

The Novel SCN^- Ion-selective Electrode Based on the 1-Benzyl-3-(4-nitrophenyl) thio-urea Ionophore

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A potentiometric sensor based on the 1-benzyl-3-(4-nitrophenyl) thio-urea was synthesized and tested as an ionophore in PVC based membrane sensor towards SCN^- ions. This membrane exhibits a linear stable response over a wide concentration range (1.0×10^{-5} to 1.0×10^{-2} M) with a slope of -59.2 mV/dec., a detection limit of $\log[\text{SCN}^-] = -5.05$, and a selectivity coefficient for thiocyanate against perchlorate anion of $\log K_{\text{SCN}^-}^{\text{pot}} = -0.133$. The selectivity series of the membrane is as follows: $\text{SCN}^- > \text{ClO}_4^- > \text{I}^- > \text{NO}_3^- > \text{HSO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{F}^- > \text{CH}_3\text{COO}^- > \text{HCO}_3^- > \text{Br}^- > \text{H}_2\text{PO}_4^- > \text{SO}_3^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. The proposed electrode showed good selectivity and a good response for the SCN^- ion over a wide variety of other anions in pH 6.0 buffer solutions and has a fast response time of about < 5 s. The influences of the membrane by pH, ionophore, and plasticizer were studied.

Key Words : Ion selective electrodes, Polymeric membrane electrode, SCN^- selective electrode, Thio-urea

Introduction

The thiocyanate ion is existing at low concentration in serum, saliva and urine when absorbed a crucifer containing glucosinolate. However, high concentration of thiocyanate in human body lead to dizziness or unconsciousness,¹ a high saliva thiocyanate concentration can be quantitatively used as an indication for exposure to tobacco smoke.² It has been found that there is a correlation between the blood cyanide, the plasma thiocyanate and the salivary thiocyanate. In addition, ability to play an important role in antimicrobial system as a substrate for peroxidase, and detoxify carcinogens has been demonstrated recently.³⁻⁵ Therefore, an accurate, simple and rapid method for the determination of thiocyanate is significant in medicine and the life sciences.⁶

The analytical methods for the determination of the thiocyanate ion concentration are spectrophotometry,⁷ ion chromatography,⁸ polarography,⁹ amperometry,¹⁰ and voltammetry methods.¹¹ Among the various methods, it is known that potentiometric analysis using an ion-selective sensitive electrode (ISE) is simple, rapid, and less expensive. These advantages of ISEs have led to the development of potentiometric sensors for many inorganic and organic species.

The PVC membrane ISEs contain various constituents, usually ionophores and lipophilic salt, as an ion exchanger, and displays the classical Hofmeister behavior,¹² in which the membrane selectivity is controlled by the free energy hydration of the ions involved with a selectivity sequence: $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- \approx \text{Sal}^- > \text{NO}_3^- > \text{NO}_2^- > \text{Br}^- > \text{Cl}^- \approx \text{HSO}_3^- > \text{CH}_3\text{COO}^- \approx \text{HCO}_3^- > \text{HSO}_4^- > \text{SO}_4^{2-} \approx \text{H}_2\text{PO}_4^- \approx \text{F}^-$. Thus, some ions behind perchlorate in this sequence are difficult to prepare useful selective electrodes in practical application. Recently, most of the SCN^- ion selective electrodes are

based on metalloporphyrines,¹³⁻¹⁵ lipophilic organometallic compounds,^{16,17} zeolite,¹⁸ vitamin B₁₂ derivatives,^{19,20} schiff-based complexes²¹ of metal ions, and nickel macrocyclic complexes,²² silver and gold tri-isobutylphosphine sulfide and 1,3-diphenylpropyl phosphine derivatives²³⁻²⁵ which have a remarkable deviation from the Hofmeister pattern. These deviations result from a direct interaction between the central metal of the membrane active components and the analytical anion and steric effect associated with the structure of the ligand.

