Study of Cobalt(III) Corrole as the Neutral Ionophore for Nitrite and Nitrate Detection via Polymeric Membrane Electrodes

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Abstract
Cobalt(III) 5,10,15-tris(4-*tert*-butylphenyl) corrole was synthesized and incorporated into plasticized poly(vinyl chloride) membranes and studied as a neutral carrier ionophore via potentiometry. This cobalt(III) complex has binding affinity to nitrite, and the resulting membrane electrode yields reversible and Nernstian response toward nitrite. Enhanced nitrite selectivity is observed over other anions, including lipophilic anions such as thiocyanate and perchlorate when an appropriate amount of lipophilic cationic sites are added to the membrane phase. Detection limit to nitrite is ca. 5 μM. Using tributylphosphate as the plasticizer with the cobalt(III) corrole species yields electrodes with enhanced nitrate selectivity.

Keywords: Ion-selective electrodes,, Nitrite, Nitrate, Polymeric membrane electrodes, Potentiometry

1 Introduction

There remains great interest in devising new ion-selective polymeric membrane electrodes (ISEs) [1–3] because they are simple, inexpensive and portable devices that can be employed for many practical analytical applications [4–7]. For the detection of anions and cations with such ISEs, plasticized polymeric membranes containing an appropriate ionophore, a lipophilic ion-exchange additive and a plasticizer are typically utilized. To achieve selectivity for the target ion over more lipophilic ionic species in the sample phase, ionophores (ion carriers) with specific binding affinity to the target ion are required within the organic membrane phase. To date, considerable research on developing new ionophores to improve selectivity has been conducted. Among all the anion-selective ionophores examined, hydrophobic metal ion-ligand complexes are among the most useful, including metallocorrins, metalloporphyrins, and metallosalophens. It has been reported that both the metal ion center and the specific ligand structure can influence selectivity [8–10]. Indeed, a strong and selective axial ligation reaction between the ionophore and target anion to form a host-guest complex is required to yield non-Hofmeister selectivity patterns (i.e., selectivity based on free energy of hydration of the anions). The degree of binding between ionophore and target anion can, however, also be altered by the specific ligand structure.

Corroles, like porphyrins, possess a tetrapyrrolic macrocycle structure with an aromatic 18π electron system. Unlike porphyrins, there is a direct linkage between two adjacent pyrrole rings so that the skeletons of corroles are contracted by one carbon [11]. Owing to the above, corroles are trianionic tetradentate ligands when chelated with metal ions, providing interesting properties. Corroles are known to form complexes with various transition and main group metal ions, including Cr(III), Mn(III), Fe(II)/Fe(III), Ru(II)/(III)/(IV), Co(III), Rh(III), Zn(II), Ge(IV), and Sn(IV) [12]. However, relatively few metallocorroles have been reported as anion ionophores for ISEs. Indeed, only 5,10,15-triphenylcorrole metallated with Mn(III), Cu(II) and Fe(III) have been studied as receptors in polymeric membrane electrodes for anion detection [13]. Selectivity toward Cl⁻ was enhanced when Mn(III) was used as the metal ion center for a corrole ligand, while enhanced selectivity toward CO_3^{2-} and HPO_4^{2-} were observed with Cu(II) and Fe(III) as the metal centers, respectively. These findings suggest that corroles complexed with other metal ion centers are worthy of investigation as new ionophore systems for ISEs.

Early research efforts exploited lipophilic vitamin B_{12} derivative complexes with cobalt(III) as the metal center to serve as a charged carrier type ionophore to detect nitrite with high selectivity over chloride [14]. However, this ISE exhibited nearly equivalent potentiometric response to thiocyanate. The core portion of the Co(III)-B_{12} derivative is a corrin ring which resembles the corrole ring, differing only in their aromaticity. Since the metal ion center plays a vital role in the anion selectivity patterns observed, a Co(III) corrole should serve as a nitrite selective ionophore as well. In fact, there have been sev-
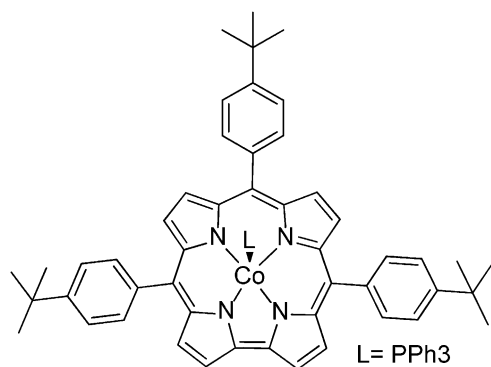
Fig. 1. Structure of Co(III) 5, 10, 15-tris(4-*tert*-butylphenyl) corrole with triphenylphosphine as the axial ligand.

eral other Co(III) complexes studied for preparation of nitrite ISEs, including Co(III) tetraphenylporphyrins [15] and Co(III) phthalocyanines [16].

