INFLUENCE OF $ZnCl_2$ CONCENTRATION ON THE SELECTIVITY OF A $Zn(NCS)_4^{2-}$-SELECTIVE ELECTRODES AND ITS APPLICATION FOR DETERMINATION SCN^- IONS IN INDUSTRIAL SOLUTIONS

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ABSTRACT

The influence of the background concentration of $ZnCl_2$ on the selectivity of $Zn(NCS)_4^{2-}$−SE based on QAS to SCN^- is studied. The introduction of $ZnCl_2$ into a solution fixes zinc released from the membrane in the form of thiocyanate complex. A high selectivity of the $Zn(NCS)_4^{2-}$−SE to SCN^- ions is due to the formation of better extractable complexes between zinc and SCN^- compared to acidocomplexes of competitive anions. An introduction of 5.0 M $ZnCl_2$ into a solution increases selectivity to SCN^- ions by 5 orders of magnitude in the presence of interfering ClO_4^- ions and more than 4.5 orders of magnitude in the presence of interfering NO_3^- ions.

Keywords: potentiometry, thiocyanate ions, tetrathiocyanozincate−selective electrode, quaternary ammonium salts.

INTRODUCTION

The thiocyanate ion is usually present in low concentrations in human serum, saliva, and urine as a result of the digestion of some vegetables (cabbage, turnip, onion juice) or by intake of thiocyanate-containing foods such as milk and cheese. Higher concentration of this ion, which is a metabolic product of cyanide, arises from tobacco smoke[1].

Thiocyanate finds many industrial applications and, though not toxic as cyanide, it is harmful to aquatic life. Thiocyanates are used in the production of thiourea and polyacrylonitrile fibers, are reactants in the processes of dyeing and printing textiles, in analytical chemistry as pesticides, in the processes of isolation and separation of rare metals, et al.

Therefore, an accurate, simple, and rapid method for the determination of thiocyanate is significant in medicine, industry and in the life sciences.

Several methods have been developed for the determination of thiocyanate. These include application of spectrophotometry[2], spectrofluorimetry[3], amperometry[4], polarography[5], chromatography[6] and ion selective electrodes [1, 7−10] for the determination of thiocyanate.

Thiocyanate-selective electrodes (SCN^-−SEs) have grown substantially over recent years and were widely used for the direct and rapid analytical detection thiocyanate ions due to their potentiometric response characteristics such as relatively fast response, wide linear response range, low detection limit, reasonable selectivity and low cost.

Unfortunately, most of these electrodes[1, 7−10] have one, two or, in some cases, all of the problems: narrow range pH and/or high detection limit and/or serious interfering effect from hydrophobic anions such as I^-, Br^-, Cl^- and, especially, ClO_4^-, NO_3^- et al. Perchlorates occupy the first place in the Hoffmeister number of hydrophobicity: $ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > NO_2^- > Cl^- > SO_4^{2-}$,[11] therefore the determination of other ions against their background makes not a simple task.

It was previously determined[12] that SCN^-−SE based on quaternary ammonium salts (QAS) is more sensitive to ClO_4^- ions than SCN^-. Selectivity coefficients of SCN^-−SE with respect to ions ClO_4^-, I^-, Br^-, Cl^- equal to 8.0, 0.2, 2 and 8×10^{-3}, respectively.

The goal of this paper was to investigate the interference of hydrophobic anions (on an example of ClO_4^- and NO_3^-) on the determination of thiocyanate ions with $Zn(NCS)_4^{2-}$−SE depending on the concentrations of supporting $ZnCl_2$ solutions.

EXPERIMENTAL

Reagents and chemicals

All reagents of salts (Sodium perchlorate $NaClO_4$, Sodium nitrate $NaNO_3$, Potassium thiocyanate KNCS, Zinc chloride $ZnCl_2\times H_2O$, Potassium chloride KCl) and Sodium hydroxide (NaOH), Hydrochloric acid (HCl) were of analytical grade. All solutions were prepared using distilled water.