The present study deal with the 1-benzyl-3-(4-nitrophenyl) thio-urea based ISE for selective determination of thiocyanate. This ISE shows a good detection limit, fast response time and slope.

Experimental

Reagents. All the salts and the membrane components anion exchanger triiododecylmethylammonium chloride (TDDMACl), polyvinyl chloride (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS) and tetrahydrofuran (THF) were obtained from Fluka. Analytical-grade sodium and potassium salts of the tested anions were used. Water doubly distilled in a quartz apparatus was used to prepare all the aqueous electrolyte solutions.

Potentiometric Measurement. The electrochemical properties of the SCN^- ISEs were investigated in the conventional configuration. Small disks were punched from the cast membranes and then mounted in Philips electrode bodies (IS-561). For all the electrodes, 0.1 M KCl was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference

electrode (Model 90-02). The electrochemical potential was measured using a 16-channel potentiometer coupled to a computer (KST101-1). The dynamic response curve was produced by adding standard solutions of anions to a magnetically stirred buffer solution (0.05 M tris-HCl). The selectivity coefficients ($\log K_{\text{SCN}^-}^{\text{pot}}$) were determined using a separate solution method (SSM). At least three-time measurements were performed, and the data were obtained from the plot. The detection limits were estimated at the intersection of two linear lines, one extrapolated from a high concentration range and the other parallel to the X-axis drawn through the mean potential value of the lowest anion concentration used in the plot of the potential value of the anion concentration used in the plot of the potential change and the SCN⁻ concentration.

Separate Solution Method (SSM). The selectivity coefficient K was determined using the SSM with the following generalized Eq. (1)²⁶:

$$\log K_{A,B}^{\text{pot}} = \frac{E_B - E_A}{S} + \left(1 - \frac{Z_A}{Z_B}\right) \log a_A \quad (1)$$

Where $\log K_{A,B}^{\text{pot}}$ is the potentiometric selectivity coefficient, S the slope of the calibration plot, a_A is the activity of thiocyanate solution and Z_A and Z_B are the charges of the SCN⁻ and the interfering anions, respectively.

Debye-Huckel Equation. The activities of the anions were based on the activity coefficient data (γ) calculated from the modified form of Debye-Huckel Eq. (2),²⁷ which is applicable to any ion and is as follows:

$$\log \gamma = -0.511Z^2 \left[\frac{\mu^{12}}{(1 + 1.5\mu^{12}) - 0.2\mu} \right] \quad (2)$$

where μ is the ionic strength and Z is the valency.

X-ray Structure Determination. The derived 1-benzyl-3-(4-nitrophenyl) thio-urea (Figure 1) was synthesized in the authors' laboratory to prepare highly selective thiocyanate electrodes. Single crystals are suitable for X-ray structural determination and were obtained by cooling saturated solutions of methylenechloride at -20 °C. The reflection data for the compound were collected on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). The hemispheres of the reflection

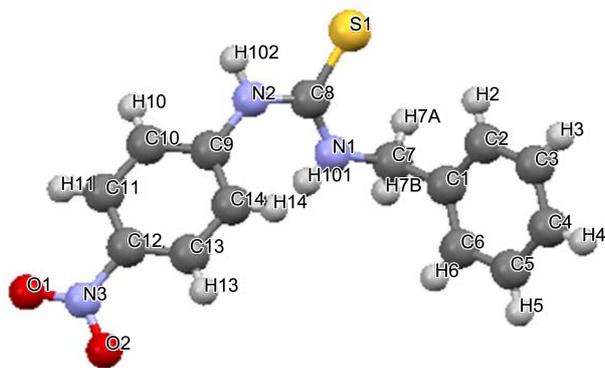


Figure 1. The structure of 1-benzyl-3-(4-nitrophenyl) thio-urea ionophore.

