics and possible saturation of the membrane [27]. Increasing the amount of [CuL], up to 5% resulted in membranes for which slopes were larger and the linear range wider. The influence of plasticizer type on the response characteristics of the perchlorate electrode was investigated by using different plasticizers including DBP, DOP and NPOE. Similar to our publications [21,28], the electrodes based on DBP and DOP showed better potentiometric responses, i.e., higher sensitivity and wider linearity of calibration plot. It seems that DBP, with a low polarity and a relatively high mobility, with respect to other plasticizer examined, provides appropriate conditions for incorporation of lipophilic perchlorate ion into membrane. The potentiometric response of the membrane was greatly improved in the presence of lipophilic cationic additive TOMAC. It is known that, lipophilic salts not only reduce the membrane resistance, but also enhance the response

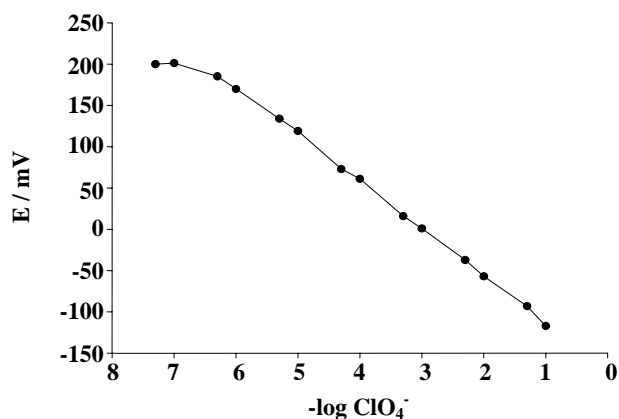


Fig. 2: Potentiometric response of the  $\text{ClO}_4^-$ -ISE to perchlorate using optimized membrane electrode.

behavior and selectivity, and reduce interference from sample cations [29]. Generally, better response characteristics were observed with an ionophore / TOMAC weight ratio of about 2.5, which corresponds to a mole ratio of about 2.3. Irrespective of ionophore concentration the slope was relatively larger when DBP / PVC weight ratio was approximately 2.0.

#### Response characteristics of the electrode

The potential response of the membrane electrode to varying concentrations of  $\text{ClO}_4^-$  was examined over the concentration range  $1.0 \times 10^{-7}$  –  $1.0 \times 10^{-1}$  M using the optimized membrane composition and conditions described above. A typical calibration plot is shown in Fig. 2, which depicts a linear range from  $7.0 \times 10^{-7}$  –  $1.0 \times 10^{-1}$  M with a Nernstian slope of  $-55.0 \pm 1.0$  mV per decade. The practical limit of detection, taken as the concentration of  $\text{ClO}_4^-$  at the point of intersection of the extrapolated linear segments of the calibration plot, was  $3.0 \times 10^{-7}$  M. The slope and detection limit of the electrode were evaluated from repeatedly carrying out calibration graphs between  $1.0 \times 10^{-7}$  and  $1.0 \times 10^{-1}$  M. The calibration parameters thus obtained are included in Table 2. As can be seen a near-Nernstian response, low detection limit and good calibration reproducibility were obtained. In practice, slopes of between 55 and 59 mV decade<sup>-1</sup> are referred to as Nernstian for analytical purposes [30]. The stability and reproducibility of EMF measurements made with currently available membrane electrode cell assemblies clearly depend on the type of electrode used, due to technical (geometry at the tip) and electrical reasons

(high resistances of the membranes). The standard deviation of the potential responses on the same portions of the sample at concentrations of  $1.0 \times 10^{-5}$ ,  $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-2}$  M were  $\pm 1.0$ ,  $\pm 0.8$ ,  $\pm 0.7$  and  $\pm 0.6$  mV, respectively.

The response time of electrochemical cells containing ion-selective electrodes is considered to be one of the most critical and limiting factors in the biological applications of potentiometric sensors. The IUPAC Commission on Analytical Nomenclature has recommended that response times should be stated in terms of  $t_{90}$  values (time required for the EMF to undergo 90% of its total change). More recently, it has been extended to be able to treat drifting systems as well. In this case, the second time instant is defined as the one at which the emf / time slope ( $\Delta E / \Delta t$ ) becomes equal to a limiting value [31]. The response time was obtained from the dynamic response curves corresponding to perchlorate concentration steps to obtain a 10-times more concentrated solution. The values obtained for different perchlorate concentrations are included in Table 2.