For ISE membranes preparation the following reagents were used: poly(vinylchloride) (PVC, Fluka AG Selectrofore®); 1-bromonaphthalene (1-BN, analytical grade) as a membrane plasticizer; solvent: tetrahydrofuran (THF, analytical grade) purified by distillation as described in[13]; 3.4.5-tris(dodecyloxy)benzyltrimethylammonium (TM), trinonyloctadecylammonium (TNODA) in bromide form with an amine content of less than 0.03% prepared in the Department of Analytical Chemistry of BSU as described in[14].

The structures of the QAS used are shown in Fig. 1.

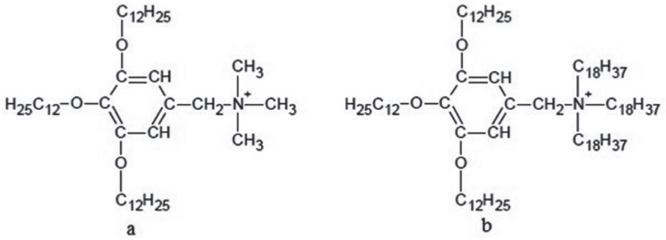

Figure. 1. Structure of QAS used: a − 3.4.5-tris(dodecyloxy) benzyltrimethylammonium (TM); b − trinonyloctadecylammonium (TNODA)

Apparatus

Potential measurement and pH control of the solutions were performed using digital potentiometer I-160 at a temperature of 24±1⁰C. Silver chloride electrode EVL-1M3 with internal 0.1 M KCl solution was used as a reference electrode.

Preparation of the electrode

The method of manufacture ISEs was described in[15]: QAS (5wt.%), PVC (33% wt.), 1-BN (62% wt.) were weighed in a glass weighing bottle and stirred for 5 min. Freshly distilled THF was added to the mixture and stirred on a magnetic stirrer for 2 h to homogenize the solution. The solution was poured on a smooth glass plate. To prevent solution spreading the teflon circular cylinders were placed on the glass plate. The plate was covered with a sheet of filter paper and then was left in a fume hood for 20−25 h to complete THF evaporation. Disc-shaped membranes were cut from the obtained elastic film and stuck to the electrode end of PVC body, using THF-PVC composition as an adhesive. The thickness of the membrane film was about 0.5 mm. 1×10^{-3} M solution of $ZnCl_2$ in the background 0.1M KNCS was poured inside the electrodes.

The electrodes were soaked in 0.1 M $ZnCl_2$ on 1.0 M KNCS background solutions for 48 h and then during the day 1×10^{-3} M $ZnCl_2$ on 0.1M KNCS background solutions.

Measurement procedure

The slope of the electrode function of $Zn(NCS)_4^{2-}$−SE is 28.5−29.5 mV×decade^{-1} (at a concentration of 0.05 to 5.0 M KNCS), which implies that double-charged $Zn(NCS)_4^{2-}$ ions are electrochemically active. Furthermore, the composition of compounds passing into the ion exchanger phase (QAS) is $Zn(NCS)_4^{2-}$ ions was established in [16, 17] as a result of anion exchange extraction study.

A series of supporting $ZnCl_2$ solutions containing 1×10^{-1}, 1×10^{-2}, 1.0

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and 5.0 M $ZnCl_2$ were prepared, their exact concentrations were found by complexometric titration[18]. Portions of KNCS were added to the prepared $ZnCl_2$ solutions to create concentrations 1×10^{-1}, 1×10^{-2}, 1×10^{-3}, 1×10^{-4} and 1×10^{-5} M SCN^-. The starting solutions of ClO_4^- with a concentration of 1.0 M in the presence of various concentrations of $ZnCl_2$ and KNCS were consecutively diluted with supporting electrolyte solutions to produce a series of ClO_4^- solutions with a concentration from 1.0 to 1×10^{-7} M. The starting solutions of NO_3^- with a concentration of 1.0 M in the presence of various concentrations of $ZnCl_2$ and KNCS were consecutively diluted with supporting electrolyte solutions to produce a series of NO_3^- solutions with a concentration from 1.0 to 1×10^{-6} M.

