Organopalladium(II) Complexes as Ionophores for Thiocyanate Ion-Selective Electrodes

Dong Wan Kim, So Hyun Lee, Junghwan Kim, Jincun Kim, Jong Keun Park,* and Jae Sang Kim*

Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Gyeongnam, Jinju 660-701, Korea. *E-mail: jaeskim@mga.gun.ac.kr

*Department of Chemistry Education, Gyeongsang National University, Gyeongnam, Jinju 660-701, Korea

Received May 12, 2009. Accepted August 24, 2009

A thio­cyanate ex­change membrane elec­tro­de based on [1,2-di­phen­yl phos­phino­ethane]di­halo­palladium(II), [(dppe)PdX2] (X = Cl (L1), X = I (L2)) has been developed. The di­iodo­palladium complex, [(dppe)PdI2]L1 displays an an­ti-Hof­meister se­lec­tiv­ity se­quence: SCN− > I− > ClO4− > NO− > HPO4− > AsO4− > NO3− > H2PO4− > CO32−. The elec­tro­de ex­hibits a Ne­rnstian re­pose (59.8 mV/decade) over a wide linear con­cen­tra­tion range of thio­cyanate (1.0 × 10−3 to 5.0 × 10−6 M), low de­tec­tion limit (1.1 × 10−6 M), fast re­sponse (t90% = 24 s), and ap­pli­cab­il­ity over a wide pH range (3.5 ~ 11). Ad­i­tion of an­ion el­e­c­tion, po­ta­sium tetra­kis[p-chlo­ro­pho­thio­cyanate (KTPCIPB) is shown to im­prove po­ten­tiom­etric an­ion se­lec­tiv­ity, sug­gest­ing that the palladium com­plex may op­er­ate as a par­ti­tioned car­rier-type iono­phore within the poly­mer mem­brane phase. The re­ac­tion me­cha­nism is dis­cussed with re­s­pect to UV-Vis and IR spec­tro­scopy. Ap­pli­ca­tion of the elec­tro­de to the po­ten­tiom­etric tit­ra­tion of thio­cyanate ion with sil­ver nitrate is re­ported.

Key Words: [(dppe)PdCl2], Thio­cyanate ion-selective electrode, Fixed inter­fer­ence method, PVC membrane

Introduction

Anions play a fac­tional role in a wide range of bio­lo­gical, med­i­cal and en­vi­ron­mental pro­ces­s­es and because of their sig­nifi­cance the de­vel­op­ment of syn­thet­ic re­cep­tors and sen­sors for an­ions has been growing in im­por­tance over the last years.1–3 The se­lec­tiv­ity of these sen­sors to­wards a spe­cific ana­lyte is gen­er­ally de­termined by the in­ter­ac­tion of the iono­phore incorporated in the sen­sor mem­brane with the test ion in so­lu­tion. Such inter­ac­tions may be based on an ion ex­change me­cha­nism, me­tal-lig­and bond for­ma­tion and ion ex­trac­tion pro­cess.4

An­ion-selective mem­brane elec­tro­des using con­ven­tion­al an­ion ex­changers, such as qua­ternary am­monium salts nor­mally fol­low the Hof­meister se­lec­tiv­ity se­quence (ClO4− > SCN− > I− > NO− > Br− > NO3− > Cl− > SO42−) in re­spon­s­ing to an­ions. This pattern de­pends on the li­po­philicity and hy­dra­tion ener­gy of the an­ions.5 The re­search to­wards an­ti-Hof­meister sen­sing ma­ter­i­als with high se­lec­tiv­ity and sen­si­ti­v­ity for gen­er­al an­ions is a rap­idly ex­pand­ing do­main in the chem­i­cal sen­sor field.

Thio­cyanate is the end prod­uct of de­toxi­fi­ca­tion of cy­anide com­pounds and is ex­creted in urine, sal­iva and se­rum.6–9 Pres­ent in and hence the deter­mi­na­tion of thio­cyanate is par­tially im­port­ant in these bod­y fluids. Over re­cent years, thio­cyanate-selective PVC mem­brane elec­tro­des based on var­i­ous iono­phores have been re­ported.10–21 Among these, a metallic­philic cy­an­ate com­plex (2–22) and cy­an­i­um com­plexes,23–26 Sch­iff base com­plexes,27–29 and calix[4]arene30,31 ap­pear to be the most prom­is­ing.