#### Influence of the concentration of internal solution

The influence of the concentration of internal solution on potential response of the  $\text{ClO}_4^-$ -selective electrode was studied. The  $\text{NaClO}_4$  concentration was changed from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-2}$  M and the potential response to the  $\text{ClO}_4^-$  ion selective was obtained. It was found that variation of the concentration of internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting near Nernstian plot. A  $1.0 \times 10^{-2}$  M concentration of the reference solution is quite appropriate for smooth functioning of the electrode system.

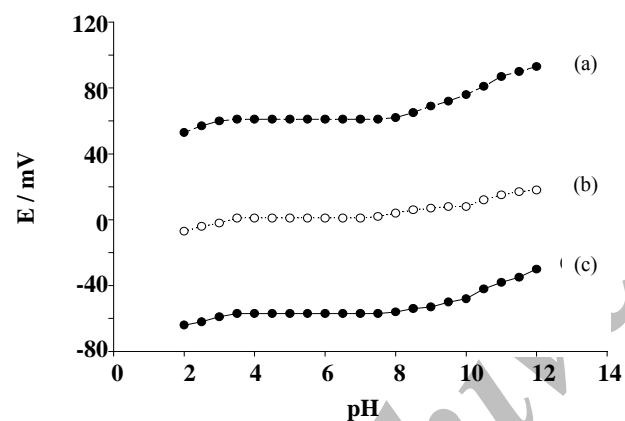
#### Influence of pH

The effect of pH on the electrode potential at various perchlorate concentrations is shown in Fig. 3. The pH was varied by adding HCl or NaOH. As can be seen, the electrode potential was independent of pH in the range 4.0-9.0 for all the perchlorate concentrations assayed. Variation of the potential at  $\text{pH} < 4.0$  could be related to protonation (due to the nitrogen sites protonation) of [CuL] in the membrane phase, which results in a loss of its ability to interaction with  $\text{ClO}_4^-$  ions or due to the

Table 3: Selectivity of coefficients, determined by use of the fixed interference method for the  $\text{ClO}_4^-$  - ISE.

Interfering Ion	$\log K^{\text{pot}}_{\text{ClO}_4^-, \text{A}^-}$ (FIM)	$\log K^{\text{pot}}_{\text{ClO}_4^-, \text{A}^-}$ (FPM)	Interfering Ion	$\log K^{\text{pot}}_{\text{ClO}_4^-, \text{A}^-}$ (FIM)	$\log K^{\text{pot}}_{\text{ClO}_4^-, \text{A}^-}$ (FPM)
$\text{F}^-$	-4.0	-3.8	$\text{PO}_4^{3-}$	-3.1	-3.9
$\text{CO}_3^{2-}$	-5.4	-4.2	$\text{S}_2\text{O}_3^{2-}$	-3.7	-3.3
$\text{Br}^-$	-2.8	-3.9	$\text{C}_2\text{O}_4^{2-}$	-3.9	-3.2
$\text{I}^-$	-2.7	-3.8	$\text{SO}_4^{2-}$	-4.3	-4.1
Sal*	-3.9	-3.3	$\text{ClO}_3^-$	-2.7	-3.9
$\text{SO}_3^{2-}$	-4.8	-4.0	$\text{BrO}_3^-$	-2.5	-2.3
OAc <sup>-</sup>	-2.8	-3.6	$\text{NO}_2^-$	-4.5	-3.9
$\text{N}_3^-$	-3.5	-4.6	$\text{HPO}_4^{2-}$	-4.4	-3.2
$\text{CN}^-$	-2.9	-3.3	$\text{Cl}^-$	-4.1	-4.9
$\text{SCN}^-$	-2.0	-2.9	-	-	-

\*Salicylate

Fig. 3: The influence of pH on the potential response of the optimized  $\text{ClO}_4^-$ -ISE Concentration of perchlorate: (a)  $1.0 \times 10^{-4}$  M, (b)  $1.0 \times 10^{-3}$  M, (c)  $1.0 \times 10^{-2}$  M.

interaction of  $\text{Cl}^-$  ions present at high concentrations with ionophore. At higher pH ( $>9.0$ ), the change of potential (positive slope) may be because of interference hydroxide ions. The working pH range, over which the electrode can be used, covers the pH of most natural and industrial waters.