Potentiometric selectivity coefficients $K^{Pot}_{SCN^-,j}$ were determinate by separate solution method, in the order of foreign ion lipophilicity increase[19].

The selectivity coefficients $K^{Pot}_{SCN^-,ClO_4^-}$ and $K^{Pot}_{SCN^-,NO_3^-}$ were calculated by the equation:

$$E=E^0+\Theta\cdot\lg([SCN^-]+K^{Pot}_{SCN^-,j}\cdot[j^-]^{s_1/s_2}), \qquad (1)$$

where $\Theta=\dfrac{2{,}3\cdot R\cdot T}{F}$; s_1 is a slope of the thiocyanate function, mV×decade^{-1}; s_2 is slope in ClO_4^- or NO_3^- solutions (j^-), s_2 = 59 mV×decade^{-1}.

Lower detection limit (LDL) was determined graphically as the intersection point of the extrapolated linear regions of the thiocyanate function graph[19].

RESULTS AND DISCUSSION

$Zn(NCS)_4^{2-}$–SE demonstrate ligand (thiocyanate) function both in the absence of Zn^{2+} ions and in its presence in various concentrations. With increasing concentration of $ZnCl_2$ the potential of the electrode falls down substantially (Fig. 2), which can be explained by the high concentration of $Zn(NCS)_4^{2-}$ ions. In addition, the influence of the nature of QAS and a plasticizer on the LDL of thiocyanates with $Zn(NCS)_4^{2-}$–SE is defined as follows: the smallest LDL achieved for the electrode based on 3.4.5-tris(dodecyloxy) benzyltrimethylammonium (TM) plasticized with 1-bromonaphthalene (1-BN) is 6.2×10^{-6} M SCN^- in the absence of $ZnCl_2$ in the background solution and in its presence is 2.8×10^{-6} M SCN^- (on 5.0 M supporting $ZnCl_2$ solutions).

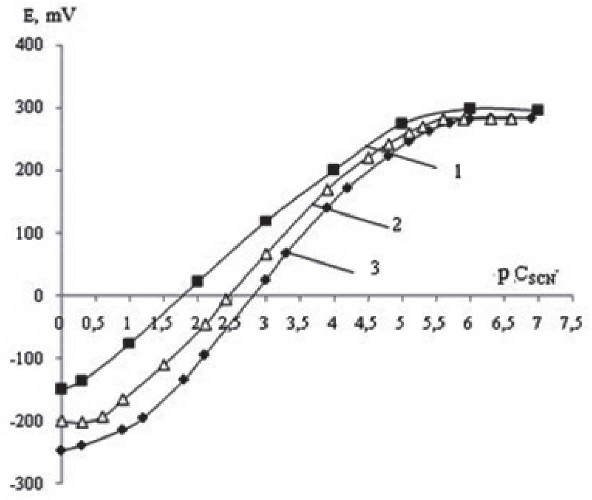

Figure 2. Thiocyanate function of a $Zn(NCS)_4^{2-}$–SE (based on TM, plasticizer 1- BN): 1– with no $ZnCl_2$ in the supporting electrolyte; 2 – in the presence of 1.0 M $ZnCl_2$; 3 – in the presence of 5.0 M $ZnCl_2$

The reasons for the appearance and the mathematical description of the thiocyanate function for a $Zn(NCS)_4^{2-}$–SE were considered in[12]. The potential change of $Zn(NCS)_4^{2-}$–SE in thiocyanates solutions is explained by the displacement from a membrane $Zn(NCS)_4^{2-}$ ions with SCN^- in the electrode layer:

$$(R_4N^+)_2Zn(NCS)_4^{2-}+2SCN^- \rightleftarrows 2R_4N^+SCN^-+Zn(NCS)_4^{2-}. \qquad (2)$$