Herein, we report on the first nitrite selective polymeric membrane electrodes prepared using a Co(III) corrole complex (cobalt(III) 5,10,15-tris(4-*tert*-butylphenyl) corrole (Co-tBC); see Figure 1). Unlike diprotonic porphyrins and monoprotonic corrins, corroles are −3 charged ligands when complexed to metal(III) ions. This forces the resulting ionophore to function via only a neutral carrier type response mechanism (i.e., binding of anion as axial ligand to the Co(III) center results in negatively charged complex). It will be shown that membrane electrodes prepared with this metal complex exhibit a Nernstian response to nitrite and display a selectivity pattern that differs significantly from the Hofmeister series when lipophilic cationic sites are added to the membrane phase. As also reported here, the optimal membrane composition for nitrite determination is achieved by varying the amount of lipophilic cationic sites and employing certain plasticizers (ortho-nitrophenyl octyl ether and dioctyl sebacate).

2 Experimental

2.1 Reagents

5,10,15-Tris(4-*tert*-butylphenyl) corrole was purchased from Frontier Scientific (Logan, UT, USA). Cobalt(II) acetate tetrahydrate (Co(OAc)$_2$·4H$_2$O), sodium acetate anhydrous (NaOAc) and ethanol (EtOH) were products of Sigma Aldrich (Milwaukee, WI, USA). Triphenylphosphine (PPh$_3$) was obtained from TCI America (Portland, OR, USA).

For membrane preparation, poly(vinyl chloride) (PVC), *o*-nitrophenyloctyl ether (*o*-NPOE), dioctyl sebacate (DOS), tributylphosphate (TBP), tridodecylmethyllammonium chloride (TDMACl), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) and anhydrous tetrahydrofuran (THF) were purchased from Fluka and used without further purification. All anion salts prepared in aqueous solutions for testing selectivity were obtained from Fluka.

2.2 Ionophore Preparation

The final ionophore Co(III) 5,10,15-tris(4-*tert*-butylphenyl) corrole was synthesized via a standard metalation reaction [17]. To prepare the ionophore, 0.104 g (0.15 mmol) of the free base corrole and 180 mg (21.96 mmol) NaOAc were dissolved in EtOH and stirred for 5 min. Then, 180 mg (7.20 mmol) Co(OAc)$_2$·4H$_2$O and 300 mg (11.46 mmol) PPh$_3$ were added to the solution. The reaction solution was stirred for 1.5 h at room temperature. The solvent was then evaporated, and the residue was purified by column chromatography with silica gel and CH$_2$Cl$_2$/hexane as the eluent. The obtained product was confirmed by NMR, UV-Vis spectroscopy and ESI-MS spectrometry.

2.3 ISE Membrane Preparation and Potentiometric Measurements

One wt % ionophore, 33 wt % PVC, 66 wt % plasticizer (*o*-NPOE or DOS) and different amounts of TDMACl (molar ratio relative to the ionophore) were dissolved in 2 mL THF and the mixture was cast in a glass ring (i.d. 24 mm) placed on a glass slide as described elsewhere [18]. A membrane was formed after solvent evaporation. To assemble the working electrode, a disk of diameter 8 mm was cut from the parent membrane and mounted into an electrode body (Oesch Sensor Technology, Sargans, Switzerland). The inner filling solution was a phosphate buffer solution (pH 4.5, 50 mM) with 10^{-2} M NaCl and 10^{-3} NaNO$_2$ or with 10^{-2} M NaCl and 10^{-3} NaNO$_3$ for nitrite sensors and nitrate sensors, respectively. Before any testing, the assembled ISEs were conditioned in solutions with same composition of the inner filling solution for 24 h. All potentiometric measurements were at ambient temperature and recorded using an EMF16 high impedance interface with EMF Suite 1.03 software (Lawson Labs, Malvern, PA). Potentiometric selectivity coefficients were determined by the separate solutions method [19].

2.4 Binding Constant Measurements

The binding constant of nitrite and nitrate with the new ionophore was measured by the segmented sandwich potentiometric method reported previously [20, 21]. Briefly, for measurement of the nitrite binding constant, two individual membranes were prepared. One contained 1.0 wt % ionophore, 33 wt % PVC, 66 wt % *o*-NPOE and 10 mol % TDMACl. The other membrane was formulated to contain essentially the same composition but without any ionophore. A series of 8-mm-diameter disks were cut from the two parent membranes and conditioned in the solution of 0.1 M NaNO$_2$ and 10^{-6} M NaCl overnight. For the following measurements, both the sample and inner filling solutions were the same as the conditioning solu-

