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Linear polyamines as carriers in thiocyanate-selective membrane electrodes

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Abstract

The polyamines, octyl-[2-(2-octylamino-ethylamino)-ethyl]-amine (L^1) and octyl-{2-[2-(2-octylamino-ethylamino)-ethylamino]-ethyl}-amine (L^2), have been used as anion ionophores in PVC-based membrane ion-selective electrodes. Different electrodes were prepared containing L^1, or L^2, and *o*-nitrophenyl octyl ether (NPOE) or bis(2-ethylhexyl)sebacate (DOS) as plasticizers. The response of the electrodes was tested in two different buffers, HEPES-KOH (pH 7) and MES-KOH (pH 5.6). Electrodes containing L^1 and L^2 with NPOE (E1 and E2, respectively) showed a Nernstian response for thiocyanate with a good response time. The detection limit, linear range and slope for electrode E1 were 3.8×10^{-6} mol dm^{-3}, 1×10^{-5} to 1×10^{-1} mol dm^{-3} and -57.2 mV decade^{-1} at pH 5.6 and 4.47×10^{-6} mol dm^{-3}, 1.95×10^{-5} to 1×10^{-1} mol dm^{-3} and -58.1 mV decade^{-1} at pH 7.0. For electrode E2 the detection limit, linear range and slope found were 2.63×10^{-6} mol dm^{-3}, 7.94×10^{-6} to 1×10^{-1} mol dm^{-3} and -58.5 mV decade^{-1} at pH 5.6 and 1.23×10^{-5} mol dm^{-3}, 7.95×10^{-5} to 1×10^{-1} mol dm^{-3} and -46.0 mV decade^{-1} at pH 7. In contrast, electrodes containing DOS as plasticizers gave only response at pH 5.6 (detection limit, linear range and slope at pH 5.6 were 3.16×10^{-5} mol dm^{-3}, 1×10^{-4} to 1×10^{-1} mol dm^{-3} and -52.6 mV decade^{-1}). Selectivity coefficients for different anions with respect to thiocyanate were calculated. The electrode E2 at pH 5.6 was also used for the determination of SCN^- by potentiometric titrations with Ag^+ ions with good results. The electrode E2 was also used to determine concentrations of thiocyanate in biological samples.

Keywords: Thiocyanate; Ion selective electrodes; PVC membranes; Potentiometry

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1. Introduction

Thiocyanate has many industrial and biological applications and its determination at low concentration levels in water, urine, saliva and industrial samples has been described as important. Thus, thiocyanate, though not as toxic as cyanide, is harmful anion. Additionally, in biological samples, where it is a metabolic degradation product from tobacco smoke containing cyanide, it has been considered a good indicator for distinguishing between smokers and non-smokers, as elevated levels of thiocyanate are related to excessive cigarette smoking.

Several methods for the determination of thiocyanate such as spectrophotometry [1–5], chromatography [6–11], polarography [12], capillary zone electrophoresis [13], amperometry [14], etc., have been reported previously. Unfortunately most of them are rather sophisticated and use high-cost equipment. As an alternative, potentiometric methods using ion-selective electrodes are simple and economical with a fast response time, low detection limit and usually good selectivity. In recently reported electrodes for thiocyanate (most of them using metal porphyrins [15–20] metal phthalocyanines [21,22], organometallic compounds [23–33] and imide pyridine derivatives [34]), the selectivity is mainly

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governed by the specific interaction between the central metal cation and the thiocyanate anion. However, some of these ionophores require extensive and time-consuming synthetic efforts to obtain final somewhat complicated hosts. Other possibilities involve the use of ionophores capable of coordinate anions via electrostatic interactions or hydrogen bonds. At this respect, polyazaalkanes are well-known anion receptors and have been extensively used in aqueous solutions in processes involving coordination with anionic species. Thus, polyamines are polybases and at neutral pH are partially protonated in water and therefore can display attractive interactions with anions. Additionally the N–H bond in amines is especially apt to give hydrogen bonding interactions [35–37]. However, although the interaction of anions with polyazaalkanes in aqueous solutions is very well documented there are relatively few examples where polyamines have been used as anion-selective ionophores in membrane-based electrodes [38–45].

In this paper, we report a study on the potential use of polyamines as carriers for the development of thiocyanate PVC membrane-based ion-selective electrodes.