Forced out of the membrane $Zn(NCS)_4^{2-}$ ions were involved in equilibrium with other complex shapes and zinc cations resulting from the step dissociation complexes. The thiocyanate function of a $Zn(NCS)_4^{2-}$–SE with no Zn^{2+} ions in solution Zn^{2+} may be described by the equation:

$$E=E^0-\frac{\Theta}{6}\lg\frac{\frac{1}{4}\cdot C\cdot K^{2SCN^-}_{Zn(NCS)_4^{2-}}\cdot\gamma^3_{Zn(NCS)_4^{2-}}\cdot[SCN^-]^2}{\alpha^2}, \qquad (3)$$

where E is electrode potential; $\Theta=\dfrac{2{,}3\cdot R\cdot T}{F}$; C is concentration QAS in $Zn(NCS)_4^{2-}$ state, M; $K^{2SCN^-}_{Zn(NCS)_4^{2-}}$ is concentration exchange constant; $\gamma_{Zn(NCS)_4^{2-}}$ is activity coefficient; $[SCN^-]$ is equilibrium concentration of thiocyanate ions in the solution, M; α is coefficient of side reaction characterizing the ratio of the total concentration of the replaced zinc to the concentration of $Zn(NCS)_4^{2-}$.

The slope of the thiocyanate function found by the equation (3) should be equal to 96–97 mV×decade^{-1}. The thiocyanate function of the $Zn(NCS)_4^{2-}$–SE in the presence of a constant concentration of Zn^{2+} ions may be described as follows:

$E_1=E_1^0+4\cdot\Theta\cdot\lg[SCN^-]$	(4)
$E_2=E_2^0+3\cdot\Theta\cdot\lg[SCN^-]$	(5)
$E_3=E_3^0+2\cdot\Theta\cdot\lg[SCN^-]$	(6)
$E_4=E_4^0+\Theta\cdot\lg[SCN^-]$	(7)
$E_5=E_5^0+\Theta\cdot\lg[Zn_{aq}^{2+}]=const$	(8)

Equation (4) describes the thiocyanate function of a $Zn(NCS)_4^{2-}$–SE in the presence of higher concentrations of Zn^{2+} ions, 1.0–5.0 M. Therein the slope should be equal to 118 mV×decade^{-1}, which was actually observed.

Fig. 3 presents the relations indicating the influence of ClO_4^- on the potential of a $Zn(NCS)_4^{2-}$–SE in the presence of KNCS in various concentrations.

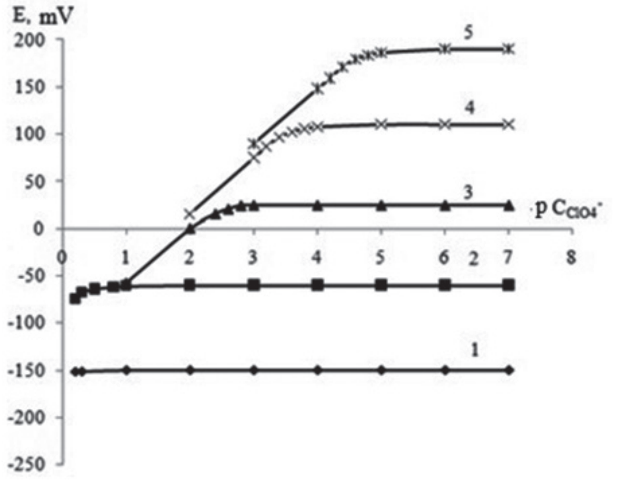

Figure 3. Influence of ClO_4^- ions on the potential of $Zn(NCS)_4^{2-}$–SE (based on TM, plasticizer – 1-BN) in the presence of KNCS, M: *1*–1×10^{-1}, *2*–1×10^{-2}, *3*–1×10^{-3}, *4*–1×10^{-4}, *5*–1×10^{-5}

Fig. 4 presents the relations indicating the influence of ClO_4^- on the potential of a $Zn(NCS)_4^{2-}$−SE in the presence of KNCS and $ZnCl_2$ in various concentrations. After the introduction of 1.0−5.0 M $ZnCl_2$ into the supporting electrolyte solution the potential of the electrode in 1×10^{-3} M KNCS was not affected by 1×10^{-1} M or higher concentration of ClO_4^- ions.