tion. Each disk was incorporated in an electrode body for an individual test before making the segmented sandwich membrane. If the cell with the membrane with ionophore and the one without ionophore had a potential value that deviated < 5 mV, those two membranes were selected. To avoid developing an aqueous phase in between the membranes, the two individual membranes were dried thoroughly with Kimwipes before making the segmented sandwich membrane ISE device. The sandwich membrane was prepared by pressing the two individual membranes disks tightly together. The sandwich membrane was immediately mounted into an electrode body after drying. During the EMF measurement, the segment containing ionophore was at the sample/membrane interface, while the segment without ionophore was at the membrane/inner filling solution interface. To calculate the membrane potential for a two-membrane system, the cell potential of an individual membrane without ionophore was subtracted from that of the cell potential measured for the sandwich membrane configuration to correct for the constant potentials coming from the inner and outer reference electrodes. The reported binding constant value was averaged for three repeated tests. For the nitrate binding constant measurement, the same procedure was followed except that one membrane was prepared with 1 wt % ionophore, 50 mol % TDMACl, 33 wt % PVC and 66 wt % TBP while the other membrane had the same formulation but without any ionophore. The conditioning solution, inner filling solution and sample solution were all 0.1 M $NaNO_3$ and 10^{-6} M NaCl.

3 Results and Discussion

The insertion of cobalt(III) into the corrole ring is quite facile with a rapid color change from dark green (free base corrole) to deep red (Co-tBC) within 10 min upon the addition of cobalt acetate. According to the literature [22–26], most well isolated and fully characterized Co(III) corroles are five- or six-coordinate complexes (with an axial ligand of triphenylphosphine or two axial ligands of pyridine). It has been shown that in the absence of axial ligands, cobalt corroles are not stable. Indeed, they oxidize and dimerize, linking two corrole rings by forming a direct C_β–C_β bond [27]. To assure a stable Co(III) complex to serve as the ionophore, triphenylphosphine was employed as an axial ligand to help stabilize the corrole ring.

3.1 Potentiometric Response Toward Nitrite

It is reported that membranes doped with metal ion-ligand complexes as ionophores have response to pH via the interaction between hydroxide and the central metal ion of the complex [28]. In a previous study with Rh(III) porphyrins [18], pH 4.5 was selected as the background electrolyte solutions for potentiometric nitrite detection. Figure 2 shows that electrodes prepared with plasticized
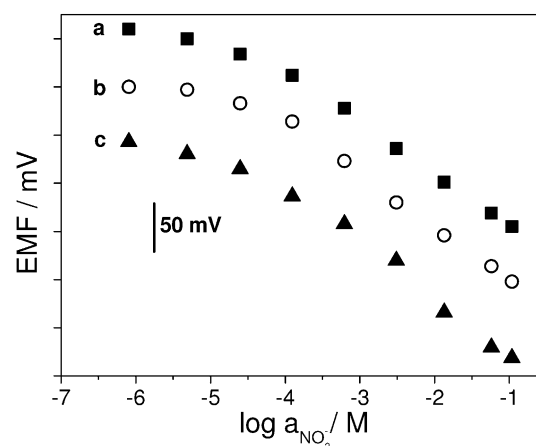
Fig. 2. Potentiometric nitrite responses in phosphate buffer solution (pH 4.5) for membrane electrodes with (a) 1 wt % Co-tBC and 10 mol % TDMACl in o-NPOE plasticized PVC; (b) 1 wt % Co-tBC and 50 mol % TDMACl in DOS plasticized PVC; and (c) 1 wt % Co-tBC, 10 mol % TDMACl and 3 wt % ETH 500 in DOS plasticized PVC.

PVC membranes doped with Co-tBC exhibit Nernstian or near Nernstian responses (with slopes of −59.6, −58.7 and −60.3 mV decade^{-1}, respectively) to nitrite over a wide range of concentrations, with a detection limit of ca. 5 μM. The membrane electrodes have relatively short response times (< 30 s) for nitrite concentrations of 30 μM and above. When switching the nitrite activity between 0.1 mM to 0.3 mM, the Co-tBC-based membrane electrodes have fast response and rapid recovery times, showing good reversibility (see Figure 3). Like other cobalt(III) complexes, the Co(III) corrole can bind with nitrite effectively and reversibly as an axial ligand to provide an ISE with Nernstian response, achieving equilibrium EMF values within a short period of time.
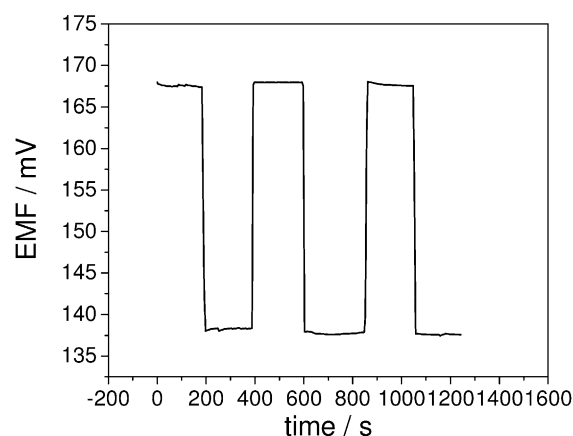
Fig. 3. Reversibility of nitrite potentiometric response in phosphate buffer solution (pH 4.5) for membrane electrode formulated with 1 wt % Co-tBC, 10 mol % TDMACl and 3 wt % ETH 500 in DOS plasticized PVC, when changing nitrite concentration back and forth between 100 mM and 300 mM.