The lifetime of the electrode was determined by recording its potential at an optimum pH value and plotting its calibration curve each day. It was observed that there was no significant change in the slope of the electrode on the following day. The electrode was tested over a period of 3 months to investigate its stability. At present, with the current knowledge of membranes and electrode bodies for solvent polymeric membrane sensors,

the lifetime of an electrode is not limited by factors such as mechanical defects, electrical shunts, chemical deterioration, or surface contamination, but rather by the loss of the ionophore or plasticizer from the membrane into the sample solution.

### Selectivity

The selectivity of any ion-selective sensor is clearly one of its most important characteristics as this property often determines whether a sensor may be used reliably in the target sample. Selectivities of solvent polymeric membrane ion-selective electrodes are quantitatively related to equilibrium at the interface between the sample and the electrode membrane. The potentiometric selectivity coefficients ( $K^{\text{pot}}_{\text{ClO}_4^-, \text{A}^-}$ ) of the perchlorate-selective electrode were determined by the Fixed Interference Method (FIM) from potential measurements of solutions prepared with a fixed concentration of the interfering ions ( $1.0 \times 10^{-3}$  M, pH=7) and varying concentrations of  $\text{ClO}_4^-$ , and the Fixed Primary Method (FPM) from potential measurements of solutions prepared with a fixed concentration of the perchlorate ion and varying concentrations of interference ion [32]. The potentiometric selectivity coefficients of the proposed electrode are summarized in Table 3. From the data given in Table 3, it is evident that the proposed perchlorate electrode is more selective with respect to potential interfering anions such as nitrate, bromide and thiocyanate. A very good degree

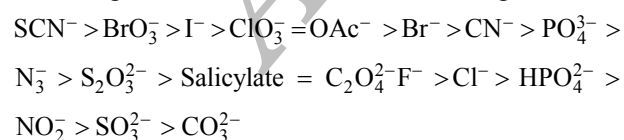
**Table 4: Comparing some of the electrode characteristics with previous  $\text{ClO}_4^-$  - ISEs.**

Reference	Slope (mV/decade)	Linear range (M)	DL ( $\mu\text{M}$ )	Interfering ions with $K^{\text{pot}} \geq 1.0 \times 10^{-2}$
Proposed electrode	$-55.0 \pm 1.0$	$7.0 \times 10^{-7} - 1.0 \times 10^{-1}$	0.3	-
34	$-56.77 \pm 0.43$	$5.0 \times 10^{-6} - 1.0 \times 10^{-2}$	1.1	$\text{SCN}^-$ , $\text{IO}_4^-$
35	$-57.8 \pm 0.4$	$8.0 \times 10^{-6} - 1.6 \times 10^{-1}$	5.0	$\text{I}^-$ , $\text{SCN}^-$
36	$-57.3 \pm 1.0$	$8.2 \times 10^{-6} - 1.0 \times 10^{-1}$	1.3	$\text{I}^-$ , $\text{Br}^-$ , $\text{Cl}^-$ , $\text{F}^-$ , $\text{IO}_4^-$
37	-59.7	$1.0 \times 10^{-5} - 1.0$	5.0	$\text{SCN}^-$ , $\text{I}^-$ , $\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{Br}^-$ , $\text{HCO}_3^-$
38	-52.5	$5.2 \times 10^{-6} - 1.0 \times 10^{-1}$	4.2	$\text{NO}_3^-$
39	-60.3	$8.0 \times 10^{-7} - 1.0 \times 10^{-1}$	0.56	$\text{SCN}^-$ , $\text{I}^-$ , $\text{IO}_4^-$ , $\text{NO}_3^-$
40	-59.9 & -58.2	$5.0 \times 10^{-7} - 4.0 \times 10^{-1}$ & $1.5 \times 10^{-7} - 2.7 \times 10^{-1}$	0.4 & 0.1	$\text{I}^-$
41	-58.6	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	0.5	$\text{SCN}^-$ , $\text{I}^-$ , $\text{CN}^-$

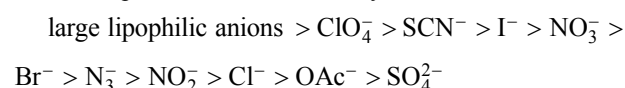
**Table 5: Determination of perchlorate ion at presence of other anions.**