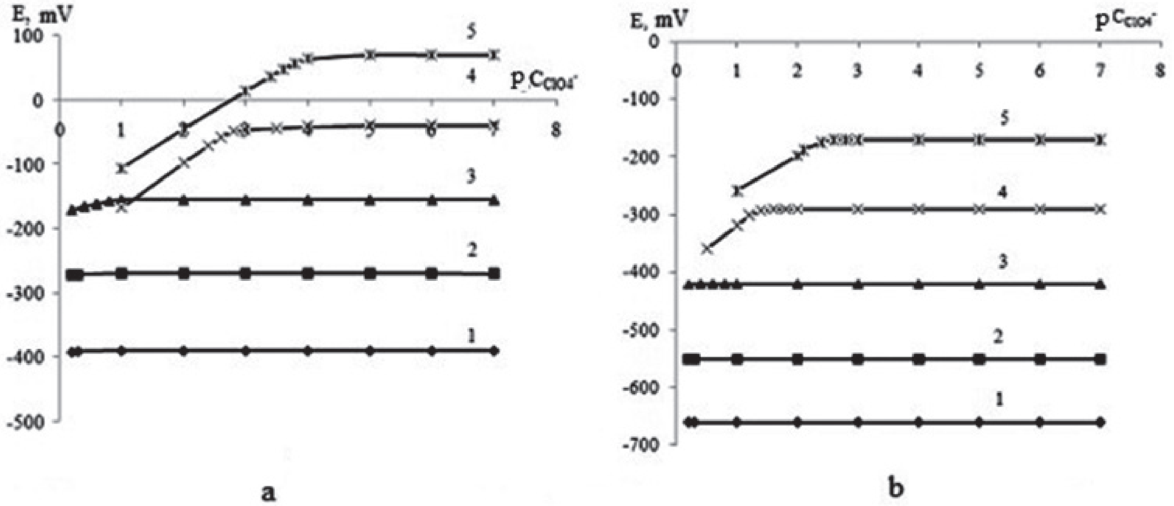

Figure 4. Influence of ClO_4^- ions on the potential of a $Zn(NCS)_4^{2-}$−SE (based on TM, plasticizer – 1-BN) in the presence of KNCS, M: *1*−1×10^{-1}, *2*−1×10^{-2}, *3*−1×10^{-3}, *4*−1×10^{-4}, *5*−1×10^{-5} and $ZnCl_2$, M: a – 1×10^{-2}, b – 5.0

Fig. 5 shows the relations indicating the influence of NO_3^- on the potential of a $Zn(NCS)_4^{2-}$−SE in the presence of various concentrations of KNCS and 5.0 M $ZnCl_2$ into the supporting electrolyte solution.

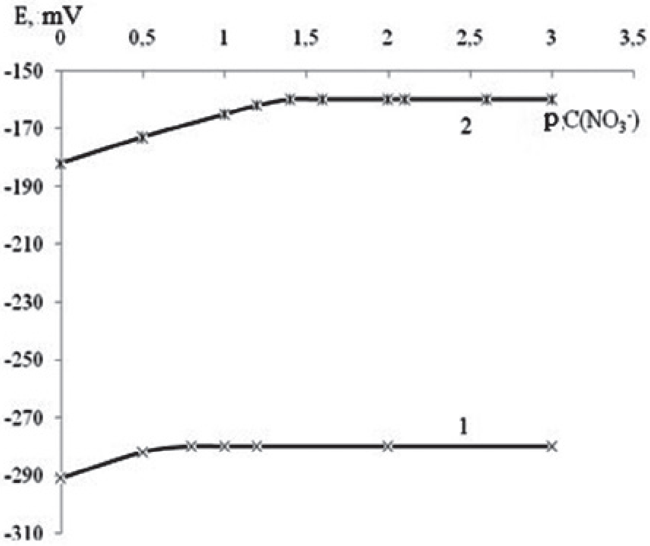

Figure 5. Influence of NO_3^- ions on the potential of $Zn(NCS)_4^{2-}$−SE (based on TM, plasticizer – 1-BN) in the presence of KNCS, M: *1*−1×10^{-4}, *2*−1×10^{-5} and 5.0 M $ZnCl_2$ into the supporting electrolyte solution