Table 1. Crystallographic data for the 1-benzyl-3-(4-nitrophenyl) thio-urea

Parameters	Compound
Formula	C ₁₄ H ₁₃ N ₃ O ₂ S
Formula weight	287.34
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	13.0169 (9)
<i>b</i> (Å)	9.7239 (7)
<i>c</i> (Å)	22.1485 (15)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	2803.45
<i>Z</i>	8
ρ_{calc} (g cm ⁻³)	1.362407
μ (mm ⁻¹)	0.235
<i>F</i> (000)	1200
<i>T</i> (K)	100(2)
Scan mode	ω and ϕ
<i>hkl</i> range	-18 ≤ <i>h</i> ≤ 18, -9 ≤ <i>k</i> ≤ 14, -31 ≤ <i>l</i> ≤ 30
Measured reflections	30302
Unique reflections [<i>R</i> _{int}]	4404 (0.0334)
Refined parameters	190
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0453
w <i>R</i> ₂ ^b of all data	0.1099
GOF on <i>F</i> ²	1.022
ρ_{fin} (max/min) (e Å ⁻³)	0.282/-0.341

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$$

data were collected as ω scan frames with 0.5°/frame and an exposure time of 10 s/frame. The cell parameters were determined and refined using the SMART program.²⁸ Data reduction was performed using the SAINT software.²⁹ The data were corrected for the Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program.³⁰ The structures of the compounds were solved using direct methods, and were refined with the full-matrix least-squares method using the SHELXTL program package, with anisotropic thermal parameters for all the non-hydrogen atoms (Figure 1 and Table 1).³¹

FT-IR Study. To identify the surface functional group under Fourier transform infrared spectroscopy (FT-IR) spectrum of the 1-benzyl-3-(4-nitrophenyl) thio-urea in the range of 500-3500 cm⁻¹ has shown in Figure 2. For the ionophore, the peaks observed frequencies at 3363 cm⁻¹ corresponds to N-H symmetric stretching. The presence of aromatic group is indicated by two peaks at 3158, cm⁻¹ and 3067 cm⁻¹ which represents the C-H stretching mode, while the band 3000 cm⁻¹ correspond to aliphatic C-H stretching. The band at 1661-1499 cm⁻¹ and 1389-1259 cm⁻¹ can be assigned to the -NO₂ functional group to asymmetric and symmetric modes. And the peak at 600-700 cm⁻¹ is the characteristic peak of the C=S bound to the nitrogen atom that shows the one peak in the stretching vibration. Besides, peaks of some other

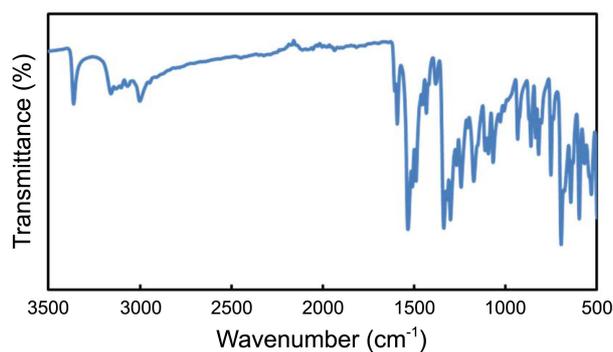


Figure 2. The FT-IR spectrum of ionophore.

corresponding to 1563-700 cm⁻¹ is caused by vibration associated with the interaction between the C-N stretch of C=S stretching.

NMR Study. The ¹H-NMR spectra were recorded on a Bruker Ultrashield 300 MHz/54 mm NMR spectrometer. CDCl₃ and tetramethylsilane (TMS) were used as the solvent and the chemical shift reference, respectively. According to the ¹H-NMR spectrum of 1-benzyl-3-(4-nitrophenyl) thio-urea shows a multiplet signal at 7.23 ppm, which may be assigned to the benzene's -C-H. The doublet peaks at 8.01 ppm, and 6.64 ppm were derived from H-N(=O)=O and -N-H of 1-benzene ring, respectively. The singlet peaks were presented at 4.0 ppm, and 2.0 ppm which correspond to aromatic C-N-H, and amine, respectively. Elemental analysis for C₁₄H₁₃N₃O₂S was found as wt %, C: 58.52; H: 4.56; N: 14.62; O: 11.14; S: 11.16.

