Potentiometric anion selectivity of polymer-membrane electrodes based on cobalt, chromium, and aluminum salens

Ibrahim H.A. Badr*

Department of Chemistry, Faculty of Science, Ain Shams University, P.O. Box 11566, Cairo, Egypt

Abstract

Metallo-salens of cobalt(II) (Co-Sal), chromium(III) (Cr-Sal), and aluminum(III) (Al-Sal) are used as the active ionophores within plasticized poly(vinyl chloride) membranes. It is shown that central metal–ion plays a critical role in directing the ionophore selectivity. Polymer-membrane electrodes based on Co-Sal, Cr-Sal, and Al-Sal are demonstrated to exhibit enhanced responses and selectivity toward nitrite/thiocyanate, thiocyanate, and fluoride anions, respectively. The improved anion selectivity of the three ionophore systems is shown to deviate significantly from the classical Hofmeister pattern that is based only on ion lipophilicity. For example, optimized membrane electrodes for nitrite ion based on Co-Sal exhibit $\log K^{\mathrm{pot}}_{\mathrm{Nitrite,Anion}}$ values of -5.22, -4.66, -4.48, -2.5 towards bromide, perchlorate, nitrate, and iodide anions, respectively. Optimized membrane electrodes based on Co-Sal and Cr-Sal show near-Nernstian responses towards nitrite (-57.9 ± 0.9 mV/decade) and thiocyanate (-56.9 ± 0.8 mV/decade), respectively, with fast response and recovery times. In contrast, Al-Sal based membrane electrodes respond to fluoride ion in a super-Nernstian (-70 ± 3 mV/decade) and nearly an irreversible mode. The operative response mechanism of Co-Sal, Cr-Sal, and Al-Sal membrane electrodes is examined using the effect of added ionic sites on the potentiometric response characteristics. It is demonstrated that addition of lipophilic anionic sites to membrane electrodes based on the utilized metallo-salens enhances the selectivity towards the primary ion, while addition of cationic sites resulted in Hofmeister selectivity patterns suggesting that the operative response mechanism is of the charged carrier type. Electron spin resonance (ESR) data indicates that Co(II) metal–ion center of Co-Sal ionophore undergoes oxidation to Co(III). This process leads to formation of a charged anion-carrier that is consistent with the response behavior obtained for Co-Sal based membrane electrodes.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Anion sensors; Polymer-membrane electrodes; Salen complexes; Response mechanism

1. Introduction

Highly selective liquid/polymeric membrane electrodes for cations (e.g., sodium, potassium, calcium, ammonium and hydrogen ions) have already replaced the conventional analytical techniques for routine analysis of many analytes (e.g., blood gases and electrolytes) [1,2]. In contrast, highly selective liquid/polymeric membrane electrodes are not available for all anions, particularly the hydrophilic anions, and are not widely used in routine analysis with very few exceptions [3]. The development of selective and sensitive liquid/polymeric membrane electrodes for anions is of increasing interest for clinical, industrial, as well as environmental applications. The need for selective and sensitive sensors stems from the fact that real samples are usually complex in nature and target analytes are typically present at low concentration levels. Classical membrane electrodes for anions that are based on various anion-exchangers exhibit similar selectivity sequence (lipophilic organic anions $> ClO_4^- > IO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > F^- \geq H_2PO_4^-$ [4]). Therefore, more lipophilic anions are preferred and anion-exchanger based membrane electrodes lack selectivity for hydrophilic anions [5]. Furthermore, anion-exchanger based membrane electrodes do not satisfy the required selectivity for the analysis of hydrophobic anions in many practical applications (e.g., analysis of thiocyanate and salicylate in physiological fluids [6]).

Ever since the first non-Hofmeister anion membrane electrode was described by Simon et al. [7,8], this type of electrodes is gaining growing research interest. Simon et al. utilized lipophilic derivatives of Vitamin B_{12} as nitrite ion-carriers in polymer membranes. Vitamin-B_{12} based membrane electrodes showed excellent nitrite/thiocyanate selectivity compared to

* Tel.: +202 417 9685; fax: +202 684 2123.
  E-mail address: ibadr1@yahoo.com.

that of the classical anion-exchanger based electrodes. Several metal–ion complexes and organometallic compounds such as metalloporphyrins [6,9,10], metallophthalocyanines [11,12], organotin [13], organopalladium [14], mercury carborane [15,16], as well as organomercury [17] compounds have been investigated as potential anion-carriers in liquid/polymeric membranes. Active research in this area led to the development of membrane electrodes with significantly enhanced selectivity for anions such as NO_2^- [7,14,18], Cl^- [15–17], F^- [19,20], SO_3^{2-} [21], and salicylate [6]. The enhanced selectivity in these cases is highly dependant on the type of the metal–ion center of the ionophore that leads to a selective ligation with a particular anion, or the existence of selective complementary interaction between the target anion and the carrier. To a less extent changing the peripheral ligand structure alters the anion selectivity [16,22]. Moreover, steric/electronic effects, in those cases, facilitate the recognition of a specific anion based on size or strength of binding to the ionophore [16,22]. In addition to utilizing metal–ion complexes and organometallic compounds as anion-carriers in liquid polymeric membranes, very useful ionophores based on different anion-recognition mechanisms have been developed. The recognition in those cases is based on selective hydrogen-bonding interactions [23–26] or reversible reaction with the host species [27,28].