Table 1 shows the values of $K^{Pot}_{SCN^-,NO_3^-}$ and $K^{Pot}_{SCN^-,ClO_4^-}$ for $Zn(NCS)_4^{2-}$−SE, as well as thoseof $K^{Pot}_{SCN^-,NO_3^-}$ and $K^{Pot}_{SCN^-,ClO_4^-}$ for SCN^-−SE based on TM and TNODA to be compared.

Table 1 indicates that for practical purposes it is sufficient to maintain the supporting electrolyte solution of $ZnCl_2$ equal to 1×10^{-1}−1.0 M.

Table 1. The values of coefficients selectivity $K^{Pot}_{SCN^-,NO_3^-}$ and $K^{Pot}_{SCN^-,ClO_4^-}$ for $Zn(NCS)_4^{2-}$−SEs and SCN^-−SEs

$Zn(NCS)_4^{2-}$−SE based on TNODA		$Zn(NCS)_4^{2-}$−SE based on TM	
$ZnCl_2$, M	$K^{Pot}_{SCN^-,NO_3^-}$	$ZnCl_2$, M	$K^{Pot}_{SCN^-,NO_3^-}$
−	4.0×10^{-4}	−	1.5×10^{-3}
1×10^{-2}	9.2×10^{-7}	1×10^{-2}	6.7×10^{-5}
$ZnCl_2$, M	$K^{Pot}_{SCN^-,ClO_4^-}$	1×10^{-1}	2.0×10^{-6}
−	4.2×10^{-1}	1.0	1.0×10^{-7}
1×10^{-2}	8.8×10^{-4}	$ZnCl_2$, M	$K^{Pot}_{SCN^-,ClO_4^-}$
1×10^{-1}	9.0×10^{-5}	−	1.6×10^{-1}
1.0	6.5×10^{-6}	1×10^{-2}	4.9×10^{-3}
5.0	8.1×10^{-7}	1×10^{-1}	4.2×10^{-4}
−	−	1.0	1.7×10^{-5}
−	−	5.0	4.3×10^{-6}
$K^{Pot}_{SCN^-,ClO_4^-}$ = 7.2 (SCN^-−SE based on TNODA)			
$K^{Pot}_{SCN^-,ClO_4^-}$ = 3.3 (SCN^-−SE based on TM)			
$K^{Pot}_{SCN^-,NO_3^-}$ = 2.0×10^{-2} (SCN^-−SE based on TM)			

In addition to perchlorate ions NO_3^- ions are considered to be among the sufficiently hydrophobic and, above all, widespread in model and real objects.

Similar experiments to study the selectivity of $Zn(NCS)_4^{2-}$−SE to SCN^- ions in the presence of ClO_4^- ions were held for ISE based on TNODA. In the absence of $ZnCl_2$ in the solution the values of $K^{Pot}_{SCN^-, ClO_4^-}$ for electrodes based on TM are lower than those of TNODA due to a high affinity of the hydrophobic ClO_4^- ions to steric accessibility QAS[20]. The reverse was observed for NO_3^- ions, which are also able to displace $Zn(NCS)_4^{2-}$ from the membrane in the electrode layer, it being greatly observed for more sterically accessible QAS (TM), to which $Zn(NCS)_4^{2-}$ ions have minimal affinity[21].

