Perchlorate-Selective Polymeric Membrane Sensor based on Unsymmetrical Schiff Base of N$_2$O$_2$ Cu (II) Complex

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Abstract
Unsymmetrical Cu(II) complex ((2E, 3E)-N-salicylidene-N’-(2-hydroxyphenylmethylene) 1,2-phenylenediamino Cu(II)) was synthesized and was studied to characterize its potential as an anion carrier in a PVC membrane electrode. The polymeric membrane electrode prepared with unsymmetrical Cu (II) complex showed excellent response characteristics to perchlorate ion. The electrode exhibited Nerstian responses to ClO$_4^-$ ion over a wide concentration range from 1.0 x 10$^{-1}$ to 1.0 x 10$^{-6}$ M. The response time of the electrode was fast (<5S) and the membrane could be used for over 3 months in a PH range of 5-10. The electrode exhibits fast response time, good sensitivity, low detection limit, long stability, appropriate selectivity toward ClO$_4^-$ relative to a variety of other common anions.

Keywords: Perchlorate ion selective electrode, PVC membrane electrode, Schiff base.

Introduction
Schiff base ligands have been available in the chemistry catalogue for over 150 years [1]. Their instant and enduring popularity undoubtedly stem from the ease with which they can be synthesized, their bewildering versatility and their wide raining complexion ability once formed. These Schiff base complexes played a seminal role in the development of modern coordination chemistry [2], inorganic biochemistry [3], catalysis [4], and optical materials [5]. Another wide-spread application of the Schiff bases is their utilization in the ISE (Ion-Selective Electrodes). They are employed as the ion-exchange material (or ionophore or ion-carrier) in the membrane of a certain ISE category; the Polymeric Membrane Electrodes/Microelectrodes. These electrodes consist of various ion-exchange materials incorporated into an inert matrix such as PVC, polyethylene or silicone rubber [6]. Perchlorate is regarded as a new emerging persistent inorganic contaminant because of its specific properties, such as high water solubility, mobility and considerable stability [7].

One of the major sources of this environmental contaminate is the manufacture or improper
storage or disposal of ammonium perchlorate which is used as a primary component of solid propellant for rockets, missiles, fireworks [8–10]. Perchlorate has also been found in food products [11-12], soil [13], milk [14], fertilizers [15], plants [16] and in human urine [17]. There are various methods for the determination of perchlorate ions, including spectroscopy, indirect atomic absorption spectroscopy, ion chromatography, conductometry, gravimetry, amperometry and potentiometry [18-22]. These methods suffer from different interferences. Thus a suitable, simple and fast method for direct determination of perchlorate ion is necessary.

In the past two decades many perchlorate selective electrodes have been reported based on ion –association complexes between perchlorate anions and different organic compounds (long-chain quaternary ammonium ions, organic bases, organic dyes and metal chalets [23-41].

We Report herein, new unsymmetrical Schiff base N₂O₂ complex of Cu (II) ((2E, 3E)-N-salicylidene-N’-(2-hydroxyphenylmethylieden) 1, 2-phenylenediamino Cu (II)) which was synthesized and used as ion carrier in PVC matrix-based anion sensors. The complex has demonstrated to work as efficient carrier of perchlorate anion in the wide working linear range with non-Hofmeister selectivity pattern indicating better selectivity for perchlorate over other inorganic and organic anions.

Experimental

Reagents

All the chemicals used were of analytical reagent grade. High molecular weight Poly Vinyl Chloride (PVC) and tetrahydrofuran (THF) were obtained from Fluka. Dibutylphthalate (DBP), benylacetate (BA), acetophenone (AP), cetyltrimethyl ammonium bromide (CTAB), salicylaldehyde, 1-hydroxy2-acetophenone, orto-phenylenediamine, pipyridine, organic and inorganic salts were obtained from Merck. All solutions and buffers were prepared with deionized distilled water. Ligand prepared by adding 2-hydroxyacetopnone (0.05 mmol) to O-phenylenediamine (0.05 mmol) and then the mixture stirred at 100 °C for 15 minutes to reach yellow solid. Then it was filtered and recrystalized in ethanol. Salicylaldehyde (0.03 mmol) was added to a solution of yellow solid (0.03 mmol) in methanol, then 20 drops of piperdine were added to resulting mixture. The mixture was stirred for 30 min at room temperature and the precipitated product was collected by filtration, washed with methanol and dried by vacuum. Ligand was recognized by IR and 1H-NMR. The IR spectrum of ligand exhibits a broad and intense band at 1612 cm⁻¹ which is assignable to the strechig vibration of two asymmetrical C=N bonds.
1H-NMR ligand (CDCl3): 2.9 Hz (3H,s), 8.16 Hz (1H,s), 6.6-7.6 (12H,m).

