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Cu(II) complexes as receptor molecules for development of new chloride sensors

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Abstract

Highly sensitive and selective chloride polymeric membrane sensors are developed that employ Cu(II) complexes as anion carriers. Optimized membrane sensors showed a near-Nernstian response towards chloride anion over a wide concentration range of 2.5×10^{-5} to 1.0×10^{-1} M and have micromolar level detection limits. These sensors have fast response time and work well in the pH range of 4.2-9.6. They exhibited enhanced potentiometric selectivity for chloride over other anions, including more lipophilic anions such as perchlorate, thiocyanate, nitrate, etc. Response characteristics (e.g. detection limit, linear range, response slope and selectivity) of these sensors remain essentially the same over a period of ~ 5 months, reflecting remarkable stability.

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1. Introduction

Carrier-based ion-selective electrodes have become increasingly useful in clinical and physiological measurements [1,2]. The development of anion-selective liquid/polymeric membrane electrodes for the assessment of anion concentrations in real samples is of increasing interest for clinical, environmental and industrial applications [3–7]. Various approaches have been attempted to develop chloride selective electrodes. Anion exchangers have been employed as electroactive species for the development of chloride sensors [8,9]. However, these sensors lack selectivity over more lipophilic anions and respond significantly to more lipophilic anions according to wellknown Hofmeister series [10]. A host of organotin compounds [11,12], utilized as anion carriers, in chloride selective sensors demonstrate a selectivity pattern that also deviates from the lipophilicity-based Hofmeister selectivity. These sensors, due to certain limitations of long response time, non-Nernstian response and potentiometric signal instability, lacked practical

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0013-4686/\$ - see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2006.05.023 applications [13]. Several approaches of reducing interferences from lipophilic anions have been reported. Chloride sensors based on neutral carrier type metal complexes such as metalloporphyrins [14,15] and mercury organic derivatives [16,17] have also been developed. However, the non-classical behavior, chemical instability and insufficient selectivity impeded the use of these electrodes in direct monitoring of chloride in physiological samples. Recently, a new chloride sensor based on ruthenium(III) Schiff's base complex has been reported [18]. The sensor was successfully applied for the determination of chloride in serum samples.

Since various inorganic anions play fundamental roles in chemical and biological systems, the development of specific receptors to monitor the targeted anions of biological and environmental interest remains a formidable challenge. Developing better chloride ionophores is of high interest, mainly because of the significance of measuring chloride in physiological applications. An attempt has been made to prepare metal complexes for use as chloride anion carriers. The design of dinuclear complexes employs a synthetic strategy where different multidentate ligand systems are coordinated around vacant coordination sites on the metal ions [19–22]. Much emphasis has been given to the molecular framework by choosing an appropriate ligand system and pendant functional groups around the metal site. The incorporation of a functionally active ligand system, its denticity, chelate ring size, donor type and substituents on or near N-donors influence the selectivity and M2-O2 structure reactivity [23,24]. In this work, a biologically significant class of ligand β -diketone was chosen primarily as it exhibits versatile coordination ability and shows bidentate chelate formation [25]. Secondly, β -ketonate complexes have proved to be efficient antitumor agents against various carcinoma [26]. The dinuclear copper complexes with two metal ions in close proximity have received great attention [27-29] due to their potential use as bimetallic catalysts modeling the enzyme activity. Schiff bases are also currently being studied extensively owing to their biological and anticancer activity [30-34]. They are versatile ligands for many transition metals and provide donor atoms suitable for the formation of di- and trinuclear complexes. On complexation, the biological activity including anticancer is considerably enhanced which has led to metal-based pharmaceuticals [35]. Diazines in aromatic heterocyclic ligands have been utilized in bringing two copper(II) centers into close proximity to study the influence of antiferromagnetic intramolecular exchange.

In the present work, Cu(II) complexes are examined as unique ion carriers in PVC-matrix-based anion sensors. They have been demonstrated to work as efficient carriers of chloride anion in the wide working linear range with non-Hofmeister selectivity pattern indicating better selectivity for chloride over other inorganic and organic anions.