It has been re­ported that organo­palladium com­plexes ex­hibit unique se­lec­tiv­ities and have been suc­cess­ful­ly used as elec­tro­active ma­ter­i­als in mem­brane sen­sors for par­tic­ular an­ions and gases.32–34 In pre­vious work, Mey­er­h­off sug­gested that the halo­geno­or­ganic palladium com­plex, ben­zyl­bis-(triphen­yl phos­phine) palladium(II) chlo­ride in a poly­car­bo­nated mem­brane works as a charged car­rier.35 It seemed worth­while to in­vesti­gate such an organo­palladium com­plex to see whether the re­sult­ing an­ion selectiv­ity might be en­hanced.

In this pa­per we re­port on the an­ion se­lec­tiv­ity of mem­brane elec­tro­des pre­pared with the palladium organophosphate com­plex ([dppe]PdCl2) as shown in Scheme 1 as the an­ion el­e­c­tion within a poly­mer mem­brane. This com­pound in­duces an an­ti-Hof­meister se­lec­tiv­ity se­quence with a sig­nifi­cantly re­spond­ing re­se­arch to thio­cyanate. Inter­est­ingly, the ad­i­tion of both a lip­ophilic an­ionic site, KTPCIPB, and a cat­ionic site, TDMACI, to the mem­brane was shown to re­sult in Ne­rnstian re­spon­s­es and to fur­ther en­hance se­lec­tiv­ity for thio­cyanate, sug­gest­ing a car­rier re­sponse me­cha­nism for the L2-based mem­brane elec­tro­des.

Experimental

Re­agents. The L1 is com­mer­cially avail­able, but is unsuit­able for ISE-exam­i­na­tions due to poor solu­bil­ity in THF. L2 was pre­pared according to the liter­ature pro­ce­dure1 shown in Scheme 1. An ex­cess of NaI was added to a solu­tion of [(dppe)PdCl2] in wa­ter/dichlo­ro­eth­ane mixture.

The mixture was stirred for 20 min during which time a yellow precipitate formed. [1,2-Bis(diphenylphosphino)ethane]dichloropalladium(II), high-molecular weight poly(vinyl chloride), o-nitrophenolyl ether(o-NPOE), tridecyl methylammonium chloride (TDMACI), potassium tetrakis[p-chlorophenyl]borate (KTPCIPB) and tetrahydrofuran (THF) were obtained from Aldrich Chemical Co. (Milwaukee, WI). All of the chemical substances were of reagent grade and were used without further purification. Stock solutions of anions were prepared using deionized water and working solutions were obtained by dilution of the stock solutions with deionized water.

Electrode preparation and potential measurements. The membrane contained ~1.0 wt.% L₂, ~66 wt.% plasticizer (o-NPOE) and ~33 wt.% PVC and a small amount of ionic additives (TDMACI or KTPCIPB). The membrane components, ~180 mg in total, were dissolved in 5 mL of THF. This solution was placed in a glass ring of 35 mm i.d. resting on a glass plate. After overnight solvent evaporation, the resulting membrane was peeled from the glass mold and discs of 7 mm i.d. were cut out. Membrane disc was then mounted in a glass tube. After filling the internal solution containing 1.0 x 10^{-2} M KSCN and contacting with an AgCl-coated Ag wire, the prepared electrode were conditioned in 1.0 x 10^{-2} M KSCN solution for 24 hours. The electrode was stored dry and reconditioned before use.

The response of the sensor for thiocyanate ion was examined by measuring the electromotive force (EMF) of the following electrochemical cell:

\[ \text{Ag} | \text{AgCl} | \text{KCl} | \text{sample solution} | \text{PVC Mem.} | 1 \times 10^{-1} \text{M KSCN solution} | \text{AgCl} | \text{Ag} \]

Dynamic response curves and calibration plots were obtained through the step addition of standard solutions to 100 mL of background electrolyte at 25 °C. The solutions were magnetically stirred during the recording of all emf values.

Apparatus. The potential differences between the ISEs and the reference electrode (Orion sleeve type double junction Ag/AgCl reference electrode; model 90-02) were measured by using a PC equipped high impedance input 16-channel analog-to-digital converter (KOSENTECH, Busan, Korea).

UV-Vis spectra were acquired with an HP 8453 spectrophotometer equipped with a quartz cell (1 cm thick standard optical cell, ca. 4 mL capacity).

IR spectra were obtained on a Fourier infrared spectrophotometer (FTIR-8400, SHIMADZU) with the samples mounted as KBr pellets.