Membrane Preparation. The compositions of the PVC based SCN⁻ ion-selective electrodes are summarized in Table 2. The ionophore, plasticizer, and PVC were dissolved in an appropriate volume of THF, and were mechanically stirred. All the membrane cocktails were cast in glass rings placed on glass plates for the conventional ion-selective electrodes. The solvent from the PVC membrane was allowed to evaporate for at least 24 h at room temperature. The resulting membrane was about 0.3 mm thick.

Results and Discussion

Working Concentration Range and Slope. In the preliminary experiments, investigations were conducted to

Table 2. Compositions of the membrane

Membrane ^a	Ionophore ^a	PVC ^a	<i>o</i> -NPOE ^a	DOP ^a	DOA ^a	DOS ^a	TDDMACI ^b
m-1	1	33	66				0
m-2	1	33	66				50
m-3	1	33		66			50
m-4	1	33			66		50
m-5	1	33				66	50
m-6	2	33	66				50
m-7	3	33	66				50
m-8	5	33	66				50

^aIn milligrams. ^bin moles percent relative to the ionophore

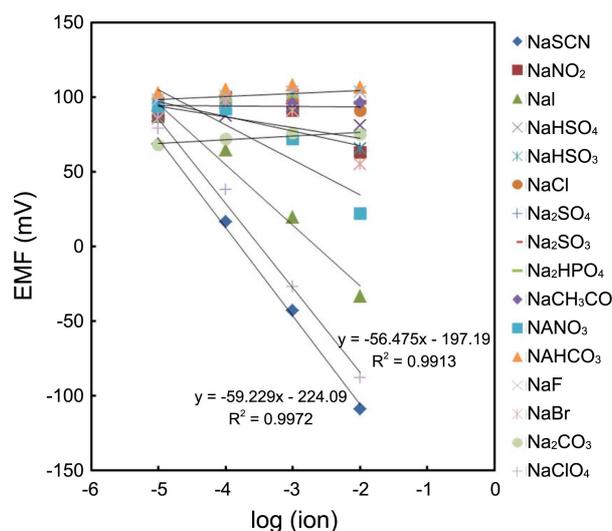


Figure 3. Potentiometric response curve for different ions.

Table 3. Limit of detection, and slope of different ion

Ions	Response Slope (mv/dec.)	LOD
SCN ⁻	-59.23	-5.04
ClO ₄ ⁻	-56.48	-5.04
I ⁻	-40.77	-4.92
NO ₃ ⁻	-23.53	-4.49

determine the potentiometric response of 1-benzyl-3-(4-nitrophenyl) thio-urea to different anions at 0.05 M tris-HCl at pH 6.0 and anion exchanger *o*-NPOE. The potential measurements of these electrodes were carried out over the concentration range from 1.0 × 10⁻⁸ to 1.0 × 10⁻² M of the respective analyte ions. The concentration range of 1.0 × 10⁻⁵ to 1.0 × 10⁻² that corresponds to the SCN⁻ ISE SCN⁻, ClO₄⁻, I⁻, and NO₃⁻ ions were compared with the Nernst slopes (-59.23, -56.48, -40.77, and -23.53 mV/dec., respectively), as shown in Figure 3 and Table 3. The results clearly indicate that the PVC membrane electrode is more sensitive and stable for thiocyanate.

