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

Dong Wan Kim, So Hyun Lee, Junghwan Kim, Jineun 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@gnu.ac.kr*
†Department of Chemistry Education, Gyeongsang National University, Gyeongnam, Jinju 660-701, Korea
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A thiocyanate poly(vinyl chloride) (PVC) membrane electrode based on [1,2-bis(diphenylphosphino)ethane]dihalopalladium(II), [(dppe)PdX_2, X = Cl (L^1), X = I (L^2)] as active sensor has been developed. The diiodopalladium complex, [(dppe)PdI_2](L^2) displays an anti-Hofmeister selectivity sequence: $SCN^- > I^- > ClO_4^- > SaI^- > Br^- > NO_2^- > HPO_4^- > AcO^- > NO_3^- > H_2PO_4^- > CO_3^{2-}$. The electrode exhibits a Nernstian response (-59.8 mV/decade) over a wide linear concentration range of thiocyanate (1.0×10^{-1} to 5.0×10^{-6} M), low detection limit (1.1×10^{-6} M), fast response ($t_{90\%}$ = 24 s), and applicability over a wide pH range (3.5 ~ 11). Addition of anionic sites, potassium tetrakis[*p*-chlorophenyl]borate (KT*p*ClPB) is shown to improve potentiometric anion selectivity, suggesting that the palladium complex may operate as a partially charged 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)PdI_2], Thiocyanate ion-selective electrode, Fixed interference method, PVC membrane

Introduction

Anions play fundamental roles in a wide range of biological, medicinal 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 due to specific 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 ($ClO_4^- > SCN^- > I^- > SaI^- > NO_3^- > Br^- > NO_2^- > Cl^- > SO_4^{2-}$) in responding to anions. This pattern depends on the lipophilicity and hydration energy of the anions.[5-7] The research to anti-Hofmeister sensing materials with high selectivity and sensitivity for given anions is an rapidly expanding domain in the chemical sensor field.

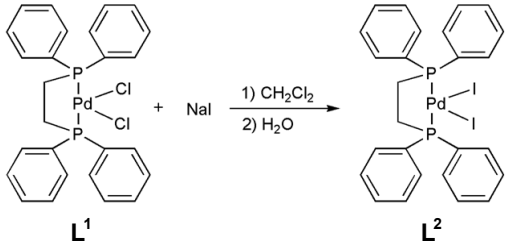
Thiocyanate is the end product of detoxification of cyanide compounds and is excreted in urine, saliva and serum.[4,8] Present in and hence the determination of thiocyanate is particularly important in these body fluids. Over recent years, thiocyanate-selective PVC membrane electrodes based on various ionophores have been reported.[9-38] Among these, a metallophthalocyanine complex,[20-22] metalloporphyrin complexes,[23-34] Schiff base complexes,[35-36] and calix[4]arene[37-38] appear to be most promising.

It has been reported that organo-palladium complexes exhibit unique selectivities and have been successfully used as electroactive materials in membrane sensors for particular anions and gases.[39,40] In previous work, Meyerhoff suggested that the halogeno-organic palladium complex, benzylbis-(triphenyl phosphine) palladium(II) chloride in a polar plasticized membrane works as a charged carrier.[39] It seemed worthwhile to investigate such an organopalladium complex to see whether the response characteristics of the resulting electrode might be enhanced.

In this paper, we report on the anion selectivity of membrane electrodes prepared with the palladium organophosphine complex ([(dppe)PdI_2]; see Scheme l) as the active ionophore within a plasticized PVC membrane. This compound induces an anti-Hofmeister selectivity pattern with a significantly enhanced response toward thiocyanate. Interestingly, the addition of both a lipophilic anionic site, KT*p*ClPB, and a cationic site, TDMACl, to the membrane was shown to resulting Nernstian response and to further enhance selectivity for thiocyanate, suggesting charged carrier response mechanism for the $\mathbf{L^2}$-based membrane electrodes.

Experimental

Reagents. The $\mathbf{L^1}$ is commercially available, but is unsuitable for ISE- examinations due to poor solubility in THF. $\mathbf{L^2}$ was prepared according to the literature procedure[41] shown in Scheme 1. An excess of NaI was added to a solution of [(dppe)$PdCl_2$] in water/dichloromethane mixture.