2. Experimental

2.1. Reagents and apparatus

Reagents grade *o*-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl)sebacate (DOS), tetrahydrofuran (THF), poly(vinyl chloride) of high molecular weight (PVC), *N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid (HEPES) and 2-(*N*-morpholino)ethanesulfonic acid (MES) were purchased from Sigma–Aldrich. Tetrahydrofuran (THF) was purchased from Merck. Thiocyanate, carbonate, nitrate, nitrite, bromide, chloride, iodide, acetate, oxalate, sulfate, phosphate, iodate, sulfite, azide, benzoate, salicylate and cyanide solutions were prepared from sodium or potassium salts and were purchased from Scharlau. All the aqueous solutions and buffers were prepared with deionised distilled water (Milli-Q water purification system). The potentiometric response measurement of the electrodes was carried out using a Crison Model GLP 22 pH/mV. Experiments were performed at 25 °C in an argon atmosphere. All the potentiometric titrations were carried out with a titroprocessor using a 25.0 ± 0.1 °C water-thermostatted vessel under argon atmosphere and an automatic burette.

2.2. Synthesis of ionophores L^1, L^2

2.2.1. Synthesis of octyl-[2-(2-octylamino-ethylamino)-ethyl]-amine (L^1).

A 1.5 ml (14 mmol) of diethylenetriamine and 4.38 ml (28 mmol) of caprylic aldehyde were dissolved in 20 ml of absolute ethanol. The reaction mixture was stirred and refluxed at 50 °C for 8 h and then 1.5 g (39.65 mmol) of $NaBH_4$ was added and the mixture heated to reflux at 50 °C for 16 h. The solvent was evaporated to dryness on a rotary evaporator. The crude reaction was dissolved in dichloromethane and washed with aqueous sodium chloride. The organic phases were dried with anhydrous magnesium sulfate and evaporated to dryness. The product was filtered and washed with hexane. Yield: 3615 mg, 71.45%: ^{1}H NMR (CDCl3): δ 0.85 (t, 6H, CH_3-$(CH_2)_7$-N), 1.1–1.4 (m, 24H, CH_3-$(CH_2)_6$-CH_2-N), 2.8-3.3 (m, 12H, CH_2-NH). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.07 (CH_3), 22.57 (CH_2), 25.83 (CH_2), 26.86 (CH_2), 29.09 (CH_2), 29.11 (CH_2), 31.7 (CH_2), 44.97 (CH_2-N), 47.39 (CH_2-N), 48.33 (CH_2-N). FAB high resolution mass spectroscopy; found 328.3697, calculated for $C_{20}H_{45}N_3$, 328.3692.

2.2.2. Synthesis of octyl-{2-[2-(2-octylamino-ethylamino)-ethylamino]-ethyl}-amine (L^2)

A 2 g (13.68 mmol) of triethylenetetramine and 4.27 ml (27.35 mmol) of caprylic aldehyde were dissolved in 20 ml of absolute ethanol. The reaction mixture was stirred and refluxed at 50 °C for 8 h, then 1.2 g (31.72 mmol) of $NaBH_4$ to the solution were added and the mixture heated to reflux at 50 °C for 16 h. The resulting solution was evaporated to dryness on a rotary evaporator. The crude reaction was dissolved in dichloromethane and washed with aqueous sodium chloride. The organic phases were dried with anhydrous magnesium sulfate and evaporated to dryness. The product was filtered and washed with hexane. Yield: 4.5 g, 98.3 %: ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 6H, CH_3-$(CH_2)_7$-N), 1.1–1.4 (m, 24H, CH_3-$(CH_2)_6$-CH_2-N), 2.6-3.2 (m, 16H, CH_2-NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.05 (CH_3), 22.58 (CH_2), 26.29 (CH_2), 26.95 (CH_2), 29.10 (CH_2), 29.15 (CH_2), 31.72 (CH_2), 45.07 (CH_2-N), 46.80 (CH_2-N), 47.74 (CH_2-N), 48.83 (CH_2-N). FAB high resolution mass spectroscopy; found 371.4119, calculated for $C_{22}H_{50}N_4$, 371.4114.

2.3. Membrane preparation

Membranes containing different PVC/plasticizer ratios and different amounts of ionophores L^1 and L^2 were studied. We found a optimum response of the membranes to thiocyanate in terms of linear range and detection limit when using the following composition: 1.0 wt.% of the corresponding ionophore (L^1 or L^2), 33 wt.% of PVC and 66 wt.% of plasticizer (DOS or NPOE). The response of the membranes was tested at different pH values and a suitable response to thiocyanate in neutral and slightly acidic aqueous solutions was found. Therefore, pH values of 7.0 and 5.6 were selected to carry out a complete electrode characterization. The membranes were prepared, characterized and evaluated according to IUPAC recommendations [46].