2. Experimental

2.1. Cu(II) complexes

Cu(II) complexes used in this work are shown in Fig. 1. Cu(II) complex 1 has been synthesized by the method reported in literature [36], whereas Cu(II) complex 2 has been synthesized by following method: to a solution of the ligand LH₂ (0.5 g, 1 mmol) in dichloromethane (25 cm³) was added CuCl₂·2H₂O (0.3 g, 2 mmol) in MeOH in 1:2 molar ratio. The colored product was isolated by slow evaporation of the resultant mixture, filtered, washed with hexane and dried in vacuo. Purple solid, yield, 70%; mp 98 °C; calculated for C₃₂H₃₀N₆O₂Cu₂Cl₂: 58.8% C, 4.1% H, 11.5% N. Found: 58.5% C, 4.1% H, 11.4% N. IR



Fig. 1. Structures of Cu(II) complexes.

(in nujol mull) (cm⁻¹): 1608 (C=N of N₂O₂ donor set), 1007 (N–N), 1490 (C–N), 1240 (C–O), 530 (Cu–N), 475 (Cu–O), 360 (Cu–Cl). UV–vis (in CH₂Cl₂) (cm⁻¹): 26,310, 18,796.

2.2. Other reagents

Poly(vinyl chloride) (PVC), dioctylsebacate (DOS), dioctylphthalate (DOP) and dibutylphthalate (DBP) were purchased from Fluka. Dried tetrahydrofuran (THF) and hexadecyltrimethylammonium bromide (HTAB) were used as received from Lancaster. Sodium salts of various interfering anions obtained from S.D. Fine-Chemicals were of analytical reagent grade. Doubly distilled de-ionized water was used throughout.

2.3. Electrode preparation and potential measurements

General procedure adopted to prepare PVC membrane was as follows: the appropriate amounts of various membrane ingredients [4.9 mg copper(II) complex **1**, 100.3 mg PVC, 2.0 mg HTAB, 200.4 mg DBP, and 5.1 mg copper(II) complex **2**, 100.0 mg PVC, 2.0 mg HTAB, 202.3 mg DBP] were dissolved in 5 mL of THF. The resulting mixture stirred vigorously and after removing air bubbles, was transferred into 50 mm petridish. The solvent was allowed to evaporate off at room temperature overnight. A flexible, transparent membrane of thickness ~0.4 mm was obtained. A membrane of suitable size was cut and fixed to PVC tube with the help of PVC glue and conditioned in 1.0×10^{-2} M NaCl solution for 2 days. Table 1 shows the optimized composition of various Cl⁻ anion-selective electrode membranes.

All emf measurements were carried out with the following cell assembly:

Ag-AgCl|3 M KCl|internal reference solution

 $(1.0 \times 10^{-2} \text{ M NaCl})|\text{PVC membrane}|\text{test solution}|$

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3 M KCl|Ag-AgCl
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Table 1

Membrane compositions and electrode characteristics of various chloride sensors prepared

The measurements of the electrode potentials were done with an Equip-tronics model EQ-602 potentiometer, and pH measurements were made with an Elico LI-model-120 pH meter.

3. Results and discussion

3.1. Response characteristics of sensors

In the preliminary experiments, the membrane electrodes were prepared incorporating Cu(II) complex **1** as ion carrier and DOP as plasticizer. The potentiometric response of these electrodes was observed for different anions such as fluoride, chloride, iodide, nitrate, salicylate and thiocyanate anions. The potential versus logarithm of concentration curves for these anions so obtained are shown in Fig. 2. It is clear from Fig. 2 that the sensor for chloride anion showed better potentiometric response as compared to other anions studied. This indicates that Cu(II) complex **1** is capable of binding chloride anion selectively than other anions. Similar experiments were preformed for Cu(II) complex **2** and this complex was also found to sense chloride anion sensitively and selectively over a wide concentration range as compared to others.

The sensitivities and selectivities obtained for a given ion carrier depend significantly on the nature of the plasticizer used in the preparation of membranes. Since it influences the dielectric property of the membrane phase and the mobility of the ion carrier in the PVC matrix, its selection is one of the most important tasks in designing a sensitive and selective anion-selective sensor. In the present study, membranes were prepared by incorporating three different plasticizers (DOP, DOS and DBP). The membrane compositions and electrode characteristics of these membranes are given in Table 1. Among all of these (membranes A–F), membrane electrodes C and F incorporating DBP as plasticizer showed best sensitivity for the sensors in terms of slope and working linear concentration range, whereas the use of DOP and DOS in membranes A, D and B, and E, respectively, resulted in a pronounced reduction in the slope of the