Introduction of $ZnCl_2$ to the solution results in the opposite effect: the replacement of TM on the QAS with the steric accessibility of the exchange center (TNODA) values of $K^{Pot}_{SCN^-, NO_3^-}$ and $K^{Pot}_{SCN^-, ClO_4^-}$ are reduced i.e. selectivity increases, due to the high affinity of the hydrophobic and large size ions $Zn(NCS)_4^{2-}$ to steric accessibility QAS[21].

The potentiometric response of the $Zn(NCS)_4^{2-}$−SE was found to be sensitive to pH changes. The results given in Fig. 6 show that the potential response remains constant over the pH range of 2.0 to 9.0. A significant change in the potential at pH <2.0 may be due to the formation HNCS, at pH>9.0 may be due to the formation of hydroxocomplexes.

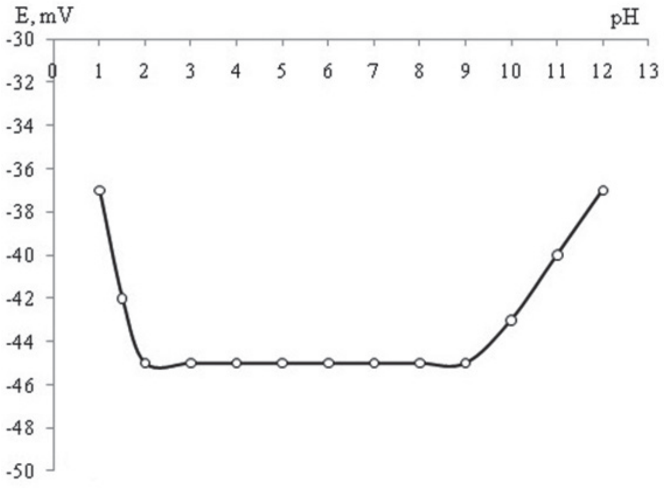

Figure 6. Effect of pH on the potential response of the $Zn(NCS)_4^{2-}$−SE (based on TM, plasticizer – 1-BN)

To compare the results obtained for $Zn(NCS)_4^{2-}$−SE the plots reflecting the influence of ClO_4^- ions on the potential of SCN^-−SE (based on TM) are shown in Fig. 7.

Fig. 7 shows that in any supporting electrolyte solution of SCN^- the influence of interfering ClO_4^- ions is clearly seen.

Thiocyanate ions participate in the displacement of complex $Zn(NCS)_4^{2-}$ ions from the membrane to the aqueous solution; the ions then undergoing stepwise dissociation.

Introduction of $ZnCl_2$ into the solution binds zinc released from the membrane as thiocyanate complexes. The high selectivity of the $Zn(NCS)_4^{2-}$−SE to SCN^- ions is due to the fact that zinc with SCN^- forms complexes that are extracted much better, i.e. possesss a higher anion-exchange affinity compared to acido complexes with the competitive anions. In the reference literature[22–25] no information about perchlorate and nitrate complexes of zinc is given.

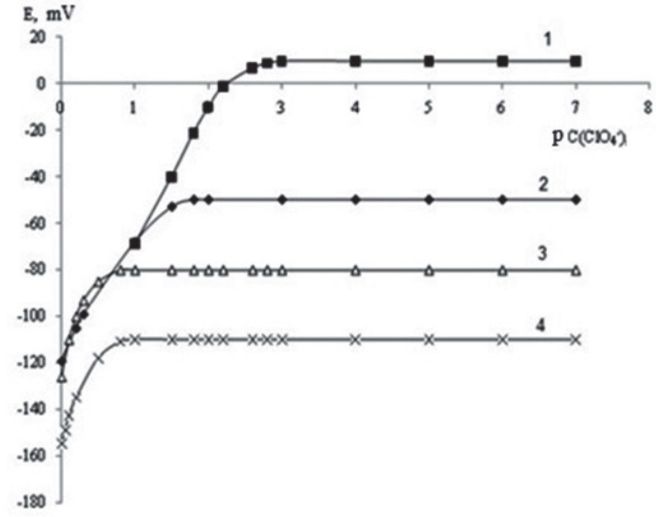

Figure 7. Influence of ClO_4^- ions on the potential of a SCN^-−SE in the presence of KNCS, M: 1−1×10^{-2}, 2−1× 10^{-1}, 3−0.5, 4−1.0

The obtained results were compared with other SCN^-−SEs in Table 2. The $Zn(NCS)_4^{2-}$−SE based on QAS displays better parameters such as selectivity and low detection limit in terms than the other SCN^-−SEs.