Scheme 1. Synthesis of compound $\mathbf{L^2}$.

The mixture was stirred for 30 min during which time a yellow precipitate formed. [1,2-Bis(diphenylphosphino)ethane]dichloropalladium(II), high-molecular weight poly(vinyl chloride), *o*-nitrophenyloctylether(*o*-NPOE), tridodecylmethylammonium chloride (TDMACl), potassium tetrakis[*p*-chlorophenyl] borate (KT*p*ClPB) 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.% $\mathbf{L}^2$, ~66 wt.% plasticizer (*o*-NPOE) and ~33 wt.% PVC and a small amount of ionic additives (TDMACl or KT*p*ClPB). 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 1.0×10^{-1} M KSCN and contacting with an AgCl-coated Ag wire, the prepared electrode were conditioned in 1.0×10^{-1} 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:

Ag | AgCl | sat. KCl | sample solution || PVC Mem. || 10^{-1} M KSCN solution | AgCl | 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-8400S, 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 $\mathbf{L}^2$ (2.0×10^{-5} M) and 5 mL of distilled water containing 100 equivalents of the respective anions (2.0×10^{-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 $\mathbf{L}^2$ 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 % $\mathbf{L}^2$) which has no additives exhibited the best response to thiocyanate over a wide concentration range (1.0×10^{-1} to 5.0×10^{-6} M), with a detection limit of 1.1×10^{-6} 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 (TDMA$^+$) and anionic sites (T*p*ClPB$^-$) to the plasticized membrane containing $\mathbf{L}^2$ also leads to a near Nernstian response in each case (see Figure 1). This behavior is quite unusual and suggests that

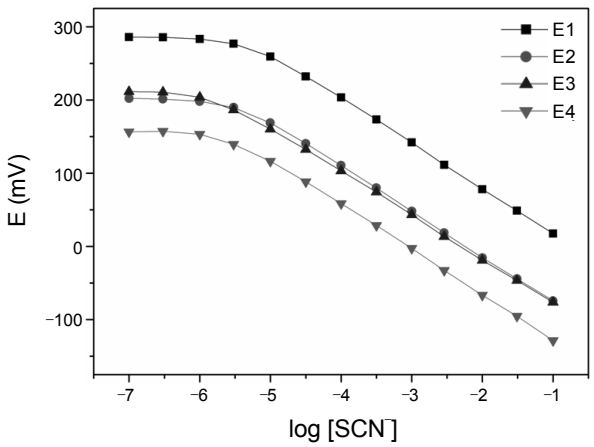


Figure 1. Calibration graphs for E1-E4 based on $\mathbf{L}^2$.

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

Electrode Type	Membrane mass composition /mg				Slopes (mV/decade)	Detection Limit (M)
	Plasticizer	PVC	Ionophore	Additive (mole %)[a]		
E1	NPOE (116.8)	62.4	1.5	40[b]	-61.10	7.2×10^{-6} M
E2	NPOE (122.8)	59.5	1.5	50[c]	-61.48	4.9×10^{-6} M
E3	NPOE (121.3)	59.4	1.5	-	-59.78	1.1×10^{-6} M
E4	NPOE (116.3)	59.4	-	100[b]	-61.56	3.3×10^{-6} M

[a]Molar amount of TDMACl or KT*p*ClPB relative to the total ionophore concentration in the membrane. [b]TDMACl. [c]KT*p*ClPB.

it may be possible for the [(dppe)PdI_2] 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.[4] 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.[42,43] 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). $\mathbf{L^2}$ has no overall net charge and, therefore, should act as an electrically neutral carrier. However, it is expected that after conditioning, $\mathbf{L^2}$ in the plasticized PVC membrane will remain as partially dissociated species ([(dppe)PdI(H_2O)]$^+$, [(dppe)PdSCN(H_2O)]$^+$, *etc*) so that it will act as a positively charged carrier.[39,43] 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.

