COMPARATIVE STUDY OF SELENOPOLYTHIONIC ACIDS $H_2Se_nS_2O_6$ AS PRECURSORS FOR FORMATION OF CHALCOGENIDES LAYERS

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Comparative studies of characteristics and properties of $H_2SeS_2O_6$, $H_2Se_2S_2O_6$, $K_2SeS_2O_6$, $K_2Se_2S_2O_6$ and $H_2Se_nS_2O_6$ of the homologous range $Se_nS_2O_6^{2-}$(n = 1 – 3) are presented with aim to applying as functional materials for chalcogenation procedures. Our results show that $H_2Se_nS_2O_6$ (n = 1.04 – 2.1) might be successfully synthesized in direct reactions as the single-source selenium precursor. Direct reactions of isolation of selenopolythionic compounds showed the strong dependence upon the conditions of reactions: concentration, temperature and admixtures. The kinetics of direct $H_2Se_nS_2O_6$ formation's reactions were studied and analyzed by three mechanisms. The comparison of five selenopolythionic compounds irrespective of species of compound showed their applicability for selenization process despite the differences of duration of its isolation, the stability and the purity. Selenium layers have been formed deposited on polycapramide (PA) surface first time using $H_2Se_nS_2O_6$ (n = 1.18-1.27).

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1. Introduction

With respect to development of new functional materials and/or optimization of properties of known chalcogenic precursors, wide investigations and systematization of fundamental characteristics of these compounds are of great importance. Over the two last decades, the formations of semiconductive chalcogenides layers on different substrates using selenopolythionates have been object of intensive investigations [1]. Anions of selenopolythionates might be considered as the substituted polythionates in which sulfur is partially substituted by selenium. As result of these changes more different forms of anions appears: at present are known following homologous ranges $Se_nS_2O_6^{2-}$(n = 1 – 6), $Se_nS_3O_6^{2-}$(n = 1 – 3), and $SeS_nO_6^{2-}$(n = 2 – 4).

Comparative studies of the homologous range $Se_nS_2O_6^{2-}$(n = 1 – 6) when composition of anion is variable and detailed investigation of characteristics and properties of an individual members of the range are mutually complementary.

Selenotrithionic acid was discovered and isolated as the potassium salt $K_2Se(SO_3)_2$ by Rathke in 1865 [2]. In crystalline form are also obtained lithium, sodium, potassium, rubidium, cesium and other metals selenotrithionates [3]. J. Janickis and V. Zelionkaite isolated the first salt of diselenotetrathionic acid, the monohydrate $K_2Se_2(SO_3)_2$ H_2O [4].

However, free, unsolvated acids had not been prepared until quite recently: V. Zelionkaite and J. Šukytė in 1970 – 1972 announced the solvent - free synthesis of selenotrithionic $H_2SeS_2O_6$, and diselenotetrathionic $H_2Se_2S_2O_6$ acids [5]. These acids were isolated from their potassium salts. Potassium selenotrithionate and diselenotetrathionate were prepared according to published procedures [1, 3]. Anions of ranges $Se_nS_2O_6^{2-}$(n = 1 – 6) and $Se_nS_3O_6^{2-}$(n = 1 – 3) were isolated only in the form of nitrone' salts and some complex cobalt cations [4].

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However, the synthesis of salts and isolation of acids from their salts is rather complicated and labor-consuming. For this reason we tried to estimate the possibility of easy selenopolythionate anion $Se_nS_2O_6^{2-}$ produce in direct experiments.

In well-known paper published almost 200 years ago, H. Schulze [6] reported that the interaction of selenous and sulfurous acids runs differently depending on the stoichiometric ratio of reagents. Mixing both acids in molar ratio H_2SO_3:H_2SeO_3 = 2:1 leads to an isolation of elemental selenium according the following equation:

$$H_2SeO_3 + 2H_2SO_3 \rightarrow Se + 2H_2SO_4 + H_2O$$

Monoselenotrithionic acid forms with an excess of H_2SO_3 solution added to the solution of H_2SeO_3 with ratio 3:1:

$$H_2SeO_3 + 3H_2SO_3 \rightarrow H_2SeS_2O_6 + H_2SO_4 + 2H_2O +$$

According H. Schulze yellow solutions of diselenotetrathionic acid forms, when H_2SO_3 solution is added to an excess of H_2SeO_3:

$$2H_2SeO_3 + 5H_2SO_3 \rightarrow H_2Se_2S_2O_6 + 3H_2SO_4 + 3H_2O$$

The qualitative observation of H. Schulze later on were confirmed by F. Foerster and W. Seidel [7] despite they were doubtful about the existing of diselenotetrathionic acid, and laid the assumption that diselenotetrathionic or triselenopentathionic acids produce in this reaction together with monoselenotrithionic acid.

All these considerations have been made on the background of only qualitative or semi quantitative observations. Quantitative studies of this reaction became possible only after the preparation of analytical methods for the solutions of selenopolythionates containing also selenous and sulfurous acids [8]. Since then the reaction has become of basic importance in chalcogens chemistry. Several later studies of various cases of above described reaction and newest interpretation of its mechanism exist [4, 8, 9] and still run. However, the reaction suffers from a serious limitation due to the inability to strongly determine the procedure and to exactly determine the conditions and the mechanism because of its complexity.

Dilute 0.01- 0.02 mol·dm^{-3} solutions of selenotrithionic and diselenotetrathionic acids together with sulfuric acid form in the reaction of dilute selenous and sulfurous acids [6]. The reaction is possible to express by following common equation:

$$nH_2SeO_3 + (2n+1)\ H_2SO_3 \rightarrow H_2Se_nS_2O_6 + (2n-1)\ H_2SO_4$$

Since the methods of preparation strongly influence the structure and properties of resulting precursor, this work aims at a systematic description of synthesis procedure.

2. Experimental

2.1 Synthesis of $H_2Se_nS_2O_6$ from selenous acid with addition of $CaCO_3$

In the study [5, 10] with aim to precipitate sulfuric acid calculated according the below reaction amount of $CaCO_3$ was added:

$$2H_2SeO_3 + 5H_2SO_3 + 3CaCO_3 \rightarrow H_2Se_2S_2O_6 + 3CaSO_4 + 6H_2O + 3CO_2$$

To 10.4 g of selenous acid dissolved in 10 ml of distilled water 12 g of $CaCO_3$ was added. The mixture was stirred before the almost complete removal of CO_2 and the formation of suspension of calcium selenite. After that 150 ml 1.4 mol·dm^{-3} H_2SO_3 was added to the suspension with mixing and cooling in glass water. At the beginning of the reaction $H_2SeS_2O_6$ was formed, which further at room temperature continuously converts to $H_2Se_2S_2O_6$ (Fig. 1, a). In order to monitor the reaction aliquots of solution were taken from the reaction vessel, diluted with distilled water to 100 ml and analyzed according to below described methods.

2.2 Synthesis of $H_2Se_nS_2O_6$ from selenous acid with addition of $KHSO_3$

Further we tried to study in more detail the reaction of selenous acid with potassium hydrogen sulfite [11]:

$$2H_2SeO_3 + 5KHSO_3 \rightarrow H_2Se_2S_2O_6 + 3K_2SO_4 + KHSO_4 + 3H_2O$$

$H_2Se_nS_2O_6$ was prepared using two different preparations with a same mixing molar ratio $2H_2SeO_3$:$5KHSO_3$ by just varying the order of reagents addition to the reaction mixture and the reaction temperature. Both reactions were performed using an excess of one of reagents H_2SeO_3 or $KHSO_3$. In order to monitor the reaction aliquots of solution were taken from the reaction vessel, diluted with distilled water to 100 ml and analyzed according to below described methods.
According the first preparation described in [11]. 50 ml of 1 mol·dm^{-3} $KHSO_3$ solution was slowly poured while stirring into same amount of 0.4 mol·dm^{-3} H_2SeO_3 solution. During reaction solution heats up, so it is cooled down using ice or solutions must be cooled down beforehand. Solution obtains greenish-yellowish color which is indication of $Se_nS_2O_6^{2-}$ ions' formation. Further solution change color to orange then to red with the formation of colloidal amorphous selenium. Solution can be stable for weeks, if refrigerated