An inner enterprise method «Measurement of sodium thiocyanate the production baths of Nitron I by a volumetric method with Silver Nitrate» was introduced at the plant Polymir (Novopolotsk, Belarus) to control thiocyanate in precipitation baths; the indicator being 2,7-dichlorophenylfluorescein. Silver nitrate is rather expensive; therefore, the development of alternative methods for thiocyanate is important.

A new method for the potentiometric determination of thiocyanate in precipitation baths was proposed. The stock solution was diluted with distilled water or a $ZnCl_2$ solution prior to the potential registration in the ratio of 1:200. The concentration of thiocyanate ions was found by the calibration graph method taking into account the initial dilution. The data of potentiometry analysis were verified by iodometry titration[26]. The values obtained are shown in Table 3 ($Zn(NCS)_4^{2-}$−SE based on TM).

The direct potentiometry determination of thiocyanate with $ZnCl_2$ background concentration provides more accurate data, the presence of 1×10^{-1} M $ZnCl_2$ being sufficient for practical purposes. The proposed method for the direct potentiometry determination of SCN^- neither takes long time nor requires expensive consumables.

Table 3. Results of titrimetric and potentiometric determination of SCN^- ions in a precipitation bath (n = 10, p = 0.95)

Titrimetry, C(SCN^-), M	RSD_{tit}, %	Potentiometry, C(SCN^-), M	RSD_{pot}, %
1.13±0.01	1.2	1.125±0.005 (with no $ZnCl_2$ in the supporting electrolyte)	1.0
		1.125±0.004 (0.1M $ZnCl_2$)	0.9
		1.124±0.003 (1.0M $ZnCl_2$)	0.8
		1.124±0.003 (5.0M $ZnCl_2$)	0.8

Table 2. Comparison of some characteristics of the proposed electrode with previous SCN^-−SEs.

S[(a)]	Ionophore	LDL[(b)]	$-\lg K^{Pot}_{SCN^-, An^-} > 2$	pH	Ref.
59.0	cobalt(III) Schiff base	8.0×10^{-7}	ClO_4^- 0.89; I^- 1.2	2.8–9.8	[1]
51.8	tris(2,2′,2″-salicylidene-imino) triethylamine-iron(III) complex	2.5×10^{-6}	F^- 1.95; Br^-1.2; I^- 0.7; NO_3^-1.95; ClO_4^- 0.36	–	[7]
55	nitron thiocyanate	1.0×10^{-5}	I^-1.7; ClO_4^- 0.3	3.0–8.0	[8]
57.2	nickel and iron phthalocyanines	5.0×10^{-6}	for I^- and ClO_4^-	3.0–10.0	[9]
57.3	N, N´-bis-(4-phenylazosalicylidene) o-phenylene diamine- Mn(II) complex	7.0×10^{-6}	I^- 1.34; ClO_4^- 1.40	5.38	[11]
118	QAS	2.8×10^{-6}	ClO_4^- 6.09; NO_3^- 7.0	2.0−9.0	This work

(a)Slope, mV×decade^{-1}; (b)Low detection limit, M

CONCLUSIONS

The minimization of interference with not only hydrophobic ClO_4^- ions also NO_3^-, etc., as well a substantial increase of the slope of the thiocyanate function up to 118 mV×decade^{-1} is attained on the introduction of $ZnCl_2$ into the supporting electrolyte, making more stable the electrode response and the stability of the potential over time. In general, all these improvements ensure the determination of thiocyanate with a relative standard deviation of 0.8%, which is comparable with the precision of a volumetric method.

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