The membrane components were dissolved in 5 ml of THF. The resulting mixture was transferred into a glass dish of 5 cm diameter. The solvent was allowed to evaporate overnight and a transparent membrane of 0.16 mm thickness was formed from which small-diameter disks were cut out and incorporated into the electrode which was finally conditioned by soaking it in a 0.1 M potassium thiocyanate solution at pH 5.6 or 7. When not in use the electrodes were kept immersed in the same solution. Previously, the membrane electrodes had also been examined with different concentrations of the inner reference solution and the optimum concentration was 0.1 M potassium, thiocyanate.

2.4. EMF measurements

The external reference electrode was a Ag–AgCl (KCl 3 M) and the internal reference electrode was a Hg–Hg_2Cl_2 (saturated KCl). The electrode cell assembly of the following type was used: Ag/AgCl (KCl 3 M)|sample solution|PVC membrane|internal solution, 0.1 M of KSCN-buffer (MES pH 5.6 or HEPES pH 7)| Hg/Hg_2Cl_2 (saturated KCl). The buffers that were used throughout the experiments were HEPES-KOH (pH 7) and MES-KOH (pH 5.6). The detection limit was defined as the intersection of the extrapolated linear regions of the calibration graph. Potentiometric selectivity coefficients were determined according to the fixed interference method using 0.01 M solutions of interfering ion. Activity coefficients were calculated according to Debye-Hückel approximation. Calibration curves were constructed by plotting the potential, E, versus the logarithm of the activity of thiocyanate at pH 5.6 and 7 [47–49].

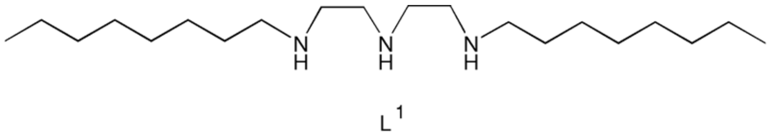
3. Results and discussion

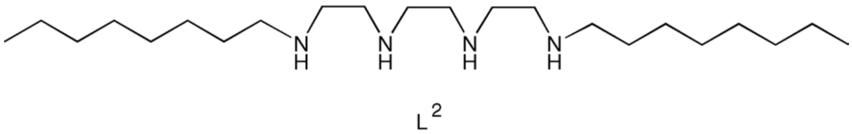
As stated in the introduction many of the recently reported ion-selective electrodes developed for thiocyanate contain metal complexes which are known to be suitable receptors for certain anions via coordination to the metal centre. As an alternative to these ionophores we have checked here the use of polyamines, which are known to display interaction with anions via hydrogen bonding and/or electrostatic forces. The receptors prepared L^1 and L^2 are simple open-chain polyamines containing three and four amino groups, respectively (see Scheme 1). They were prepared by condensation of diethylenetriamine or triethylenetetramine with caprylic aldehyde to give the corresponding di-imines that were further reacted with sodium borhydride to yield the amines L^1 and L^2. The ^1H, ^{13}C spectra and FAB high resolution mass spectroscopy were in agreement with the proposed formulation.

3.1. The emf response characteristics

It is known that, apart from the role of the ionophore, the electrode response is dependent on the composition of the membrane, the nature and amount of plasticizer and the addition of ionic additives. For this reason, different PVC membrane electrodes containing the ionophores L^1 or L^2 were prepared using two plasticizers of very different dielectric constants; bis(2-ethylhexyl)sebacate (DOS, $\varepsilon = 4$) and *o*-nitrophenyl octyl ether (NPOE, $\varepsilon = 24$). The response of these electrodes was additionally tested in two different buffers, HEPES-KOH (pH 7) and MES-KOH (pH 5.6). The electrodes containing L^1 or L^2 polyamines were introduced in the membranes in their unprotonated form and after the conditioning period (0.1 M potassium thiocyanate solution at pH 5.6 or 7) the electrodes gave response to anions. This anionic response without the necessity of adding ionic salts suggested that the ionophores are finally at least partially protonated in the membrane. From the different anions tested a good response was observed for SCN^-. The characteristics of the ion-selective electrodes in the presence of thiocyanate are shown in Table 1.