Samples	% Recovery for $\text{ClO}_4^-$
Solution with concentrations of $1.0 \times 10^{-2}$ ( $\text{SCN}^-$ , $\text{ClO}_4^-$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{F}^-$ )	101.5 ( $\pm 2.6$ )
Solution with concentrations of $1.0 \times 10^{-3}$ ( $\text{SCN}^-$ , $\text{ClO}_4^-$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{F}^-$ )	94.2 ( $\pm 3.1$ )
Solution with concentrations of $1.0 \times 10^{-2}$ ( $\text{SCN}^-$ , $\text{ClO}_4^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{Br}^-$ )	97.6 ( $\pm 2.9$ )
Solution with concentrations of $1.0 \times 10^{-2}$ ( $\text{SCN}^-$ , $\text{ClO}_4^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{N}_3^-$ )	95.4 ( $\pm 3.2$ )
Solution with concentrations of $1.0 \times 10^{-2}$ (Tap Water)	100.3 ( $\pm 3.0$ )

of selectivity with respect to most anions was found. According to the tabulated data in Table 3, the interfering effect of the ions is in the following order:



The sequence is characterized by the Hofmeister series:



The electrode selectivity coefficients do not comply with the Hofmeister series but show a selectivity which is close to it. However, the anion lipophilicity still plays

an important role and only the simultaneous consideration of both the lipophilicity and the anion interaction with copper allows one to explain the selectivity patterns [33].

In Table 4, the response characteristics of the proposed electrode are compared with those of the several recently reported selective electrodes for  $\text{ClO}_4^-$  ion [34-41]. As is quite obvious from Table 4, in some cases, the linear range, detection limit and the selectivity coefficients of the proposed electrode are superior to those of other electrodes reported in the literature.

#### Analytical applications

The proposed membrane electrodes were found to work well under laboratory conditions. To assess the applicability of the membrane electrode real for samples an attempt was made to determine  $\text{ClO}_4^-$  in several water samples and biological samples (human blood serum) using the spike method. The proposed electrode was applied to the recovery of perchlorate ion from tap water sample and also for the determination of perchlorate in the presence of other anions and the results are given in Table 5. In the case of water the determination was also carried out in the presence of perchlorate. Perchlorate was measured by direct potentiometry using the standard addition technique. Also, this electrode was applied to the recovery of perchlorate ion from blood serum samples. The quality of the results was evaluated by performing a recovery test. The results indicate that the proposed

electrode can be successfully applied to the determination of perchlorate at concentrations normally present in some biological samples and water samples.

## CONCLUSIONS

On the basis of these results discussed in the paper, compound N, N'-4-nitro-phenylmethanebis-(salicylaldehyde-imino) copper (II) can be regarded as a carrier for construction of a novel PVC-based on membrane-ISE for perchlorate. The proposed electrode showed better selectivity than most previous electrodes and was proved suitable for the determination of perchlorate in the presence of a much higher other anion concentration. It is easy to prepare and use. This electrode can be used for determination of perchlorate in real samples. The present electrode permits the direct measurement of perchlorate in real samples without prior separation steps, thus considerably simplifying the determination procedure with respect to the other analytical methods used.

## Acknowledgment

The authors express their appreciation to the University of Payam Noor of Ardakan Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