CHN Found: N: 6.81, H: 4.90, C: 64.73 (Caled: N: 6.87, H: 4.94, C: 64.77).

2E, 3E)-N-salicylidene-N’-(2-hydroxyphenylmethylidene) 1, 2-phenylenediamino copper (II) was synthesized as described elsewhere [42] and identified by IR and CHN.

**Electrode preparation and Emf measurement**

Different composition of membrane ingredients, including ionophore, the plasticizers DBP, BA, AP, DBS, the additive CTAB (cetyltrimethyl ammonium bromide) and PVC (as shown in Table 1), were thoroughly dissolved in 3 ml THF. The solvent was evaporated solely until an oily concentrated mixture was obtained. Glass tube (3 mm i.d.) was dipped into the mixture for about 30 s. Then the tube was pulled out and kept at room temperature for 12 h, and a membrane of about 0.3 mm thickness was formed at the end of the tube. The tube was then filled with an internal solution of 1.0 x 10^{-3} M perchlorate. The electrode was finally conditioned for 24 h by soaking in a 1.0 x 10^{-2} M perchlorate solution. Potentials were measured using a coring ion analyzer PH/mV meter relative to a double junction saturated calomel electrode (SCE) with the chamber filled with an ammonium nitrate solution at constant temperature (25 ± 0.1°C). A silver/silver chloride electrode containing a 3M solution of KCl was as the internal reference electrode. The electrode cell assembly of the following type was used:

Ag-AgCl | KCl (3M) | internal solution 1.0 x 10^{-3} M ClO_4^- | PVC membrane | tested solution | Hg-Hg_2Cl_2, KCl (saturated).

Membranes containing different PVC/plasticizer ratios were studied and the optimum composition found was 30.0 wt% of powdered PVC, 62 wt% of plasticizer (DBP, 5 wt% of additive (CTAB) and 3 wt% of the complex. These were mixed in 3 ml of THF and transferred into a glass dish of 5 cm diameter. The solution was left for the solvent to evaporate slowly and an oily mixture was obtained. A Pyrex tube (3 mm i.d.) was dipped into the mixture for about 30 s. Then the tube was pulled out and kept at room temperature for 12 h, and a membrane for 0.3 thicknesses was formed at the end of the tube. The tube was then filled with an internal solution of 1.0 x 10^{-3} M perchlorate. The electrode was finally conditioned for 24h by soaking in a 1.0 x 10^{-2} M perchlorate solution. A silver/silver chloride was used as an internal reference electrode (Figure 1).
**Results and Discussion**

Our preliminary experiments revealed that (2E, 3E)-N-salicylidene-N’-(2-hydroxyphenylmethylidene) 1, 2-phenylenediamino copper (II) and the plasticized PVC-based membrane electrodes containing this complex as ionophore after conditioning for about 24 h in $1.0 \times 10^{-2}$ M NaClO$_4$ solution generates stable potential responses in solutions containing perchlorate. The membrane demonstrated a remarkable selectivity toward perchlorate compared to other anions tested. The preferential response of the ionophore towards ClO$_4^-$ is believed to be associated with the coordination of perchlorate with the metal center in this complex and it is the relative affinity of ClO$_4^-$ as a suitable ligand for Cu (II) that dictates the observed selectivity pattern of the electrodes.

The potential responses of the polymeric membrane electrode containing this complex Cu (II) as ionophore for a variety of anions are shown in Figure 2.
Optimization of membrane components

It is well known that the sensitivity, selectivity and linearity of ion selective sensors does not only depend on the nature of ionophores used, but also considerably on the membrane composition and the properties of the plasticizers used [43-48]. Thus, the effect of the membrane composition, the amount of the plasticizer on the potential response of the ClO₄⁻ sensor were investigated and the results are summarized in Table 1. As seen from Table 1, in the absence of ionophore, the electrode showed a negligible response slope (No. 1). Based on the results obtained on the optimization of the membrane composition, the membrane 2 with the optimized composition of DBP: PVC (powdered high molecular weight): ionophore: CTMAB ratio of 62: 30: 3:5 was selected for the preparation the polymeric membrane electrode for perchlorate ion.