Membranes containing L^1 or L^2 with NPOE (electrodes E1 and E2) gave suitable responses at both pH 5.6 and 7, although a slightly better detection limit and a faster response time was found when working at pH 5.6. Thus, for instance, the E1 electrode at pH 5.6 gave a linear response in the concentration range 1×10^{-5} to 1×10^{-1} M, a detection limit of 3.80×10^{-6} M and a Nernstian potentiometric response of -57.2 mV decade^{-1} of thiocyanate activity. A very similar response was also found for electrode E2 at pH 5.6 (linear range of 7.94×10^{-6} to 1×10^{-1} M, detection limit of 2.63×10^{-6} and sensitivity of -58.5 mV decade^{-1}). These results using NPOE contrast with those found with the less polar DOS plasticizer. Thus, the electrode containing L^1 and DOS (E3) at pH 5.6 displayed a sub-Nernstian response with a slope of -52.6 mV decade^{-1} and gave a detection limit





Scheme 1.

Table 1
Response characteristics of E1, E2 and E3 electrodes

Number	Ionophore	Plasticizer	pH	Detection limit (M)	Lineal range (M)	Slope (mV decade^{-1})	Response time (s)
E1	L^1	NPOE	5.6	3.8×10^{-6}	1×10^{-5} to 1×10^{-1}	−57.2	2
E1	L^1	NPOE	7.0	4.47×10^{-6}	1.95×10^{-5} to 1×10^{-1}	−58.1	7
E2	L^2	NPOE	5.6	2.63×10^{-6}	7.94×10^{-6} to 1×10^{-1}	−58.5	3
E2	L^2	NPOE	7.0	1.23×10^{-5}	7.95×10^{-5} to 1×10^{-1}	−46.0	9
E3	L^1	DOS	5.6	3.16×10^{-5}	1×10^{-4} to 1×10^{-1}	−52.6	9

(3.16×10^{-5} M) and linear range (1×10^{-4} to 1×10^{-1} M) in the presence of thiocyanate worse than those found for the E1 and E2 electrodes (see Table 1). The electrodes prepared display quite a short response times, measured as the time elapsed in reaching the 95% of the final response after changing the activity of the anion sample form 10^{-4} to 10^{-2} or from 10^{-2} to 10^{-4}. The response time measured for the different electrodes was of 2 and 7 s for the electrode E1 at pH 5.6 and 7, respectively, and of 3 and 9 s for E1 at pH 5.6 and 7.

The membrane electrodes prepared with NPOE showed no decay of the slope below 50 mV decade^{-1} for at least 30 days. However, with DOS as plasticizer the electrodes prepared could only be used for 1 week. The rest of studied electrodes present very unstable responses with times of life of approximately 2 or 3 days.

3.2. The effect of pH

The effect of pH on the response of the membranes containing L^1 and L^2 and NPOE (electrodes E1 and E2) was studied over the 2–11 pH range at a fixed concentration of thiocyanate of 1×10^{-4} M. The pH was varied by adding potassium hydroxide and hydrochloric acid. The results for E2 (L^2 and NPOE as plasticizer) are shown in Fig. 1. As can be observed, the potential response of the electrode is independent of pH in the pH range 4–8, whereas at approximately pH greater than 8 the potential decreases, probably due to either, an increasing competition of the OH^- with the SCN^- anion or due to a deprotonation of the ligand L^1. A similar potential variation and hydroxyl competition at basic pH was observed for electrode E1 (L^1 and NPOE). At pH lower than 4, the potential also decreases probably due to competition of the Cl^- anion.

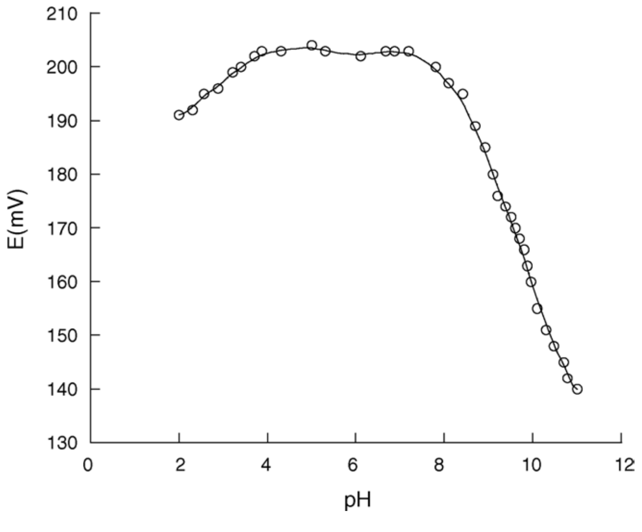


Fig. 1. The pH effect on the potential of the membrane electrode E2 containing L^2, PVC and NPOE as plasticizer.