| ISEs | PVC ^a | HTAB ^a | Complex ^a | | Plasticizer ^a | | | Slopes (mV per decade) | Linear range (M) |
|------|------------------|-------------------|----------------------|------|--------------------------|-------|-------|------------------------|---|
| | | | 1 | 2 | DOP | DOS | DBP | | |
| A | 102.4 | 2.0 | 5.1 | _ | 200.5 | _ | _ | -49.49 | $2.5 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| В | 100.5 | 2.0 | 5.0 | _ | _ | 200.7 | _ | -46.52 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| С | 100.3 | 2.0 | 4.9 | _ | _ | _ | 200.4 | -56.49 | $2.5 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| D | 102.0 | 2.0 | _ | 5.2 | 208.1 | _ | _ | -49.97 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| Е | 100.0 | 1.9 | _ | 4.9 | - | 201.9 | _ | -47.21 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| F | 100.0 | 2.0 | _ | 5.1 | _ | _ | 202.3 | -55.17 | $2.5 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| G | 103.2 | _ | 5.0 | _ | _ | _ | 203.9 | -34.87 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| Н | 100.4 | 2.0 | 10.1 | _ | - | _ | 201.5 | -52.28 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| Ι | 101.0 | 1.9 | 15.2 | _ | - | _ | 203.1 | -50.22 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| J | 100.4 | 2.0 | _ | 9.9 | _ | _ | 200.5 | -49.35 | $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ |
| Κ | 100.0 | 2.0 | _ | 15.3 | - | _ | 200.5 | -44.62 | $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ |
| L | 100.2 | 3.0 | 5.2 | _ | _ | _ | 205.7 | -41.48 | $2.5 \times 10^{-5} - 1.0 \times 10^{-2}$ |
| М | 100.2 | 5.0 | 5.0 | - | _ | _ | 200.6 | -37.37 | $5.0\times 10^{-5} 1.0\times 10^{-2}$ |
| | | | | | | | | | |

HTAB: hexadecyltrimethylammonium bromide, DOP: dioctylphthalate, DOS: dioctylsebacate, DBP: dibutylphthalate. ^a Compositions (in mg).



Fig. 2. Potentiometric responses for representative individual anions obtained with sensors based on Cu-complex 1.

electrode response. The electrodes C and F based on Cu(II) complexes **1** and **2** showed near-Nernstian slopes of -56.49 and -55.17 mV per decade, respectively, in the linear concentration range of 2.5×10^{-5} to 1.0×10^{-1} M (Fig. 3). The detection limits of these sensors were found to be 7.586×10^{-6} and 9.772×10^{-6} M for C and F, respectively, with the internal reference solution of 1.0×10^{-2} M NaCl solution.

Ion-carrier-based electrodes are considerably influenced by the nature of the ion carrier as well as composition of the membrane. We also investigated the influence of membrane compositions on the potential response of chloride sensors (Table 1). Various membranes with varying amounts of additive and ion carrier were prepared. As is obvious from Table 1, increasing the amount of ion carrier in the membranes resulted in decreased sensitivity with relative decrease in slope values of the sensors (membranes C, H and I for ion carrier **1** and F, J and K for ion



Fig. 3. Potentiometric responses of chloride sensors C and F based on Cu(II) complexes 1 and 2, respectively, incorporating DBP as plasticizer.

carrier 2). Both Cu(II) complexes are expected to act as neutral carriers for anions. Accordingly, membrane electrodes prepared without lipophilic cationic additives should show a little anionic response, while a better anionic response is expected only in the presence of cationic sites in the membranes [37]. These cationic additives induce the anion permselectivity of the membrane and work as the counterion for the chloride complex of ion carriers. It is also well known that the cationic additives (HTAB) can reduce ohmic resistance [38] and improve the response of anionselective electrodes [39,40]. It is clear from Table 1 that the presence of HTAB in the membrane composition (membrane G without any additive as compared to membrane C) increases the sensitivity of the sensors. However, the addition of increasing amount of HTAB (membranes L and M) decreases the sensitivity of the sensors for chloride anions. The membranes with the optimum ratio of ion carrier/HTAB: 5 mg/2 mg, revealed near-Nernstian response to the concentration of chloride anion.

The effect of concentration of internal reference solution was also studied. The potentiometric response was recorded at three different concentrations, i.e., 1.0×10^{-1} , 5.0×10^{-2} and 1.0×10^{-2} M NaCl of internal reference solution. No significant change in potential response of the sensors was observed with the variation of the concentration of internal reference solution except for an expected change in the intercept of the curves. Thus, 1.0×10^{-2} M NaCl solution was found quite appropriate for smooth functioning of the electrode system.