Extraction study and absorbance measurements (UV-Vis and IR). A solution of 5 mL of dichloromethane containing L₂ (2.0 x 10^{-3} M) and 5 mL of distilled water containing 100 equivalents of the respective anions (2.0 x 10^{-3} M) were mixed and shaken for 24 hr in order to reach extraction equilibrium. After phase separation, the organic phase was used for the UV-Vis spectrophotometric measurements. After removal of the solvent, the resulting solid was used for the IR study.

Results and Discussion

Performance characteristics of the sensor. It is well known that the sensitivity and selectivity obtained for a given neutral carrier depend significantly on the membrane composition and the properties of the solvent mediator employed as well as the PVC/plasticizer ratio used.

The organopalladium(II) complex L₂-based thiocyanate ion selective electrode was prepared with four different membrane compositions and the slopes, working ranges and detection limit (DL) obtained are listed in Table 1. As shown the electrode E3 (PVC/o-NPOE, 1.0 wt% L₂) which has no additives exhibited the best response to thiocyanate over a wide concentration range (1.0 x 10^{-1} to 5.0 x 10^{-4} M), with a detection limit of 1.1 x 10^{-5} M and a response slope of -59.8 mV/decade. It is noted that this corresponds to one of the electrodes for which no ionic additives are present.

Nevertheless, addition of both lipophilic cationic sites (TDMACI) and anionic sites (KTPCIPB) to the plasticized membrane containing L₂ also leads to a near Nernstian response in each case (see Figure 1). This behavior is quite unusual and suggests that

![Figure 1. Calibration graphs for E1-E4 based on L².](image_url)

**Table 1.** Effect of the membrane composition on the characteristics of the proposed thiocyanate-ISE.

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Membrane mass composition/mg</th>
<th>Slopes (mV/decade)</th>
<th>Detection Limit (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plasticizer</td>
<td>PVC</td>
<td>Ionophore</td>
</tr>
<tr>
<td>E1</td>
<td>NPOE (116.8)</td>
<td>62.4</td>
<td>1.5</td>
</tr>
<tr>
<td>E2</td>
<td>NPOE (122.8)</td>
<td>59.5</td>
<td>1.5</td>
</tr>
<tr>
<td>E3</td>
<td>NPOE (121.3)</td>
<td>59.4</td>
<td>1.5</td>
</tr>
<tr>
<td>E4</td>
<td>NPOE (116.3)</td>
<td>59.4</td>
<td>-</td>
</tr>
</tbody>
</table>

*Molar amount of TDMACI or KTPCIPB relative to the total ionophore concentration in the membrane. *TDMA⁺. *KTPCIPB.
Thiocyanate Ion-Selective Electrodes


it may be possible for the $[\text{dppe}Pd(II)]$ complex to interact with thiocyanate by a charged carrier mechanism in the membrane phase, where both the neutral form and the charged form of the Pd(II) complex participate in ion exchange-complexation with thiocyanate within the membrane phase.

For membrane ion sensors based on electrically neutral carriers, the presence of ionic sites with a charge sign opposite to that of the primary ions is necessary to establish the permselectivity of the membrane and, therefore, result in a Nernstian response. On the other hand, it was recently shown that the use of ionic sites with the same charge sign as the primary ion can significantly improve the response slope and selectivities of certain ISEs based on electrically charged carriers. This means that, in this case, charged-carrier based ISEs also respond well if the charge sign of the sites is opposite to that of the analyte; however, their selectivity is no longer influenced by the ionophore (Hofmeister selectivity sequence). $L^1$ has no overall net charge and, therefore, should act as an electrically neutral carrier. However, it is expected that after conditioning, $L^1$ in the plasticized PVC membrane will remain as partially dissociated species ($[\text{dppe}Pd(II)]H^+$,$[\text{dppe}PdSCN(H_2O)_5]$$^+$, etc.), so that it will act as a positively charged carrier. The data indicate that the response of the sensor reflects an associated exchange mechanism and that the palladium complex acts as partially positively charged ion exchanger.

**Selectivity of the electrode.** The most important characteristic of an ISE is its selectivity for the analyte ion of interest over other ions in solution. The selectivity coefficients were determined graphically (see Figure 2) by the fixed interference method using the expression \[ \log K_{BCN} = \log a_B(DL)/a_B(G) \] where \(a_B(DL)\) is the primary ion activity at this detection limit and \(a_B(G)\) is the interfering ion activity in the background (1.0 × 10⁻³ M concentration level), and \(z_B\) and \(z_J\) is the charge of the primary and interfering ion. The resulting selectivity coefficients are summarized in Table 2.