Dielectric constants of plasticizers used to formulate the polymeric membrane can influence the ion-selective electrode performance for detection of nitrite. Plasticizers with higher dielectric constants require a lower concentration of lipophilic ionic additives in the membrane phase to provide a Nernstian response toward nitrite. Indeed, when using o-NPOE ($\varepsilon = 23.9$) as the plasticizer, with the addition of 10 mol % TDMACl, the response slope toward nitrite is -59.6 mV/decade, while 50 mol % TDMACl is required to yield Nernstian response if DOS ($\varepsilon = 3.9$) is employed. However, by introducing more lipophilic ionic sites via the addition of 3 wt % ETH 500 (without changing the neutrality of the entire membrane), and with the presence of 10 mol % TDMACl, a Nernstian response toward nitrite is also observed with DOS plasticized PVC membrane electrodes.

3.2 Selectivity and Binding Constant

As shown in Figure 4, polymeric membrane electrodes, prepared with membranes containing 1.0 wt % Co-tBC in o-NPOE plasticized PVC membranes, and the addition of 10 mol % TDMACl exhibit relatively high selectivity to nitrite over other anions. Compared with the classical anion-exchanger-based membrane electrodes, Co-tBC-

based electrodes have a very different selectivity pattern from the Hofmeister sequence ($ClO_4^- > SCN^- > NO_3^- > Br^- > Cl^-$) with enhanced nitrite response (e.g., shift of ~4 logarithmic units in the case of perchlorate and chloride; shift of ~3 logarithmic units in the case of thiocyanate, nitrate and bromide), suggesting that nitrite can preferentially interact with the Co-tBC species to form an anion/ionophore complex within the polymeric membrane. This selectivity sequence is also somewhat different from that reported for electrodes formulated previously with other cobalt(III) complexes [14–16]. Such selectivity differences may be the result of the corrole ligand itself as well as the presence of the strongly bound triphenylphosphine fifth ligand.

For ionophore-based ISEs, it is well known that the presence of a suitable amount of lipophilic ion-exchanger within the membrane can enhance the potentiometric selectivity toward the target ion. As shown in Figure 4, in the case of o-NPOE plasticized membranes, improvement of nitrite selectivity over other anions can be achieved by adding 10 mol % TDMACl. As the TDMACl level increases beyond this level, the selectivity pattern changes toward the classical Hofmeister sequence. For example, when there is 25 mol % of TDMACl present in the membrane, sensors have nitrite selectivity over most anions
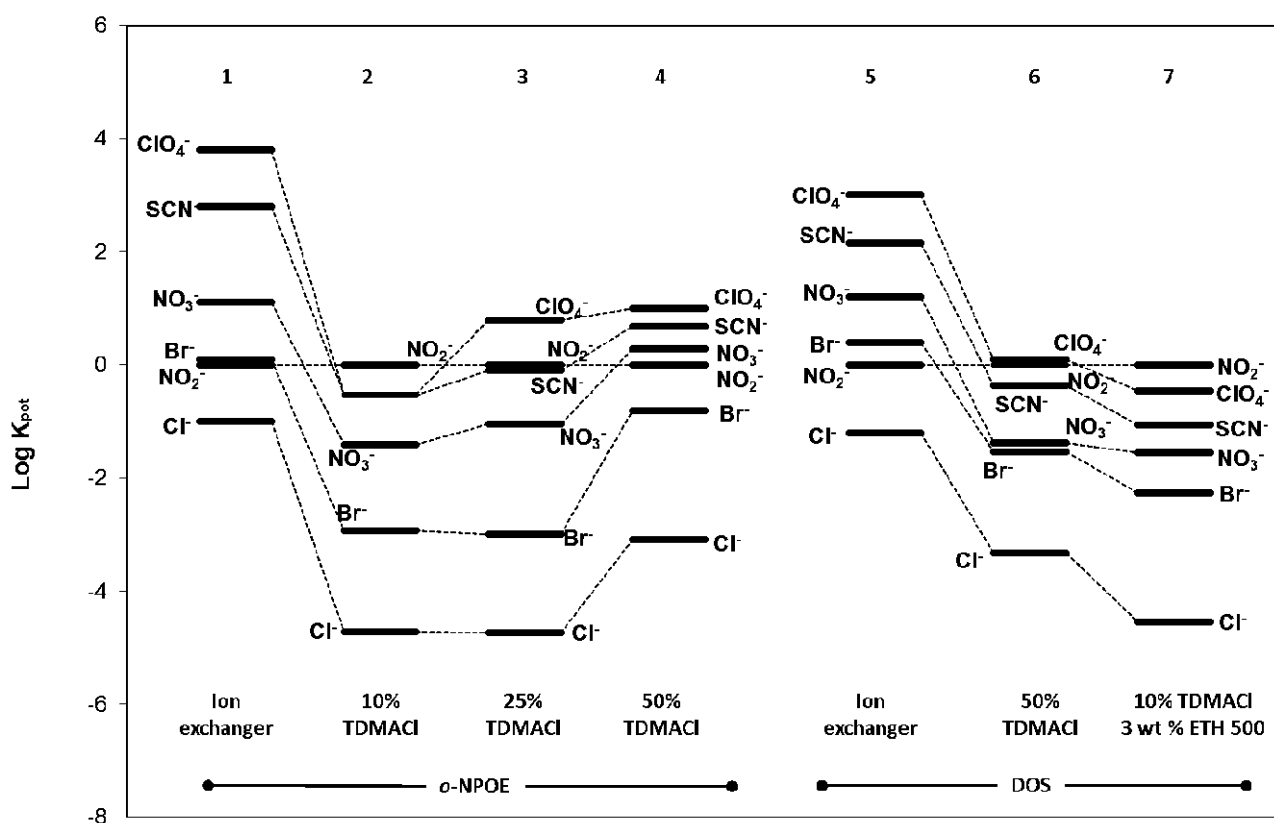