3.2. Effect of pH and response time of sensors

The pH dependence of chloride sensors based on Cu(II) complexes was examined over a pH range of 1–12 at different concentrations of chloride anion solutions. Fig. 4 demonstrates the variation of the electrode potentials of chloride sensors C and F, with pH at a chloride anion concentration of 1.0×10^{-2} M. From the plots shown in Fig. 4, it is evident that for every sensor



Fig. 4. Plots showing the variation of electrode potential of chloride sensors with pH at 1.0×10^{-2} M NaCl solution.



Fig. 5. Response time curve of chloride sensor F, based on Cu-complex 2 for step changes in concentration of Cl^- anion.

the electrode potential remained constant over a wide pH range of 4.2–9.6, which was taken as the functional pH range of the sensor. The observed drift at higher pH values could be due to the simultaneous response of the sensors to chloride and hydroxide ions. Pure solutions of sodium chloride do not need any pH adjustment, since their pH lies in the functional pH ranges of the sensors.

The average time required for the chloride sensors to reach a potential within $\pm 1 \text{ mV}$ of the final equilibrium value after successive immersion of a series of NaCl solutions, each having a 10-fold difference in concentration, was measured. Fig. 5 shows the potential versus time trace for chloride sensor, F, from lower $(1.0 \times 10^{-4} \text{ M})$ to higher $(1.0 \times 10^{-1} \text{ M})$ concentration of NaCl solutions. The sensor yielded steady state potentials within 20 s, and the electrode potential remained constant for more than 5 min, after which a very slow divergence was observed. Similarly response time recorded for chloride sensor, C, was reasonably short (within 20s), and the stability of the potentiometric signal was quite satisfactory. The sensing behavior of the membrane sensors remained unchanged when the potential was recorded either from low to high concentration or vice versa. The present type of sensors gave reproducible potentials with the standard deviation of $\pm 1 \text{ mV}$ and their potentials remained constant for more than 5 min. In terms of lifetime of the sensors, these could be used over a period of 5-6 months without any significant change in the value of slope, working concentration range and response time.

Table 2 Selectivity coefficient values, log $K_{Cl^- X^-}^{Pot}$, of chloride sensors

| Diverse anions | С | F |
|----------------------------------|-------|-------|
| NO ₂ - | -2.46 | -2.44 |
| NO ₃ ⁻ | -2.45 | -2.73 |
| ClO ₄ - | -2.53 | -2.57 |
| SCN ⁻ | -0.12 | +0.03 |
| HCO ₃ ⁻ | -2.50 | -2.52 |
| HPO_4^{2-} | -3.45 | -3.26 |
| $H_2PO_4^-$ | -2.62 | -3.05 |
| Salicylate ⁻ | -2.58 | -2.42 |
| F ⁻ | -2.37 | -2.35 |
| Br ⁻ | -0.08 | -0.29 |
| I- | +0.31 | +0.15 |
| CH ₃ COO ⁻ | -2.66 | -2.65 |
| SO_4^{2-} | -3.33 | -3.48 |
| CO ₃ ²⁻ | -3.47 | -3.53 |

3.3. Selectivity

One of the most important characteristics of any ion-selective electrode is its relative response to the primary ion over other ions in solution, which is expressed in terms of potentiometric selectivity coefficients. The selectivity coefficients have been determined using fixed interference method (FIM) based on the semi-empirical Nicolskii-Eisenman equation. In this method, the concentration of primary ion, chloride anion, is varied, whereas the concentration of secondary interfering ions is kept constant in the test solutions which is 1.0×10^{-2} M concentrations of interfering ions in present case. The potentiometric selectivity coefficients $(\log K_{Cl^-,X^-}^{Pot})$ of chloride sensors for various interfering ions are given in Table 2. The potentiometric selectivity sequence for sensor C was found to be in the order of $I^- > Br^- > SCN^- > F^- > NO_3^- \approx$ $NO_2^- > HCO_3^- > CIO_4^- > salicylate > H_2PO_4^- > CH_3COO^- > SO_4^{2-} > HPO_4^{2-} > CO_3^{2-}$, whereas that for sensor F was found as $I^- > SCN^- > Br^- > F^- > salicylate > NO_2^- > CO_3^{2-} > SO_4^{2-} > SO_4$ $HCO_3^- > CIO_4^- > CH_3COO^- > NO_3^- > H_2PO_4^- > HPO_4^{2-} > SO_4^{2-} > CO_3^{2-}$. The non-Hofmeister selectivity sequence so obtained for both chloride sensors C and F is assumed to be associated with an interaction between the central metal of the carrier and chloride ion. Most of the anions were found to induce negligible disturbance on the normal functioning of the chloride sensors. Thiocyanate, bromide and iodide anions were observed to be interfering anions but the selectivity values calculated for these anions were found to be better than those reported earlier in literature (Table 3). As can be seen from Table 2, the selectivity coefficients for these sensors were quite