Table 1. Composition and optimization of membranes ingredients complex.

<table>
<thead>
<tr>
<th>No</th>
<th>Composition in membranes (%)</th>
<th>Slope (mV/decade)</th>
<th>Linear range</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30  65(DBP)       -          5   29.2     1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9305</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30  62(DBP)       5           3   32.81    1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9654</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30  62(DBP)       -           5   25.63     1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>30  62(DBP)       5           10  32.59    1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9569</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30  62(DBP)       3           5   31.21    1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>30  62(BA)        5           3   12.87     1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9952</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>30  62(AP)        5           3   5.5063     1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9759</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>30  62(DBS)       5           3   23.8     1<em>10⁻¹ to 1</em>10⁻⁶</td>
<td>0.9842</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Cetyltrimethyl ammonium bromide
Effect of internal reference solution

The influence of the concentration of the solution on the potential response of the ClO$_4^-$ ion selective was studied. The NaClO$_4$ concentration was changed from $1.0 \times 10^{-3}$ to $1.0 \times 10^{-4}$ M and the potential response of the ClO$_4^-$ ion selective was obtained. It was found that variation of the concentration of the internal solution did not cause any significant difference in the potential response; except for an expected change in the intercept of resulting Nernstian plot. A $1.0 \times 10^{-3}$ M concentration of internal reference solution is quite appropriate for smooth functioning of the electrode system.

Effect of PH

The pH dependence of potential response of the proposed membrane sensors at two different concentrations of ClO$_4^-$ ions in the PH rang 1-12 was tested and the results are shown in Figure 3. The pH was varied by adding either HCl or NaOH. The results indicated that the optimum pH was in the range of 5-10. At higher pH values the potential decreased due to the simultaneous response of the electrode to ClO$_4^-$ and OH- anions. On the other hand, at pH values lower than 3 the electrode potential decreased most probably due to higher Cl- ion concentration and simultaneous response of the electrode to perchlorate and chloride ions.

![Figure 3](image.png)

**Figure 3.** Influence of pH test on the potential response of the perchlorate selective electrode at different ClO$_4^-$ concentrations: $1.0 \times 10^{-3}$ and $1.0 \times 10^{-4}$ M.

Response characteristics of the perchlorate-selective electrode

Ion-selective electrode characterization preformed with a mathematical and computational
program is very useful for the determination of detection limits and selectivity constants [49-50]. Accordingly, the slope, detection limit and selectivity coefficients of the perchlorate electrode were determined by fitting calibration data to the Nikolskii-Eisenman equation or to the formalism of Bakker et al. [51] for mixed-ion solutions of primary and interfering ions of different charge. The slope and detection limit of the electrode were evaluated from data generated repeatedly from calibration graphs between $1.0 \times 10^{-1}$ and $1.0 \times 10^{-6}$ M. The calibration parameters thus obtained are included in Table 2. As can be seen a near-Nerstian response, low detection limit and good calibration reproducibility were obtained. The response time was obtained from the dynamic response curves corresponding to perchlorate concentration steps to obtain a 10 fold concentrated solution. The values obtained for different perchlorate concentrations are included in Table 2 which show a very rapid response even for low concentration. The experimental results showed that the lifetime of the electrode was more than 3 months. During this period the detection limit and slope of the electrodes remained almost constant.

Table 2. Response characteristics of the percholrate-selective electrode.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (mV/decade)</td>
<td>32.81</td>
</tr>
<tr>
<td>Linear range (mol/L^{-1})</td>
<td>$1.0 \times 10^{-1}$ to $1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Response time (s)</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Working pH range</td>
<td>3-10</td>
</tr>
<tr>
<td>Lifetime (months)</td>
<td>&gt;3</td>
</tr>
</tbody>
</table>

**Conclusion**

The electrode based on (2E, 3E)-N-salicylidene-N’-(2-hydroxyphenylmethyldiene) 1, 2-phenylenediamino copper (II) complex can be useful analytical tool for the determination of perchlorate ions in different samples. Response time of the electrode is fast and the membrane could be used over 3 months in PH range of 5-10. The electrode showed good sensitivity, low detection limit, appropriate selectivity toward ClO$_4^-$ compared to a variety of other common anions.

**References**