Fig. 4. Logarithm of potentiometric selectivity coefficients (relative to nitrite) of Co-tBC-based polymer membrane electrodes in comparison with dissociated ion-exchanger-based membrane electrodes; Polymer membranes formulated with (1, 5) 0.5 wt % TDMAC; (2–4) 1.0 wt % Co-tBC and different mole percent of TDMACl relative to the ionophore; (6) 1.0 wt % Co-tBC and 50 mol % TDMACl; (7) 1.0 wt % Co-tBC, 10 mol % TDMACl and 3.0 wt % ETH 500. To compare the effect of membrane plasticizers, membranes 1–4 were made with o-NPOE, and membranes 5–7 were prepared with DOS.

(thiocyanate, nitrate, bromide and chloride) and only exhibit significant interference from perchlorate (data not shown), the most lipophilic anion. However, when the amount of TDMACl in the polymeric membrane reaches 50 mol%, the resulting electrodes show nitrite selectivity over only bromide and chloride and experience significant interference from more lipophilic anions, indicating the selectivity pattern reverts considerably towards the Hofmeister sequence.

The impact of different membrane plasticizers on potentiometric selectivity was also examined by using two plasticizers with different dielectric constants (o-NPOE, $\varepsilon = 23.9$; DOS, $\varepsilon = 3.9$). Unlike polymeric membrane electrodes plasticized with o-NPOE, PVC-DOS membrane electrodes require higher levels of TDMACl additive to avoid sub-Nernstian response to nitrite and to provide significant nitrite selectivity. When the TDMACl level reaches 50 mol%, the electrodes display Nernstian response to nitrite, have nitrite selectivity over most other anions (including thiocyanate, nitrate, bromide and chloride), and have equivalent response to nitrite and perchlorate. Generally, membrane electrodes with o-NPOE as the plasticizer offer better performance than those with DOS as the plasticizer in terms of response slope and selectivity. However, if more lipophilic ionic sites are introduced into the membrane via addition of ETH 500 (i.e., increasing ionic strength within the membrane phase), the selectivity pattern is similar to that of o-NPOE plasticized PVC membranes (see Figure 4, membrane 7). With TDMACl levels of 10 mol%, sensors have nitrite selectivity over all other anions examined. Selectivity worsens and reverts to the Hofmeister pattern when TDMACl levels are increased. Ion selectivity provided by ion-exchanger based sensor electrodes is governed by the ratio of single ion partition coefficient in polymeric membranes with different plasticizers. With the presence of ionophore, the observed potentiometric selectivity is governed by both the single anion partition coefficient and the relative anion-ionophore complexation constant.

The complex formation constant can be determined by the following equation (without considering ion pairing) [21]:

$$\beta_{xI_n} = \left(I_T - \frac{nR_T}{z_x} \right)^{-n} \exp\left(\frac{E_M z_x F}{RT} \right)$$