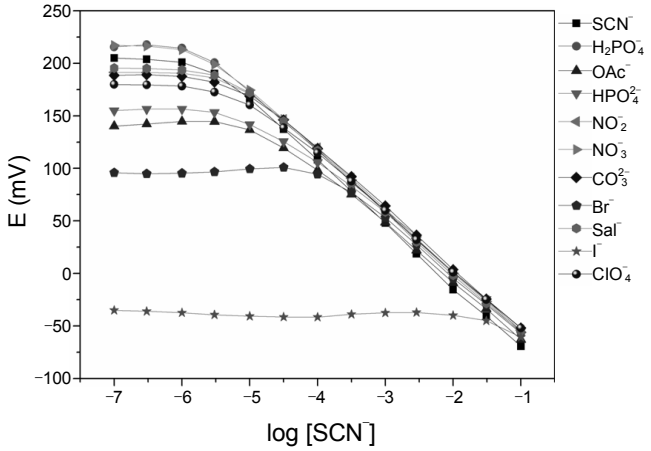


Figure 2. Selectivity pattern for the electrode (E2). The initial concentration of the diverse anions is 10^{-3} M.

Table 2. Selectivity coefficients ($K_{SCN,X}^{pot}$) obtained by fixed interference method.

Interfering ion	E1	E2	E3	E4
$H_2PO_4^-$	2.51×10^{-3}	1.73×10^{-3}	1.12×10^{-3}	2.13×10^{-3}
AcO^-	5.01×10^{-3}	1.34×10^{-2}	2.51×10^{-3}	4.78×10^{-3}
HPO_4^-	6.30×10^{-3}	1.58×10^{-2}	4.67×10^{-3}	4.07×10^{-3}
NO_2^-	5.37×10^{-3}	5.24×10^{-3}	5.01×10^{-3}	3.46×10^{-3}
NO_3^-	1.58×10^{-2}	1.86×10^{-3}	2.04×10^{-3}	1.90×10^{-2}
CO_3^{2-}	2.62×10^{-4}	1.94×10^{-4}	3.01×10^{-4}	2.51×10^{-4}
Br^-	1.14×10^{-2}	1.25×10^{-2}	1.18×10^{-2}	4.78×10^{-3}
Sal^-	1.12×10^{-1}	4.07×10^{-3}	1.51×10^{-2}	1.38×10^{-1}
I^-	1.94×10^{-1}	3.38	2.88×10^{-1}	1.99×10^{-1}
ClO_4^-	6.6×10^{-1}	6.19×10^{-3}	3.32×10^{-2}	5.01

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[44] using the expression $\log K_{SCN,J}^{pot} = \log a_I(DL)/a_J(BG)^{Z_I/Z_J}$ where $a_I(DL)$ is the primary ion activity at this detection limit and $a_J(BG)$ is the interfering ion activity in the background (1.0×10^{-3} M concentration level), and z_I and z_J is the charge of the primary and interfering anions. The resulting selectivity coefficients are summarized in Table 2.

As displayed in Table 2, the $\mathbf{L^2}$/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: $SCN^- > I^- > ClO_4^- > Sal^- > Br^- > NO_2^- > HPO_4^- > AcO^- > NO_3^- > H_2PO_4^- > CO_3^{2-}$. This order (anti-Hofmeister) strongly suggests that thiocyanate ions can preferentially interact with the $\mathbf{L^2}$ 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 is also due to the lipophilicity of the sample ion.

For comparison purposes, selectivity data for the classical anion exchanger-based membrane (PVC/*o*-NPOE, 0.5 wt% TDMACl; E4) is also provided. However, addition of lipophilic cation sites (TDMACl) to membranes containing $\mathbf{L^2}$ 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 (KT*p*ClPB) 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 $\mathbf{L^2}$ is a positively charged carrier one. Indeed, with the palladium metal ion initially ligated to two weakly coordinated iodide ligands in the $\mathbf{L^2}$ 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 $\mathbf{L^2}$ 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