Effect of Membrane Composition. The influence of the membrane composition, lipophilic additive, plasticizer on the potential response of the membrane was investigated. The effect of plasticizer on SCN⁻ ISE membrane electrodes

Table 4. Linear range, limit of detection, and slope of each membrane

Membrane	Linear range (M)	LOD (log[SCN ⁻])	Slope (mV/dec)	R ²
m-1	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-4.94	-2.34	0.6019
m-2	1.0 × 10⁻² to 1.0 × 10⁻⁵	-5.05	-59.23	0.9972
m-3	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-5.15	-51.13	0.9874
m-4	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-5.01	-53.45	0.9879
m-5	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-5.00	-51.55	0.9907
m-6	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-4.96	-58.57	0.984
m-7	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-4.80	-55.91	0.9577
m-8	1.0 × 10 ⁻² to 1.0 × 10 ⁻⁵	-4.72	-60.61	0.9411

is shown in Table 4. According to Table 4, it is clear that *o*-NPOE is a more effective mediator than others plasticizer. It is noteworthy that the character of plasticizer influences both the dielectric constant of the polymeric membranes and the mobility of an ionophore and its complex with SCN⁻.³²

The membrane electrodes were prepared from different capacity of the ionophore, a dynamic response occurred. It was noted that the potential slope of the membranes with more than 1.0 mg ionophore (m-6, m-7, m-8) was decreased than that of the membrane with 1.0 mg ionophore (m-2). So the optimal capacity of ionophore seems to be about 1.0 mg in the PVC membrane. This is most probably due to some inhomogeneities and possible saturation of the membrane.³³

The membrane electrodes were prepared in the absence and presence of the additive. The membranes without additive gave the worse sensitivity and selectivity than those with the other additive (TDDMACl). These data confirm that the lipophilic slats not only reduce the ohmic resistance^{33,34} but also improving the response behavior and selectivity.^{35,36} Moreover, the additives might be catalyzed the exchange kinetics at the sample membrane interface.³⁵

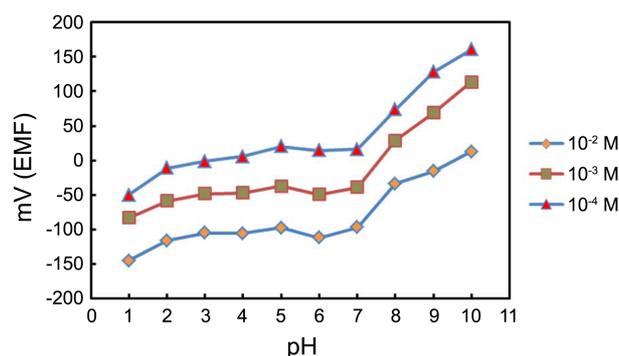
The prepared membranes were observed on the effect of inner reference solution. It was found that the concentration and composition of the internal solution affected on the potentiometric response insignificantly. Thus, 0.1 M KCl as a reference solution is proper for smooth activating of the membrane system. So, the best response was observed with the membrane composed of the following ingredients: 1% ionophore, 33% PVC, 66% *o*-NPOE, 50% of ionophore TDDMACl.

pH Effect. The influence of pH of the test solution on the response of the membrane electrode was examined in the pH range 1.0-10.0 (adjusted with either HCl or NaOH) and the results are shown in Figure 4 and Table 5. As seen, the potentials are constant in the pH range 3-7.

Variation of the potential at pH < 3 could be related the increase of the Cl⁻ ion concentration and simultaneous response of the electrode to SCN⁻ and Cl⁻ ion. Over pH 7.0, deteriorating potentiometric response can be explained by coordination competition between SCN⁻ and OH⁻ ion.

The hydroxide activities have been calculated from experimental pH values according to Eq. (3).

$$a_{OH^-} = 10^{pH-14} \quad (3)$$

**Figure 4.** The influence of pH on the response for 10⁻² M, 10⁻³ M, 10⁻⁴ M SCN⁻.

So, the selectivity coefficient for OH⁻ as the interferent for an SCN⁻ ion has been calculated to be

$$\log K_{SCN^-, OH^-}^{pot} = -5 \text{ at pH } 6.$$

Among the pH range 3-7 that experimental results show that at pH 6.0, the analytical signal of the electrode presented better detection limits and slope for thiocyanate.