3.3. Response towards thiocyanate

As is already known, ion-selective electrodes bearing neutral carriers can only work when a charge opposite to that of the analyte is on the membrane, whereas when using charged ionophores the addition of ionic sites is not necessary. The L^1 and L^2 ionophores are included in the membrane as neutral amines. However, they show a clear Nersnstian response with anions such as thiocyanate, strongly suggesting that they will be in their protonated form after stabilisation of the membrane (5 days in contact with a solution 0.1 mol dm^{-3} of thiocyanate at pH 5.6 or 7). The Fig. 2 shows the potentiometric response curves for thiocyanate and other inorganic anions using electrode E2 (L^2 and NPOE) at pH 5.6 (MES-KOH buffer solutions). As can be seen, of the different anions tested, the largest sensitivity was obtained for SCN^-, salicylate, iodide and nitrate, a poorer response was observed with

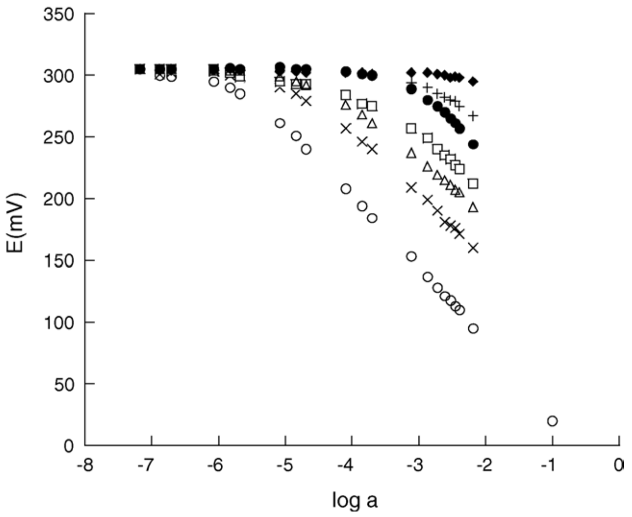


Fig. 2. Response of the PVC-based membrane E2 electrode (L^2 with NPOE) at pH 5.6 in the presence of certain anions: (◯) thiocyanate, (×) iodide, (△) salicylate, (☐) nitrate, (●) benzoate, (+) azide, (♦) cyanide.

benzoate and the responses to other anions were practically negligible.

A complete characterization of the E1 and E2 electrodes as thiocyanate electrodes was carried out. One of the most important characteristics of ion-selective electrodes is the relative response towards a certain ion over others, which is expressed in terms of potentiometric selectivity coefficients. In order to determine the selectivity coefficient of the ion-selective electrodes E1 and E2, the potential responses were investigated in the presence of various interfering anions. The potentiometric selectivity coefficients (K_{SCN^-,X^-}) of thiocyanate sensors based on ionophores L^1 and L^2 were evaluated using the fixed interference method, considering thiocyanate as the principal anion and the concentration of the interfering ion being 1.0×10^{-2} M in HEPES-KOH or MES-KOH buffer. The role of membrane plasticizer in the potentiometric anion selectivity of PVC membranes was also examined by determining the selectivity coefficients for the electrode E3 containing L^1 and DOS as plasticizers (see Table 2 and Fig. 3).

The selectivity coefficients of the electrodes E1 and E2, both containing NPOE, at pH 5.6 are very similar. Thus the selectivity sequence for the electrode E1 was thiocyanate > salicylate > I^- > NO_3^- > benzoate > N_3^- ≈ Br^- > NO_2^- = phosphate ≈ IO_3^- = CN^- = HCO_3^- > Cl^- ≈ CH_3COO^- > $C_2O_4^{2-}$ ≈ SO_4^{2-} ≈ SO_3^{2-} and a very similar selectivity sequence was found for the E2 electrode at pH 5.6 (see Table 2). These selectivity sequences do not deviate greatly from the Hofmeister series [50], suggesting that the interaction of the ionophores with most of the anions is mainly through electrostatic forces. Except for iodide and salicylate, all selectivity coefficients obtained for L^1 and L^2 as ionophores and NPOE as plasticizer are in the order of 10^{-2} or lower, indicating that other anions would not significantly disturb the determination of SCN^- using the E1 or E2 ion-selective electrodes. The response of the electrodes, in terms of selectivity coefficients, is also similar at different pH values (see, for instance, the values of the selectivity coefficients of the E1 electrode at pH 5.6 and 7 in Table 2). In contrast, relatively lower selectivity coefficients were found for membranes containing NPOE than DOS as plasticizer (compare for instance values for E2 and E3 electrodes at pH 5.6 in Table 2). Both electrodes E1 and E2 gave a low detection limit and good calibration reproducibility for thiocyanate.