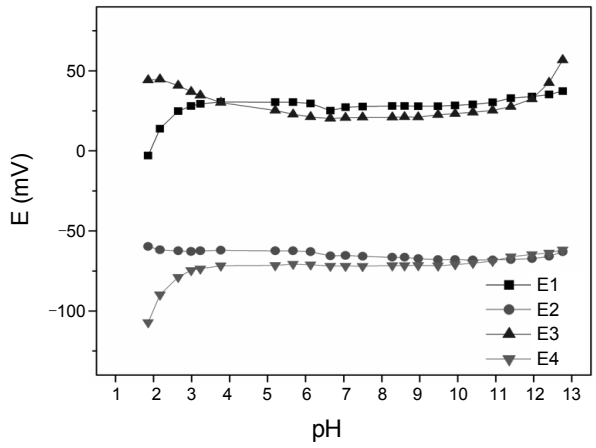


Figure 3. Effect of pH of the test solution on the potential response of the proposed E1-E4 electrodes at 10^{-2} M SCN^- concentration.

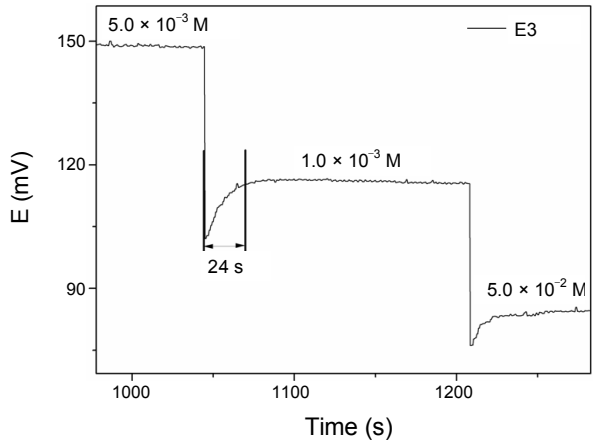


Figure 4. Dynamic EMF responses of E3 toward changes in thiocyanate activity (5.0×10^{-3} M ~ 5.0×10^{-2} M).

pH response for the optimized thiocyanate-sensitive membranes formulated with $\mathbf{L^2}$ or $\mathbf{L^2}$ 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 π-acceptor ligand (OH^-)[45,46] 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 Fig. 4. As can be seen the electrode reaches the equilibrium response in a relatively short time. When the concentration of thiocyanate was changed from 5.0×10^{-3} M to 5.0×10^{-2} M, the response time $t_{90\%}$ 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 carrier from the PVC membrane to aqueous sample solution.

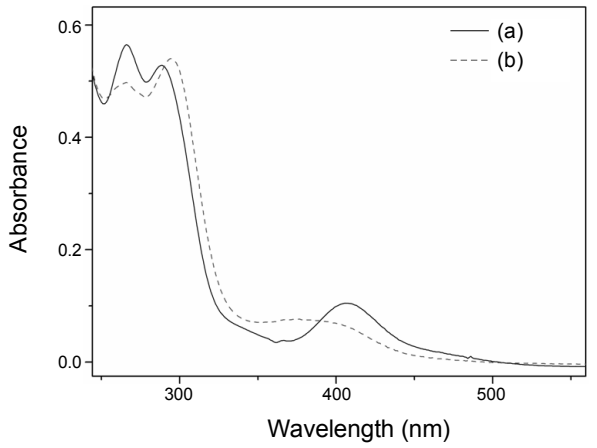


Figure 5. Absorption spectral changes for $\mathbf{L^2}$ (a) in CH_2Cl_2 (1.0×10^{-5} M), and (b) after extraction using 100 equiv. of KSCN in aqueous phase with an extraction time of 24 h.

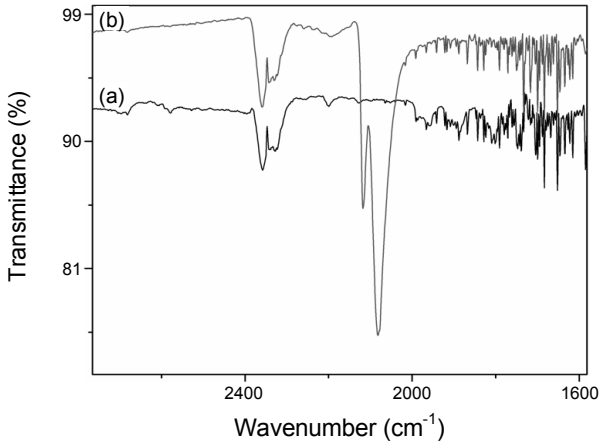


Figure 6. The C ≡ N stretching (2000 ~ 2200 cm^{-1}) region in the infrared spectra of (a) $\mathbf{L^2}$ and (b) the corresponding palladium thiocyanate complex.