As displayed in Table 2, the $L^2$/NPOE-based PVC membrane electrode E3 without additives showed excellent thiocyanate selectivity over the other anions present, even more lipophilic anions, such as perchlorate, iodide, bromide, nitrate, and nitrite. The selectivity sequence obtained with the membrane electrode E3 is as follows: SCN > I > ClO₄ > S₂O₃² > Br > NO₂ > HPO₄² > AcO > NO₃ > H₂PO₄ > CO₃². This order (anti-Hofmeister) strongly suggests that thiocyanate ions can preferentially interact with the $L^2$ complex within the polymeric membrane phase of the electrode.

In PVC membrane sensors, the selectivity not only depends on the specific interaction of the ion with the carrier, but also due to the lipophilicity of the sample ion.

For comparison purposes, selectivity data for the classical anion exchanger-based membrane (PVC/u-NPOE, 0.5 wt% TDMACI; E4) is also provided. However, addition of lipophilic cation sites (TDMACI) to membranes containing $L^1$ results in a small enhancement of selectivity with a Nernstian response but a return to the Hofmeister selectivity pattern. On the other hand, addition of lipophilic anionic sites (KTPCIPB) improves the thiocyanate selectivity except for iodide ion that has a stronger interaction with palladium. Clearly, these observations suggest that the operative mechanism in the case of $L^2$ is a positively charged carrier ion. Indeed, with the palladium metal ion initially liganded to two weakly coordinated iodide ligands in the $L^2$ structure, it is more likely that the positively charged form (loss of one or two iodide) will be the predominant ionic form in the membrane phase. This type of behavior is quite unusual and suggests that it may be possible for the organophosphino Pd(II) complex to interact with thiocyanate by a partially charged carrier complexation mechanism, where both the neutral form and the charged form of the Pd(II) complex participate in complexation with thiocyanate within the membrane phase.

**Effect of pH.** The calibration curves of four different membrane electrodes prepared by the use of $L^2$ as ionophore were plotted between pH 2.0 and 13.0 in order to determine the pH range for which the electrodes give the best response against thiocyanate ions. The pH was adjusted by adding concentrated hydrochloric acid, or concentrated potassium hydroxide solution. The sensors prepared with the palladium(II) complex do not exhibit proton/hydroxide response in the range of pH 3.0 ~ 11.0 and this is a potential advantage over previously reported. This may be explained by the OH⁻ entering as a fourth ligand at high pH values to replace the iodide ion. This type of reaction is more difficult for the Pd(II)-complex due to the chelate effect of the ligand. It is of interest to further understand the lack of

---

**Figure 2.** Selectivity pattern for the electrode (E2). The initial concentration of the diverse anions is 10⁻³ M.

**Table 2.** Selectivity coefficients ($K_{BCN}$) obtained by fixed interference method.

<table>
<thead>
<tr>
<th>Interfering Ion</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPO₄&lt;sup&gt;−&lt;/sup&gt;</td>
<td>2.51 × 10⁻¹</td>
<td>1.73 × 10⁻³</td>
<td>1.12 × 10⁻³</td>
<td>2.13 × 10⁻¹</td>
</tr>
<tr>
<td>AcO&lt;sup&gt;−&lt;/sup&gt;</td>
<td>5.01 × 10⁻³</td>
<td>1.34 × 10⁻²</td>
<td>2.51 × 10⁻³</td>
<td>4.78 × 10⁻¹</td>
</tr>
<tr>
<td>HPO₄&lt;sup&gt;−&lt;/sup&gt;</td>
<td>5.30 × 10⁻³</td>
<td>1.58 × 10⁻²</td>
<td>4.67 × 10⁻³</td>
<td>4.07 × 10⁻¹</td>
</tr>
<tr>
<td>NO₂&lt;sup&gt;−&lt;/sup&gt;</td>
<td>5.37 × 10⁻³</td>
<td>5.24 × 10⁻³</td>
<td>5.01 × 10⁻³</td>
<td>3.46 × 10⁻¹</td>
</tr>
<tr>
<td>NO₃&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1.58 × 10⁻³</td>
<td>1.86 × 10⁻³</td>
<td>2.04 × 10⁻³</td>
<td>1.90 × 10⁻¹</td>
</tr>
<tr>
<td>CO₃²&lt;sup&gt;−&lt;/sup&gt;</td>
<td>2.62 × 10⁻³</td>
<td>1.94 × 10⁻²</td>
<td>3.01 × 10⁻²</td>
<td>2.51 × 10⁻¹</td>
</tr>
<tr>
<td>Br⁻</td>
<td>1.14 × 10⁻⁵</td>
<td>1.12 × 10⁻⁵</td>
<td>1.18 × 10⁻⁵</td>
<td>4.78 × 10⁻¹</td>
</tr>
<tr>
<td>S₂O₃²&lt;sup&gt;−&lt;/sup&gt;</td>
<td>1.12 × 10⁻⁵</td>
<td>4.07 × 10⁻⁵</td>
<td>1.51 × 10⁻⁵</td>
<td>1.38 × 10⁻⁵</td>
</tr>
<tr>
<td>I⁻</td>
<td>1.94 × 10⁻⁴</td>
<td>3.38</td>
<td>2.88 × 10⁻⁴</td>
<td>1.99 × 10⁻¹</td>
</tr>
<tr>
<td>ClO₄&lt;sup&gt;−&lt;/sup&gt;</td>
<td>6.5 × 10⁻⁴</td>
<td>6.19 × 10⁻⁴</td>
<td>3.32 × 10⁻⁴</td>
<td>5.01</td>
</tr>
</tbody>
</table>
pH response for the optimized thiocyanate-sensitive membranes formulated with L\(^2\) or L\(^3\) plus additive. As mentioned previously, membranes doped with both anionic and cationic sites do not exhibit any pH response over a wide pH range (see Figure 3). In this case, the weak \(\pi\)-acceptor ligand \((\text{OH})_3\)\(^{2-}\) is unable to coordinate as a fifth ligand to the Pd complex.