Received : May 11, 2009 ; Accepted : Jan. 11, 2010

## REFERENCES

- [1] Urbansky E.T., Brown S.K., Magnuson M.L., Kely C.A., Perchlorate Level in Samples of Sodium Nitrate Fertilizer Derived from Chilean Caliche, *Environ. Pollut.*, **112**, p. 299 (2001).
- [2] Urbansky E.T., Perchlorate as an Environmental Contaminant, *Environ. Sci. Pollut. Res. Int.*, **9**, p. 187 (2002).
- [3] Motzer W.E., Perchlorate: Problems, Detection, and Solutions, *Environ. Forencics*, **2**, p. 301 (2001).
- [4] Rodriguez A.F., Davidson H.G., Villadiego M.S., Fernandez A.M., Lacave I.M., Sanz J.F., Induction of Thyroid Proliferative Changes in Rats Treated with Antithyroid Compound, *Anatomy, Histology, and Embryology*, **20**, p. 289 (1991).
- [5] Wolff J., Perchlorate and the Thyroid Gland, *Pharmacological Reviews*, **50**, p. 89 (1998).
- [6] National Academy of Sciences, "Health implications of perchlorate ingestion", Prepublication copy, National Research Council of the National Academics, (2005).
- [7] USEPA, "US EPA Headquarters Press Release: EPA Sets Reference Dose for Perchlorate", Retrieved 14 March (2005).
- [8] Atwood D.A., Harvey M.J., Group 13 Compounds Incorporating Salen Ligands, *Chem. Rev.*, **101**, p 37 (2001).
- [9] Johnson C.P., Atwood J.L., Steed J.W., Bauer C.B., Rogers R. D., Transition Metal Complexes of p-Sulfonatocalix [5] Arene, *Inorg. Chem.*, **35**, p. 2602 (1996).
- [10] Alizadeh N., Ershad S., Naeimi H., Sharghi H., Shamsipur M., Synthesis of a New Naphthol-Derivative Salen and Spectrophotometric Study of the Thermodynamics and Kinetics of Its Complexation with Copper(II) Ion in Binary Dimethylsulfoxide-Acetonitril Mixtures, *Pol. J. Chem.*, **73**, p. 915 (1999).
- [11] Bühlman P., Prestsch E., Bakker E., Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 2. Ionophores for Potentiometric and Optical sensors, *Chem. Rev.*, **98**, p. 1593 (1998).
- [12] Bakker E., Bühlman P., Prestsch E., Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics, *Chem. Rev.*, **97**, 3083 (1997).
- [13] Shamsipur M., Sadeghi S., Naeimi H., Sharghi H., Iodide Ion-Selective PVC Membrane Electrode Based on a Recently Synthesized Salen-Mn(II) Complex, *Pol. J. Chem.*, **74**, p. 231 (2000).
- [14] Mazloun Ardakani M., Mashhadizadeh M. H., Karimi M. A., Azimi M.S., Iranpoor F., Salavati-Niasari M., Potentiometric Membrane Electrode for Nitrate Based on 1,8-Bis(Salicylaldiminato)-3,6-Dioxaoctane Ni(II), *Chem. Anal.* **52**, p. 1 (2007)
- [15] Jain A.K., Jahan M., Tyagi V., Liquid-Membrane Perchlorate-Selective Electrode, *Analyst*, **112**, p. 1355 (1987).
- [16] Hassan S.S.M., Elsaied M.M., A New Liquid-Membrane Electrode for Selective Determination of Perchlorate, *Talanta*, **33**, p 679 (1986).
- [17] Bäck S., Selectivity Studies on Anion-Selective Membrane Electrodes, *Anal. Chem.*, **44**, p. 1696 (1972).