Interaction mode between SCN^- and $\mathbf{L^2}$. The selective response towards thiocyanate is believed to be associated with the coordination of thiocyanate to the ionophore, [(dppe)PdI_2]. In order to investigate the potential interaction between thiocyanate and the ionophore, UV-Vis spectra of dichloromethane solution containing the ionophore (2.0×10^{-5} 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 λ = 405 nm was observed.

The IR spectra in the region 2800 - 1600 cm^{-1} of $\mathbf{L^2}$ 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 conforms that $\mathbf{L^2}$ forms an [(dppe)Pd (SCN)(NCS)] complex, which the mixed mode of thiocyanate coordination being already reported.[47]

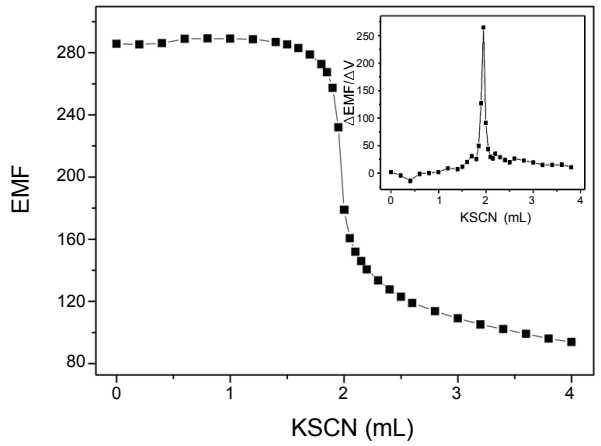


Figure 7. The titration of 1.0×10^{-3} M $AgNO_3$ (100 mL) with 5.0×10^{-2} M KSCN by using a thiocyanate-selective electrode based on the electrode E1.

Application to an end-point indication of the electrode. The optimized SCN^--ISE (E2 in Table 1) was found to work well under laboratory conditions. The recovery of thiocyanate from tap water samples with its concentration of 1.0×10^{-5} to 1.0×10^{-4} M by the electrode was found to be 100 ± 3%. It was also investigated whether the use of the thiocyanate-selective electrode could be employed as an indicator electrode in the determination of silver by potentiometric titration. For this purpose, 1.0×10^{-3} M $AgNO_3$ solution was prepared, 100 mL samples were taken from this solution and each was titrated with 0.1 M KSCN. The titration curves each showed a sharp inflection break (260 mV) at the 1:1 reaction point. Typical potentiometric titration curves are shown in Figure 7. Hence it was concluded that the electrode developed could be conveniently used as an indicator electrode in the potentiometric titration of silver.

Conclusions

New ionophore $\mathbf{L^2}$-based electrodes were successfully developed. They are applicable to the determination of thiocyanate anion in the concentration range from 5.0×10^{-6} to 1.0×10^{-1} M at pH 3.5 - 11. They have the advantage of a good detection limit of 1.1×10^{-6} M and a relatively fast response time of less than $t_{90\%} = 24$ s.

The proposed thiocyanate-selective electrode can be an alternative for most of thiocyanate PVC membrane selective electrodes reported in literature[9-38] as regard to ion selectivities, life time, and working pH range.

The response mechanism operating for the $\mathbf{L^2}$ membrane electrodes was examined using the effect of added ionic sites on the potentiometric response characteristics. It was demonstrated that addition of lipophilic anionic sites to the membrane electrodes based on the $\mathbf{L^2}$ enhances the selectivity towards the primary SCN^- ion, while addition of cationic sites resulted in Hofmeister selectivity patterns suggesting that the operative response mechanism is then of the positively charged carrier type.

It has also been demonstrated that the present thiocyanate-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 $\mathbf{L^2}$ selectively extracts thiocyanate. Thus, a specific relationship between sensing properties and extraction phenomena has been observed in the present study.

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