Table 2
Potentiometric selectivity for thiocyanate (log K_{SCN^-,X^-}) in ion-selective PVC membranes containing L^1 and L^2 as ionophores and DOS and NPOE as plasticizers

	L^1 NPOE pH 5.6	L^1 NPOE pH 7	L^2 DOS pH 5.6	L^2 NPOE pH 5.6
Salicylate	−1.29	−1.32	–	−1.32
Iodide	−1.38	−1.25	−1.28	−1.43
Nitrate	−2.15	−2.28	−2.14	−2.13
Benzoate	−2.27	−2.39	−1.98	−2.39
Azide	−2.36	−2.43	−2.16	−2.43
Bromide	−2.39	−2.38	−2.19	−2.44
Nitrite	−3	−3.1	−2.12	−2.5
Phosphate	−3	−3.95	−2.1	−3.13
Iodate	−3.09	−3.18	−2.34	−3.05
Carbonate	−3.1	−3.13	−2.12	−3.11
Cyanide	−3.1	−3.14	−2.2	−3.14
Chloride	−3.14	−2.85	−2.27	−2.98
Acetate	−3.15	−3.23	−2.23	−3.25
Oxalate	−4.07	−4.15	−3.21	−4.15
Sulfate	−4.17	−4.16	−3.33	−4.23
Sulfite	−4.21	−3.32	−3.23	−4.22

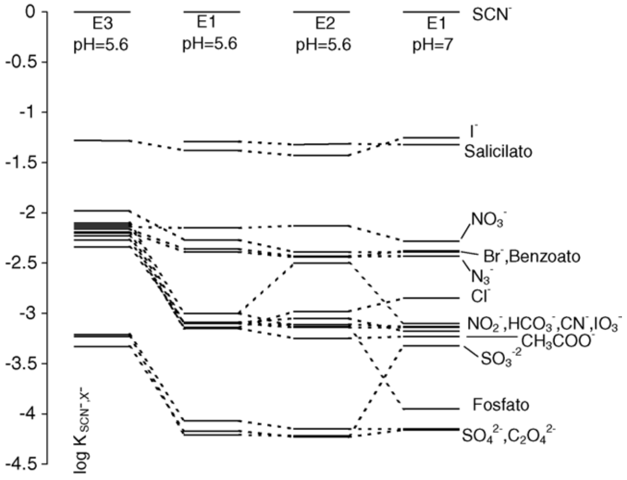


Fig. 3. Potentiometric anion selectivity coefficients of electrodes containing the ionophores L^1 and L^2.

For the sake of comparison Table 3, shows the characteristics of recently reported thiocyanate electrodes, most of them based on the use of metal complexes. However most of these reported ionopores are quite complex, are not easy to prepare, and in most cases the electrodes require cationic additives in order to enhance the electrode characteristics. In contrast the electrodes E1 and E2 use linear polyamines as relatively simple ionophores and display similar linear range, slope and detection limits than those reported in Table 3.

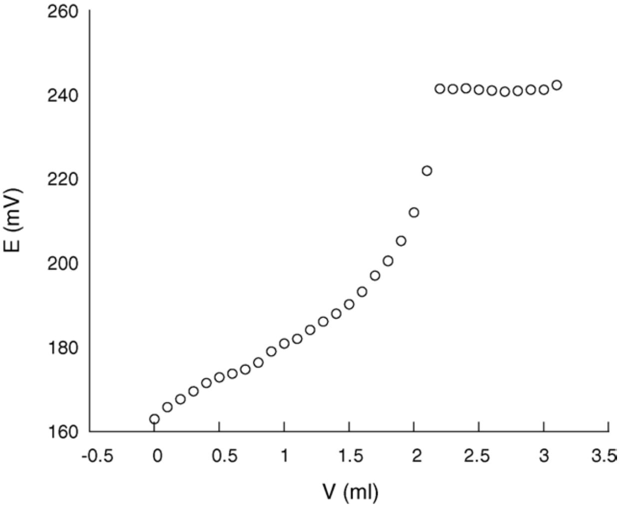


Fig. 4. Potentiometric curve of thiocyanate with 1×10^{-2} M of $AgNO_3$ as titrant in water.