Metallo-salens are interesting class of metal–ion complexes that exhibited non-Hofmeister selectivity pattern when doped in polymer membranes [29–38]. Such complexes are easily prepared and they can be made highly hydrophobic by using a lipophilic amine as a starting material. Several substitutes can be introduced to the peripheral ligand to induce various electronic and steric effects [29]. To date a host of non-Hofmeister membrane electrodes based on metal–ion complexes of salen ligands have been investigated. For example, membrane electrodes based on salen complexes of Hg^{2+}–Co^{2+} [29,39,40], Sn^{4+}–Al^{3+} [41,42], and Mn^{2+}–Co^{2+} [43,44] were shown to exhibit non-Hofmeister selectivity pattern with enhanced potentiometric responses towards iodide, salicylate, and thiocyanate, respectively.

In this study, salen complexes containing Co(II), Cr(III), and Al(III) are examined as anion carriers in liquid/polymeric membrane electrodes. Lipophilic Cr(III) and Al(III) salen complexes, have not been explored before in liquid/polymeric membrane electrodes as ionophores for thiocyanate and fluoride anions, respectively. Although some Schiff-base complexes of Co(II) have been previously evaluated as anion carriers [29,40,44], herein we show that the electrically neutral Co(II)-salen is oxidized during the conditioning process to form a positively charged Co(III)-salen that accounts for the charged carrier operative response mechanism obtained for nitrite/thiocyanate (see below).

2. Experimental

2.1. Reagents

High molecular weight poly(vinyl chloride) (PVC), *o*-nitrophenyloctylether (*o*-NPOE), dioctylsebacate (DOS), potas-
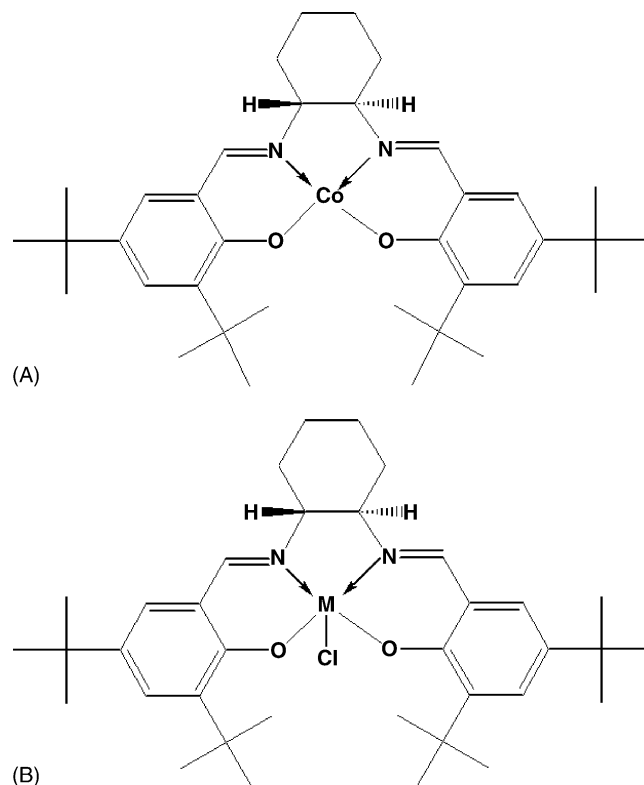

(A)

(B)

Fig. 1. Chemical structure of the salen complexes used in this study: (*R,R'*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (A), and (*R,R'*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride, and (*R,R'*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminoaluminum(III) chloride (B).

sium tetrakis[bis(3,5-trifluoromethyl)phenyl] borate (KTFPB), tridodecylmethylammonium chloride (TDMAC) and Selectphore® grade tetrahydrofuran (THF) were obtained from Fluka (Ronkonkoma, NY). (*R,R'*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (Co-Sal), (*R,R'*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (Cr-Sal), and (*R,R*)-*N,N'*-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexane diamino aluminium(III) chloride (Al-Sal) ionophores were obtained from Aldrich (Milwaukee, WI) (see Fig. 1 for chemical structure). Tris-hydroxymethylaminomethane (TRIS) and 2-morpholinoethanesulfonic acid (MES) were purchased from Research Organics (Cleveland, OH). The sodium salts of fluoride, thiocyanate, and sulfate were obtained from Matheson (Cincinnati, OH). Sodium salts of iodide, nitrite and nitrate were purchased from J.T. Baker (Philipsburg, NJ). Sodium salts of perchlorate, salicylate, bromide, and acetate, were obtained from Sigma (St. Louis, MO). Sodium chloride was obtained from Fisher Scientific (Cincinnati, OH). MES-NaOH buffer was prepared by titrating 50 mM solution of the acid form with concentrated sodium hydroxide to a pH-value of 5.00 ± 0.01. TRIS-SO_4 buffer was prepared by titrating 50 mM of the basic form of TRIS using concentrated solution of H_2SO_4 to a pH-value of 7.40 ± 0.01. Eighteen megaohms deionized water was used for the preparation of all aqueous solutions.