Response Mechanism. The preferential response towards thiocyanate is believed to be associated with the coordination of SCN⁻ to the ionophore. In order to investigate the potential interaction between thiocyanate and the ionophore, the UV spectra were carried out. Figure 5 displays a THF solution of thio-urea treated with and without a 10⁻³ M

Table 5. The limit of detection and slope in various pH values for m-2 membrane

pH	slope	DL (log[SCN ⁻])	R ²
1	-37.00	-4.70	0.9321
2	-49.65	-5.07	0.9966
3	-52.22	-5.11	0.9989
4	-53.816	-5.06	0.9987
5	-57.02	-5.15	0.9991
6	-59.23	-5.05	0.9972
7	-53.09	-5.11	0.9968
8	-43.66	-4.89	0.9618
9	-62.88	-5.09	0.9816
10	-65.90	-5.10	0.9693

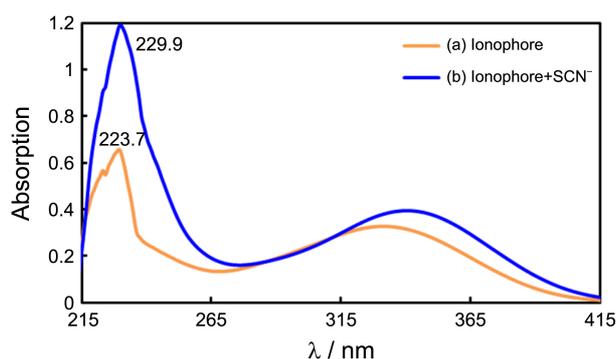


Figure 5. UV absorption spectra of (a) ionophore and (b) with treated by 10^{-3} M NaSCN solution in THF solution.

NaSCN solution for 2 h. The peak showing a considerable red shift of about 10 nm and a substantial increase in absorbance suggests that interaction took place between the carrier and thiocyanate ion.

Response Time and Life Time. The response time of the ISEs analysis plays an important role in the application. Figure 6 shows the concentration of thiocyanate ion changed from 1.0×10^{-3} to 1.0×10^{-2} M, the potential changed dynamically. The static response time thus obtained was less than 5s; however, at a concentration lower than 1.0×10^{-6} M, the potential was constant. The sensing behavior of the membrane electrode remained unchanged when the potentials were recorded either from low to high concentration, or *vice versa*.

As can be seen, the proposed thiocyanate-selective electrode shows superiority response time and good Nernstian slope. Thus, the proposed 1-benzyl-3-(4-nitrophenyl) thio-urea is advancement over the reported systems (Table 5).

The lifetime studies are based on monitoring the change in electrodes slope and linear response range with time. The membranes would be stored in pH 6.0 buffer solution when not in use. After about 2 weeks, the electrodes were responding at 98% of the initial response. By the end of one month, the response observed was still 96% of the initial value. This influence may be due to slight leaching of the plasticized PVC membrane components.

The reproducibility of the electrode was also tested. The standard deviation of 3 times measurements at slope was ± 0.5 mV, respectively.

Selectivity Coefficient. The selectivity coefficients of the new membranes are very important for determining quality as ISEs. The selectivity coefficients represent their response

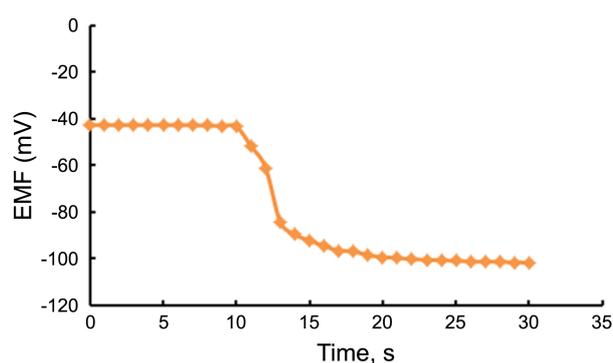


Figure 6. Response time of concentration of thiocyanate ion changed from 10^{-3} M to 10^{-2} M.