Where x is the tested ion, and I is the ionophore. The symbol I_T is the total concentration of ionophore in the membrane, E_M is the membrane potential of the asymmetric sandwich membrane, and R_T is the total concentration of ion additives in the membrane phase. The value of n is the complex stoichiometry which is 1 in this case and z is the charge of the ion which is -1. The calculated logarithmic value of the binding constant, from the above equation, between nitrite and Co-tBC is 5.57 ± 0.13 (for $n = 3$ experiments, with the potential change of 211 ± 8 mV (see Section 2 for methodology)); based on the membrane electrode formulated with 9.9 mmol/kg Co-

tBC, 4.95 mmol/kg TDMACl in o-NPOE plasticized PVC membrane). For the ion-exchanger-based membrane electrodes, selectivity is only determined by the ratio of single ion partition coefficients of the interfering ion and primary ion [29]. When the ionophore is incorporated into the membrane, the selectivity is dependent on both the ratio of partition coefficients of the interfering ion and analyte ion and the ratio of binding constants of those two ions with the ionophore. Comparing the calculated complex formation constant and the selectivity results, the presence of the ionophore with such binding affinity to nitrite is able to discriminate perchlorate ion by ~4.7 orders of magnitude compared to an ionophore-free membrane. This suggests the stronger binding affinity between the Co(III) complex and nitrite overcomes the single ion partition coefficient resulting from ion lipophilicity (poor hydration energy) in the case of perchlorate.

To date, there is no reported complex formation constant for nitrite and a neutral ionophore such as Co-tBC. To the best of our knowledge, the only reported binding constant between nitrite and a nitrite-selective ionophore is measured with Nitrite Ionophore I [30] which is a charged-carrier type structure. The formation constants determined in that work were calculated as 10.58 ± 0.04 or 10.59 ± 0.08 (with membranes prepared with PVC-DOS and PVC-NPOE, respectively), which is much larger than the complex formation constant between nitrite and Co-tBC found in this work. The weaker binding is possibly due to the presence of triphenylphosphine as a fifth axial ligand. With such a structure, the cobalt(III) center is in an approximately square pyramidal coordination environment and displaced a little off the corrole plane toward the phosphorous atom [23], making nitrite binding to the metal ion center on the opposite side less favorable.

3.3 Lifetime of Membrane Electrodes

According to previous studies, the lifetime of carrier-based polymeric ion-selective electrodes is limited by the loss of ionophore, plasticizer, and ionic site additives from polymeric membrane to the aqueous phase. Response slopes and selectivity are often influenced by this change of membrane composition. In this work, the long-term performance of electrodes with two different membrane formulations was examined. One membrane had the formulation of 1 wt% ionophore and 10 mol% TDMACl in an o-NPOE plasticized PVC membrane. The other had a formulation of 1 wt% ionophore, 10 mol% TDMACl and 3 wt% ETH 500 in a DOS plasticized PVC membrane. Starting from day 3, a slight slope drop to -57.1 mV/dec and -58.9 mV/dec for both electrodes was observed. On day 7, only sub-Nernstian response slopes were observed for these two electrodes, one with -53.8 mV/dec and the other with -54.3 mV/dec. Both formulations of the membranes exhibited nitrite selectivity during this one-week period. As soaking time reached day 14, slopes of sensors with both formulations dropped
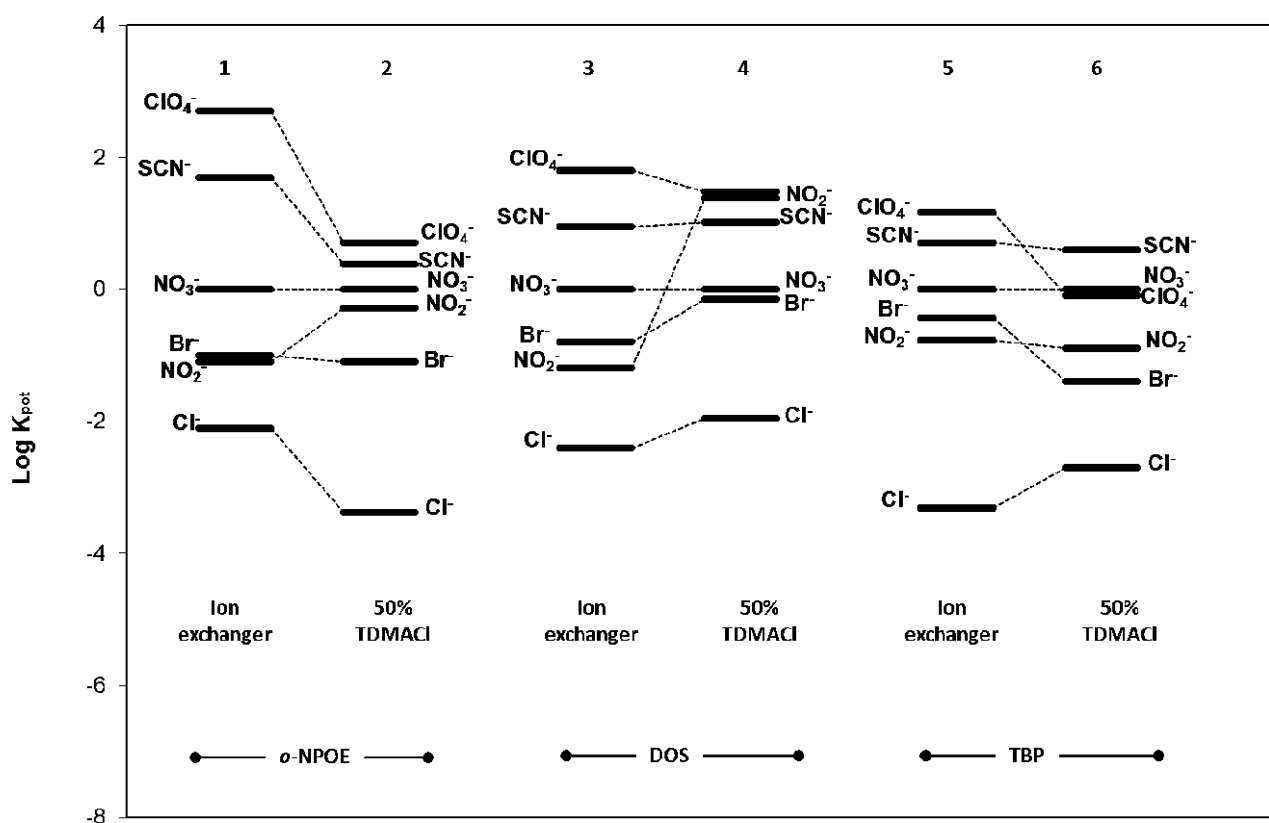
Fig. 5. Logarithm of potentiometric selectivity coefficients of Co-tBC based polymer membrane electrodes (relative to nitrite) in comparison with ion-exchanger based electrodes; Polymer membrane doped with (1, 3, 5) 0.5 wt % TDMAC; (2, 4, 6) 1.0 wt % Co-tBC and 50 mol % TDMACl relative to the ionophore. To compare the effect of membrane plasticizers, membranes 1–2 were formulated with *o*-NPOE, membranes 3–4 were prepared with DOS and membranes 5–6 were cast with TBP as the plasticizer.