Table 3

Comparison of selectivity coefficient values, $\log K_{Cl^-,X^-}^{Pot}$, of proposed chloride sensors with those reported in literature

| Interfering anion | Sensor C | Sensor F | Ref. [41] | Ref. [42] | Ref. [43] | Ref. [44] | Ref. [45] |
|--------------------|----------|----------|-----------|-----------|-----------|-----------|-----------|
| SCN- | -0.12 | +0.03 | +1.0 | +3.8 | +0.6 | +3.4 | -0.16 |
| I ⁻ | +0.31 | +0.15 | +0.5 | +3.4 | +0.8 | +2.4 | +2.34 |
| Br ⁻ | -0.08 | -0.29 | +0.4 | +1.4 | +0.1 | +0.9 | +1.04 |
| NO_3^- | -2.45 | -2.73 | +0.7 | +2.1 | -0.9 | +1.2 | -2.71 |
| HCO ₃ - | -2.50 | -2.52 | - | - | -1.9 | - | - |

Table 4 Determination of chloride anion concentration in synthetic water samples using chloride sensor F

| Amount of Cl ⁻ added (mM) | Amount of Cl ⁻ recovered (mM) | Recovery (%) | | |
|---|---|--------------|--|--|
| 80 | 77.8 | 97.2 | | |
| 50 | 47.2 | 94.4 | | |
| 30 | 28.7 | 95.7 | | |
| 20 | 18.8 | 94.0 | | |
| 10 | 9.1 | 91.0 | | |

high for iodide anion and it was expected to cause interference in normal functioning of the sensors. In order to examine the performance of the sensors in the presence of this interfering anion, various experiments were carried out at 1.0×10^{-2} , 1.0×10^{-3} , 1.0×10^{-4} and 5.0×10^{-5} M concentrations of the interfering I⁻ anion in the background. The limiting concentration of I⁻ anion that can be tolerated in the determination of Cl⁻ anion was found to be 5.0×10^{-5} M. In comparison with the anion-exchanger-based membrane electrodes that suffer severely from lipophilic anion interferences, the high chloride selectivity of Cu(II) complexes-based chloride sensors over biologically important anions should allow the determination of chloride in physiological fluids. It is worth mentioning that the presence of bromide in physiological fluids (e.g. serum) is very infrequent, and other physiologically important anions such as bicarbonate, phosphate and sulfate induce minimal interference as indicative from the selectivity values. This high discrimination against these anions indicates that they should not interfere with the chloride determination in physiological fluids.

In order to access the application of these sensors, experiments were conducted to measure Cl^- anion concentration in synthetic water samples containing known concentration of Cl^- anion with chloride sensor F (Table 4). As can be seen, the recovery of chloride anion from different samples is almost quantitative; these sensors could be used as indicator electrode for chloride determination.

4. Conclusion

A new class of anion carriers, Cu(II) complexes, has been utilized for the development of new chloride sensors. The best performance was obtained with the sensors having membrane compositions as follows: 4.9 mg copper(II) complex **1**, 100.3 mg PVC, 2.0 mg HTAB, 200.4 mg DBP, and the other sensor with 5.1 mg copper(II) complex **2**, 100.0 mg PVC, 2.0 mg HTAB, 202.3 mg DBP. These PVC-matrix-based sensors were found to work well in the pH range of 4.2–9.6 with low detection limits and displayed a short response time and fast recovery. The proposed sensors induced a selectivity pattern completely different from the Hofmeister series, including most of the lipophilic anions. The selectivity coefficient values were found to fulfill the required values for chloride sensors in physiological fluids. In addition, these sensors could be used for determination of chloride anion in various synthetic samples.

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