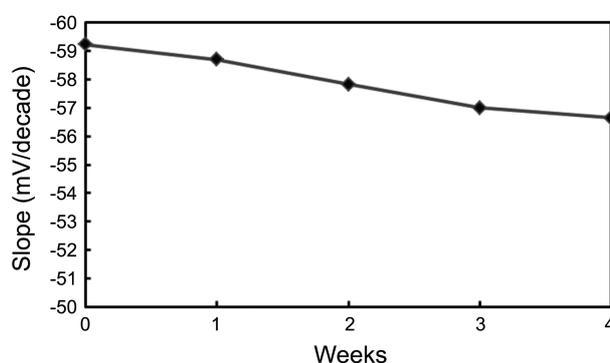


Figure 7. The life time of thiocyanate selective electrode m-2.

Table 7. Selectivity coefficients for various interfering ions for the membrane (m-2) electrodes obtained *via* SSM

j	$\log K_{\text{SCN}^-}^{\text{pot}}_{\text{SCN}^-}$
SCN^-	0
ClO_4^-	-0.133
I^-	-1.015
NO_3^-	-2.108
HSO_3^-	-2.514
Cl^-	-2.651
HSO_4^-	-2.670
F^-	-2.676
CH_3COO^-	-2.684
HCO_3^-	-2.686
Br^-	-2.6967
H_2PO_4^-	-4.1918
SO_3^{2-}	-4.2169
SO_4^{2-}	-4.244
CO_3^{2-}	-4.3580

Table 6. Comparison of the potentiometric parameters of proposed electrode with previous SCN^- ISEs

Ionophore	Linear range	slope mV/dec	Detection limit (M)	Response time (s)	pH	Ref
$\text{Rh}[(\text{trpy})(\text{bby})\text{Cl}](\text{PF}_6)_2$	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	-58.7	-5.3	15	3.0-8.0	37
Calix[4]arene	$3.0 \times 10^{-5} - 1.0 \times 10^{-1}$	-52	-4.6	10-15	2.0-3.0	38
Hexa-imidepyridine	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	-58.3	-5.3	10 <	2.0-8.0	39
Urea-functionalized porphyrin	$5.0 \times 10^{-5} - 1.0 \times 10^{-2}$	-58	-4.3	-	7	40
1-Benzyl-3-(4-nitrophenyl) thio-urea	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	-59.2	-5.05	5 <	3.0-7.0	Present work

to the species to be measured over other ions present in solution. The selectivity coefficients of the electrodes were determined by the separate solution method (SSM). The selectivity coefficients are shown Table 7. Although the Hofmeister series is $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- \approx \text{Sal}^- > \text{NO}_3^- > \text{NO}_2^- > \text{Br}^- > \text{Cl}^- \approx \text{HSO}_3^- > \text{CH}_3\text{COO}^- \approx \text{HCO}_3^- > \text{HSO}_4^- > \text{SO}_4^{2-} \approx \text{H}_2\text{PO}_4^- \approx \text{F}^-$. The selectivity series of the membrane (m-2) gives the follow as $\text{SCN}^- > \text{ClO}_4^- > \text{I}^- > \text{NO}_3^- > \text{HSO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{F}^- > \text{CH}_3\text{COO}^- \approx \text{HCO}_3^- > \text{Br}^- > \text{H}_2\text{PO}_4^- > \text{SO}_3^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. This series is totally different with Hofmeister series. This ionophore based ISE exhibited excellent selectivity for SCN^- anion.

Conclusion

At the final point, the membrane electrode incorporating 1-benzyl-3-(4-nitrophenyl) thio-urea is considered to be an ionophore (ionophore:PVC:o-NPOE:TDDMACI as 1:33:66:50 mol % of ionophore) for the development of a thiocyanate ISE in pH 6. This electrode exhibits good Nernstian response (-59.23 mV/dec.), the limit of detection as $\log[\text{SCN}^-] = -5.05$, comparatively fast response time > 5 s and better long life time. It can be concluded that the membrane electrode has a rapid potential response and selectivity towards thiocyanate ion over other interfering metal ions.

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