Response time. The response time of an ion-selective electrode is an important factor in analytical applications and it depends slightly on the concentration change. Therefore, it was determined by recording the time elapsed to reach a stable potential value after the electrode and the reference electrode were immersed in calibration solutions that corresponded from low to high thiocyanate ion concentrations. The typical dynamic responses to thiocyanate of the membrane electrode E3 is shown in Figure 4. As can be seen, the electrode reaches the equilibrium response in a relatively short time. When the concentration of thiocyanate was changed from \(5.0 \times 10^{-5}\) M to \(5.0 \times 10^{-3}\) M, the response time \(t_{\text{res}}\) of the proposed electrode is less than was 24 s. After 8 weeks use, the potentiometric response characteristics of the same electrode were found to be lower. The limited life time was due to the leaching of the carriers from the PVC membrane to aqueous sample solution.

Interaction mode between SCN\(^-\) and L\(^2\). The selective response towards thiocyanate is believed to be associated with the coordination of thiocyanate to the ionophore, \((\text{dppe})\text{PdL}\).

In order to investigate the potential interaction between thiocyanate and the ionophore, UV-Vis spectra of dichloromethane solution containing the ionophore \((2.0 \times 10^{-3}\) M) were compared with those of the same solutions after being extracted with 100 equiv. of thiocyanate anions in aqueous solution (see Figure 5). After being equilibrated with 100 equivalent of the KSCN, the UV-Vis spectrum showed a strong absorption at 302 nm with a shoulder at ca 365 nm, while a disappearance of the LMCT band of Pd-I at \(\lambda = 405\) nm was observed. The IR spectra in the region 2800 - 1600 cm\(^{-1}\) of L\(^2\) before and after extraction with SCN\(^-\) are illustrated in Figure 6. As shown in Fig. 6 (b), strong bands present at 2082 and 2177 cm\(^{-1}\) for the extracted Pd(II) complex with thiocyanate are characteristic of C=N stretching bands of SCN\(^-\), due to S- and N-bonded thiocyanate respectively. This confirms that L\(^2\) forms an \((\text{dppe})\text{Pd} \text{(SCN)}(\text{NCS})\) complex, which the mixed mode of thiocyanate coordination being already reported.
selective electrode can be used as an indicator electrode in titrations carried out involving thiocyanate and/or silver nitrate.

In a dichloromethane-water extraction study, the ionophore $L^2$ selectively extracts thiocyanate. Thus, a specific relationship between sensing properties and extraction phenomena has been observed in the present study.

Acknowledgments. The authors wish to acknowledge the sabbatical leave in the Program Year 2008-2009 of Gyeongsang National University.

References


Figure 7. The titration of $1.0 \times 10^{-5}$ M AgNO$_3$ (100 mL) with $5.0 \times 10^{-2}$ M KSCN by using a thiocyanate-selective electrode based on the electrode E1.