- [18] Kataoka M., Kambara T., A Liquid Membrane Type Perchlorate Ion-Selective Electrode, *J. Electroanal. Chem.*, **73**, p. 279 (1976).
- [19] Mazloum Ardakani M., Salavati M., Dastanpoor A., A Highly Selective Nitrate Electrode Based on a Tetramethyl Cyclotetra- Decanato- Nickel(II) Complex, *J. Electroanal. Chem.*, **568**, p. 1 (2004).
- [20] Mazloum Ardakani M., Salavati M., Jamshidpoor M., Selective Nitrate Poly(Vinylchloride) Membrane Electrode Based on Bis(2-Hydroxyacetophenone) Ethylenediimine Vanadyl (IV), *Sens. and Actuators B Chemical*, **101**, p. 302 (2004).
- [21] Mazloum Ardakani M., Salavati M., Sadeghi A., Novel Selective thiocyanate PVC Membrane Electrode Based on New Schi\_Base Complex of 2.2-[(1,3-Dimethyl- 1,3-Propanediylidene) Dinitrilo] Bis[Benzenethiolato Cadmium(II), *New J. Chem.*, **28**, p. 595 (2004).
- [22] Amini M.K., Mazloum Ardakani M., Ensafi A.A., Lead Selective membrane Electrode Using Cryptant (2,2,2) Neutral Carrier, *Fresenius J. Anal. Chem.*, **364**, p. 690 (1999).
- [23] Kamata S., Bhal A., Fakunaga Y., Marata A., Copper(II)-Selective Electrode Using Thiuram Disulfide Neutral Carriers, *Anal. Chem.*, **60**, p. 2464 (1988).
- [24] Amemiya S., Bühlmann P., Pretsch E., Cationic or Anionic Sites Selectivity Optimization of Ion-Selective Electrodes Based on Charged Ionophores, *Anal. Chem.*, **72**, p. 1618 (2000).
- [25] Schaller U., Bakker E., Pretsch E., Carrier Mechanism of Acidic Ionophores in Solvent Polymeric Membrane Ion-Selective Electrodes, *Anal. Chem.* **67**, p. 3123 (1995).
- [26] Mazloum Ardakani M., Jalayer M., Naeimi H., Zare H.R., Moradi L., Perchlorate-Selective Membrane Electrode Based on a New Complex of Uranil, *Anal. Bioanal. Chem.*, **381**, p. 1186 (2005).
- [27] Ammann D., Pretsch E., Simon W., Lindner E., Bezegh A., Pungor E., Lipophilic Salts as Membrane Additive and their Influence on the Properties of Macro- and Micro-Electrodes Based on Neutral Carriers, *Anal. Chim. Acta*, **171**, p. 119 (1985).
- [28] Mazloum-Ardakani M., Iranpoor F., Karimi M. A., Salavati-Niasari M., A New Selective Membrane Electrode for Oxalate Based on N,N'-Bis(Salicylidene)-2,2-Dimethylpropane-1,3 Diamine Ni(II), *Bull. Korean Chem. Soc.*, **29**, p. 398 (2008).
- [29] Huser M., Gehrig P.M., Morf W.E., Simon W., Lindner C., Jeney J., Toth K., Pungor E., Membrane Technology and Dynamic Response of Ion-Selective Liquid-Membrane Electrodes, *Anal. Chem.*, **63**, p. 1380 (1991).
- [30] Wegmann D., Weiss H., Ammann D., Morf W.E., Pretsch E., Sagahara K., Simon W., Anion-Selective Liquid Membrane Electrodes Based On Lipophilic Quaternary ammonium Compounds, *Mikrochim. Acta* **1-2**, p. 1 (1984).
- [31] Buck R. P., Ion Selective Electrodes, Potentiometry, and Potentiometric Titrations, *Anal. Chem.*, **44**, p. 270 (1972).
- [32] Buck R. P., Lindner E., Recommendation for Nomenclature of Ion-Sensitive Electrodes, *Pure Appl. Chem.*, **66**, p. 2527 (1994).
- [33] Danuert S., Wallace S., Florida A., Bachas L. G., Anion-Selective Electrodes Based on Electropolymerized Porphyrin Films, *Anal. Chem.*, **63**, p. 1676 (1991).
- [34] Sanchez-Pedreno C., Ortuno J. A., Hernandez J., Perchlorate-Selective Polymeric Membrane Electrode Based on a Gold(I) Complex: Application to Water and Urine Analysis, *Anal. Chim. Acta*, **415**, p. 159 (2000).
- [35] Shamsipur M., Soleymanpour A., Akhond M., Sharghi H., Hasaninejad A. R., Perchlorate Selective Membrane Electrodes Based on a Phosphorus(V) Tetraphenylporphyrin Complex, *Sens. and Actuators B*, **89**, p. 9 (2003).
- [36] Olmos R.P., Rios A., Martin M.P., Lapa R.A.S., Lima J. L. F. C., Construction and Evaluation of Ion Selective Electrodes for Perchlorate with a Summing Operational Amplifier: Application to Pyrotechnics Mixtures Analysis, *Analyst*, **124**, p. 97 (1999).
- [37] Tatyana A. B., Thomas C. H., Long-Lived Solid State Perchlorate Ion Selective Sensor Based on Doped Poly (3,4-Ethylenedioxythiophene) (PEDOT) Films, *Anal. Chim. Acta*, **551**, p. 30 (2005).
- [38] Sabater J.L., Seguí M.J., Lloris J.M., Martínez-Mañez R., Pardo T., Sancenón F., Soto J., New Membrane Perchlorate-Selective Electrodes Containing Polyazacycloalkanes as Carriers, *Sens. and Actuators B Chemical*, **101**, p. 20 (2004).

- [39] Rezaei B., Meghdadi S., Bagherpour S., Perchlorate-Selective Polymeric Membrane Electrode Based on Bis(Dibenzoylamethanato) Cobalt(II) Complex as a Neutra Carrier, *J. Haz. Mat.*, **161**, p. 641 (2009).
- [40] Soleymanpour A., Hamidi asl E., Nabavizadeh S. M., Perchlorate Selective Membrane Electrodes Based on Synthesized Platinum(II) Complexes for Low-Level Concentration Measurements, *Sens. and Actuators B Chemical*, **120**, p. 447 (2007).
- [41] Arvand M., Pourhabib A., Shemshadi R., Giahi M., The Potentiometric Behavior of Polymer Supported Metallophthalocyanines as Anion Selective Electrodes, *Anal. Bioanal. Chem.*, **387**, p. 1033 (2007).

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