Table 3
Characteristics of some reported thiocyanate-selective electrodes

Ionophore	Elec. type	Lineal range (M)	Limit of detection (M)	Slope (mV decade^{-1})	Ref
Co(III)-TP	A	1×10^{-5} to 1×10^{-1}	–	−49	15
$(FeTPP)_2O$	A, G	1×10^{-6} to 1×10^{-1}	3.98×10^{-4}	−53	16
MnTPPCl	A, G	1×10^{-5} to 1×10^{-1}	–	–	17
$(p\text{-}OCH_3)$MnTPPCl	A, G	1×10^{-5} to 1×10^{-1}	–	–	17
$(2\text{-}NO_2)$MnTPPCl	A, G	1×10^{-5} to 1×10^{-1}	–	–	17
Mn(TPP)Cl	B, F	1×10^{-7} to 1×10^{-1}	5×10^{-8}		19
Mn(III)-OBPCl	A, G	4.8×10^{-7} to 1	3.2×10^{-7}	−58.3	20
	A, F	4.8×10^{-7} to 1	–	−59.5	
Ni(II)Pc	B, G	5×10^{-7} to 1×10^{-1}	5×10^{-7}	−58.4	21
Fe(III)PcCl	B, G	5×10^{-6} to 1×10^{-1}	2×10^{-6}	−57.2	
Co(II)Pc, Mn(II)Pc	B	1×10^{-6} to 1×10^{-1}	5×10^{-7}	–	22
Au(III)-TIBPS	D, G	–	1.1×10^{-6}	−55	23
	A, G	–	1.1×10^{-6}	−51	
Mn(II)-PSPD	A, G	4.51×10^{-5} to 1×10^{-1}	–	−53.8	24
	A, E	7×10^{-6} to 1×10^{-1}	–	−57.3	
CBSED	A, G	1×10^{-6} to 1×10^{-1}	7×10^{-7}	−59.1	25
BenzoN4 nickel(II)	A, G	1.4×10^{-7} to 1×10^{-1}	1.4×10^{-7}	−59.7	26
TBOP	A, G	1×10^{-5} to 1×10^{-1}	−5.9	−53.7	27
	A, E	1×10^{-5} to 1×10^{-1}	−6	56.5	
Ni(II)-TBOP	A, G	1×10^{-5} to 1×10^{-1}	−5.1	−53.7	
PMBP-En-Co	A, G	2×10^{-6} to 1×10^{-1}	-	−60.2	28
DBHCT-Ni(II)	C, F	3.3×10^{-6} to 1×10^{-1}	3×10^{-6}	−58.4	29
$Hg(MBO)_2$	B, E	1×10^{-6} to 1×10^{-1}	6×10^{-7}	−60.6	30
$Hg(PT)_2$	B, E	1×10^{-6} to 1×10^{-1}	6×10^{-7}	−57.5	30
CdL	A, E	1×10^{-6} to 1×10^{-1}	5×10^{-7}	−58.9	31
$Rh[(trpy)(bpy)Cl](PF_6)_2$	A, E	1×10^{-5} to 1×10^{-1}	4×10^{-6}	−58.7	32
$[Cu(L)](NO_3)_2$	B, E	5×10^{-7} to 1×10^{-2}	8×10^{8}	−57.6	33
Di-imidepyridine	A, E	1×10^{-5} to 1×10^{-2}	5×10^{-6}	−56.8	34
Tetra-imidepyridine	A, E	9×10^{-6} to 1×10^{-2}	5×10^{-6}	−56.3	34
Hexa-imidepyridine	A, E	1×10^{-5} to 1×10^{-2}	5×10^{-6}	−58.3	34