to < −50 mV/dec due to significant composition changes of membranes.

3.4 Enhanced Nitrate Response

Interestingly, further investigation of the influence of the specific plasticizer on the Co-tBC-based membrane electrode response toward anions suggested that incorporation of tributylphosphate as the plasticizer yields an electrode with rather different anion selectivity pattern. With 50 mol % TDMACl present in the TBP-plasticized polymeric membrane containing 1 wt % Co-tBC, the electrodes exhibit enhanced nitrate response in terms of response slope and selectivity (see Figure 5). In fact, with this membrane formulation, modest selectivity for nitrate over nitrite is observed (ca. 10-fold). In the absence of ionophore and only the TDMACl species, membrane electrodes formulated with different plasticizers have significantly different selectivity patterns, which is due to variations in the ratio of single anion partition coefficients into the organic membrane phase. The selectivity pattern of sensors plasticized with TBP (column 5 in Figure 5) looks "compressed", especially for the lipophilic ions (perchlorate, thiocyanate, etc.). With the ionophore in the membrane, selectivity coefficients toward nitrate with respect to perchlorate and thiocyanate were reduced

~2 orders of magnitude compared to when *o*-NPOE was employed as the plasticizer (column 2 in Figure 5). With the membrane formulation of 1 wt % of ionophore, 50 mol % of TDMACl in TBP plasticized PVC membrane, the resulting electrode responds to nitrate equally as well as perchlorate. This modestly enhanced selectivity to nitrate indicates that some interaction between nitrate and the ionophore may occur, especially in the presence of the TBP plasticizer. The logarithmic value for the nitrate binding constant measured via the segmented sandwich method was calculated as 2.49 ± 0.06 with the potential change of 39 ± 3.6 mV. However, no reports on the binding of nitrate ion as an axial ligand to a metal ion center or other parts of cobalt(III) corrole complex have been reported previously. At this point, additional studies are required to assess the exact mechanism by which nitrate might be interacting weakly with the Co-tBC complex.

4 Conclusions

In summary, a Co(III) corrole species was synthesized from free 5,10,15-tris(4-*tert*-butylphenyl) corrole via metallization reaction with cobalt acetate and stabilized using a triphenylphosphine axial ligand. The resulting Co(III)

complex was incorporated and tested as a neutral carrier within polymeric membrane electrodes, and the resulting electrodes exhibited selectivity patterns that differ significantly from the classical Hofmeister series. Sensors with proper amounts of lipophilic cationic sites showed greatly enhanced nitrite response and selectivity, indicating a strong ligation interaction between the Co(III) corrole and nitrite. Indeed, the complex formation constant (logarithm value) of nitrite and the ionophore provided by the segmented sandwich membrane method was 5.57, which helps to decrease the observed EMF response to more lipophilic ions by ~4 orders of magnitude (when compared to that observed with membranes formulated with quaternary ammonium anion exchanger only). The nature of the membrane plasticizer also had substantial impact on sensor's EMF response. Generally, membranes formulated with plasticizers of a higher dielectric constant required lower amounts of lipophilic cationic sites additives in the polymeric membrane to exhibit optimal Nernstian nitrite response and good nitrite selectivity. The observed selectivity over thiocyanate for the Co-tBC-based membranes with o-NPOE is the best reported to date for nitrite sensors prepared with Co(III) complexes. However, moderately enhanced nitrate response was observed when sensors were plasticized with tributylphosphate (equivalent selectivity coefficient with perchlorate), indicating some weak interaction between nitrate and the ionophore. To better understand this possible interaction, more studies regarding the binding mechanism of nitrate with this ionophore are needed.