Ionophore: Co(III)-TP, (α, β, χ, δ-tetraphenylporphyrin)cobalt(III); $(FeTPP)_2O$, (μ-oxotetraphenylporphyrinato) iron (II); MnTPPCl, chloro (5,10,15,20-tetraphenyl porphyrinato) manganese; (p-OCH_3)Mn TPPCl, chloro [5,10,15,20-tetra(p-methoxyphenyl) porphyrinato] manganese; (2-NO_2)MnTPPCl, chloro (2-nitro-5,10,15,20-tetraphenyl porphyrinato) manganese; MnTPPCl: chloro (5,10,15,20-tetraphenyl porphyrinato) manganese; Ni(II)Pc, nickel(II) phthalocyanine; Fe(III)PcCl: iron(III) phthalocyanine chloride; Co(II)Pc: Co-phthalocyanines; Mn(II)Pc, Mn-phthalocyanines; Au(III)-TIBPS, gold(III)-triisobutylphosphine sulfide; Mn(II)-PSPD, Mn(II)-N,N'-(4-phenylazosalicylidene) o-phenylene diamide; Mn(III)-OBPCl, octabromotetraphenylporphyrinato) manganese (III) chloride; CBSED, cadmium {N,N'-bis(salicylidene)-1,2-ethylenediamine} complex; BenzoN4 nickel(II), 2,4,10,12-tetramethyl-1,5,9,13-(benzo)tetrazacyclopentadecinato (2-)nickel(II); TBOP, 3,3′-(trimethylenedinitrilo)-bis(α-oximinopropiophenone); Ni(II)-TBOP, Ni(II)-3,3′-(trimethylenedinitrilo)-bis(α-oximinopropiophenone); PMBP-En-Co, bis(1-phenyl-3-methyl-4-benzoylpyrazolone-5)ethylenediimine cobalt(II); DBHCT-Ni(II), 1,8-dibenzyl-1,3,6,8,10,13-hexaazacyclotetradecane-Ni(II); $Hg(MBO)_2$, bis(2-mercaptobenzoxazolato)mercury(II); $Hg(PT)_2$, bis(2-pyridinethiolato)mercury (II); CdL, 2,2-[(1,3 dimethyl-1,3-propanediylidene)-dinitrilo]bis-benzenethiolato cadmium (II); $[Cu(L)](NO_3)_2$, [Cu(4,7-bis(3 aminopropyl)-1thia-4,7-diazacyclononane]$(NO_3)_2$.

Electrode type: A, PVC membrane electrodes with internal reference solution; B, PVC membrane graphite electrodes; C, PVC membrane Pt-electrode; D, PVC membrane epoxi electrode; E, PVC membrane with cationic additive; F, PVC membrane with anionic additive; G: PVC membrane without additive.

3.4. Analytical applications

The thiocyanate electrode based on the L^2 ionophore with NPOE as plasticizer (E2) at pH 5.6 was used for potentiometric determination of SCN^- via Ag^+ titrations. The electrode and an Ag/AgCl double junction reference electrode were immersed in a beaker containing MES-KOH buffer of pH 5.6 containing a thiocyanate solution. Fig. 4 shows the titration curve of 20 mL of a 1.00 mmol dm^{-3} thiocyanate solution titrated with 1×10^{-2} M of $AgNO_3$. A typical sigmoidal shaped curve was found. The titration volume was measured at the inflection point of the titration curve and a concentration of thiocyanate of 1.05 mmol dm^{-3} was determined.

We have also used the electrode E2 for the determination of thiocyanate in biological samples. Thus, it has been reported that the concentration of thiocyanate in saliva provides a suitable index to distinguish smokers from non-smokers. Saliva samples were diluted by a factor of 10 by phosphate buffer (pH 5.6). From calibration plots using electrode E2 the thiocyanate concentration was determined and the results compared with the standard spectrophotometric method [51]. Table 4 shows the thiocyanate concentrations in human saliva from smokers and non-smokers obtained by

Table 4
Determination of thiocyanate in different samples

Sample	E2 electrode ($\mathrm{mmol\,l^{-1}}$)[a]	Spectrophotometric method ($\mathrm{mmol\,l^{-1}}$)[a]
Smoker saliva	0.96 ± 0.04	1.00 ± 0.03
Non-smoker saliva	0.46 ± 0.03	0.44 ± 0.03

[a] Mean value ± standard deviation (three determinations).

using the proposed electrode E2 and the colorimetric protocol. As it is shown, there is a quite good agreement between both the potentiometric and spectrophotometric procedures.

3.5. Conclusions

To sum up, we have shown that the use of plain functionalised linear amines can be used as suitable ionophores in the development of new thiocyanate-selective PVC membrane electrodes. Two new electrodes E1 and E2, containing a triamine and a tetraamine respectively, have been prepared using NPOE as plasticizer. These electrodes show a Nernstian response, detection limits of near $10^{-6}\,\mathrm{mol\,dm^{-3}}$ and a low response time of a few seconds in the presence of thiocyanate. The electrode E2 was used as indicator electrode in potentiometric titrations of thiocyante with silver. The electrode was also successfully applied for monitoring concentrations levels of thiocyanate in biological samples.

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