Acknowledgement

References

[1] J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.* **2008**, *108*, 329.
[2] E. Bakker, M. Telting-Diaz, *Anal. Chem.* **2002**, *74*, 2781.
[3] E. Bakker, Y. Qin, *Anal. Chem.* **2006**, *78*, 3965.
[4] S. C. Ma, V. C. Yang, M. E. Meyerhoff, *Anal. Chem.* **1992**, *64*, 694.
[5] P. W. Dierkes, S. Neumann, G. Klees, W.-R. Schlue, *Electrochim. Acta* **2003**, *48*, 3373.
[6] A. Knowles, S. Shabala, *J. Membrane Biol.* **2004**, *202*, 51.
[7] N. Tinkilic, O. Cubuk, I. Isildak, *Anal. Chim. Acta* **2002**, *452*, 29.
[8] E. Bakker, E. Malinowska, R. D. Schiller, M. E. Meyerhoff, *Talanta* **1994**, *41*, 881.
[9] D. Ammann, M. Huser, B. Kräutler, B. Rusterholz, P. Schulthess, B. Lindemann, E. Halder, W. Simon, *Helv. Chim. Acta* **1986**, *69*, 849.
[10] N. A. Chaniotakis, A. M. Chasser, M. E. Meyerhoff, J. T. Groves, *Anal. Chem.* **1988**, *60*, 185.
[11] S. Licoccia, R. Paolesse, in *Metal Complexes with Tetrapyrrole Ligands III*, Vol. 84, Springer, Berlin **1995**, pp. 71–133.
[12] A.-H. Iris, G. Zeev, *Coord. Chem. Rev.* **2011**, *255*, 717.
[13] L. Lvova, C. Di Natale, A. D'Amico, R. Paolesse, *J. Porphyrins Phthalocyanines* **2009**, *13*, 1168.
[14] P. Schulthess, D. Ammann, B. Krautler, C. Caderas, R. Stepanek, W. Simon, *Anal. Chem.* **1985**, *57*, 1397.
[15] E. Malinowska, M. E. Meyerhoff, *Anal. Chim. Acta* **1995**, *300*, 33.
[16] L. Jun-Zhong, W. Xiao-Chun, Y. Ruo, L. Hui-Gai, Y. Ru-Qin, *Analyst* **1994**, *119*, 1363.
[17] M. Atif, G. Ilona, G. Israel, G. Zeev, *Chem. Eur. J.* **2001**, *7*, 4259.
[18] M. Pietrzak, M. E. Meyerhoff, *Anal. Chem.* **2009**, *81*, 3637.
[19] E. Bakker, P. Bühlmann, E. Pretsch, *Chem. Rev.* **1997**, *97*, 3083.
[20] M. M. Shultz, O. K. Stefanova, S. B. Mokrov, K. N. Mikhelson, *Anal. Chem.* **2001**, *74*, 510.
[21] Y. Mi, E. Bakker, *Anal. Chem.* **1999**, *71*, 5279.
[22] R. Paolesse, *The Porphyrin Handbook,* Vol. 2, Academic Press, New York, **2000**.
[23] R. Paolesse, S. Licoccia, G. Bandoli, A. Dolmella, T. Boschi, *Inorg. Chem.* **1994**, *33*, 1171.
[24] V. A. Adamian, F. D'Souza, S. Licoccia, M. L. Di Vona, E. Tassoni, R. Paolesse, T. Boschi, K. M. Kadish, *Inorg. Chem.* **1995**, *34*, 532.
[25] R. Paolesse, S. Mini, F. Sagone, T. Boschi, L. Jaquinod, D. J. Nurco, K. M. Smith, *Chem. Commun.* **1999**, 1307.
[26] Y. Murakami, S. Yamada, Y. Matsuda, K. Sakata, *Bull. Chem. Soc. Jap.* **1978**, *51*, 123.
[27] B. Ramdhanie, L. Zakharov, A. Rheingold, D. Goldberg, *Inorg. Chem.* **2002**, *41*, 4105.
[28] V. V. Egorov, E. M. Rakhman'ko, A. A. Rat'ko, *J. Anal. Chem.* **2002**, *57*, 46.
[29] W. E. Morf, *The Principles of Ion-selective Electrodes and of Membrane Transport*, Elsevier, Amsterdam **1981**.
[30] Y. Qin, E. Bakker, *Talanta* **2002**, *58*, 909.