2.3 Synthesis of $H_2Se_nS_2O_6$ from $KHSO_3$ with addition of selenous acid

According the second preparation the freshly prepared cooled (1 - 4 °C) 50 cm^3 of 0.4 mol·dm^{-3} H_2SeO_3 was slowly added to the cooled (1 - 4 ° C) 50 cm^3 of 1 mol·dm^{-3} $KHSO_3$ with constant stirring. The reaction was started in spontaneously and completed within ~ 10min. The reaction solution is pale green at the beginning, and remains without significant changes about month when kept in the refrigerator at 4°C. Further reaction kinetics was investigated at 25°C using thermostatic arrangement.

2.4 Analysis

Complete analysis of the mixture of reaction of selenous acid with sulfurous acid with edition of $CaCO_3$ or selenous acid with potassium hydrogen sulfite includes a determination of total number of moles of selenopolythionates m, the concentration of monoselenotrithionic and diselenotetrathionic acids, average number of atoms of selenium in molecule of selenopolythionic acid n, the residue of non-reacted selenous acid H_2SeO_3 and also possible admixtures of the products of its decomposition, namely el. Se, sulfurous and sulfuric acids. We used analytical methods proposed by V. Zelionkaitė [8].

Monoselenotrithionic acid oxidizes by iodine in bicarbonate medium according an equation:

$$SeS_2O_6^{2-} + 3I_2 + 10OH^- \rightarrow SeO_3^{2-} + 2SO_4^{2-} + 6I^-$$

In bicarbonate medium sulfurous ion SO_3^{2-} also oxidizes using two mole-equivalents of iodine. The titration by iodine in bicarbonate medium with preliminary blocking SO_3^{2} with formalin gives an amount of selenotrithionic acid. Diselenotetrathionic acid by action of bicarbonate decomposes to monoselenotrithionic acid with release of one mole of Se:

$$Se_2S_2O_6^{2-} \rightarrow Se + SeS_2O_6^{2-}$$

The determination of released Se and monoselenotrithionic acid in the mother solution allows finding the concentration of $H_2SeS_2O_6$ and $H_2Se_2S_2O_6$ in their mixture. Selenous acid was determined according the known procedure after oxidizing with I_2 and further titration with sodium thiosulfate [8]:

$$H_2SeO_3 + 4I^- + 4H^- \rightarrow Se + 2I_2 + 3H_2O$$

Elemental red released Se was oxidized with el Br_2 to H_2SeO_3 and the following was determined according the above procedure [8]. The concentration of sulfuric acid was determined turbidimetrically [12] or was calculated according the balance of sulfur in the reaction mixture.

2.5 Formation of selenium layer on the surface of flexible substrate

Selenium films have been deposited on polycapramide (PA) surface by chemical bath method at 4°C, using 0.2, 0.1, 0.05 and 0.01 $mol \cdot dm^{-3}$ solutions of $H_2Se_nS_2O_6$ ($n = 1.18 – 1.27$) with deposition period of 48 h. The PA samples in 0.2 $mol \cdot dm^{-3}$ solution were also deposited 96 h. The PA samples color was changed from colorless to yellow–reddish after deposition. The samples were taken out after deposition, washed with water and dried. Films of Se on PA were characterized using optical absorption studies. UV-VIS spectra were recorded on a Spectronic^R Genesys^{TM} 8 UV/VIS spectrophotometer with compensation of PA in the range of 190–800 nm.

3. Results and discussion

Several studies of various cases of above described reactions exist [5, 11]. In the study [5, 10] with aim to precipitate sulfuric acid calculated according the below reaction amount of $CaCO_3$ was added:

$$2H_2SeO_3 + 5H_2SO_3 + 3CaCO_3 \rightarrow H_2Se_2S_2O_6 + 3CaSO_4 + 6H_2O + 3CO_2$$

At the beginning of the reaction $H_2SeS_2O_6$ was formed, which further at room temperature continuously converts to $H_2Se_2S_2O_6$ (Fig. 1, a).

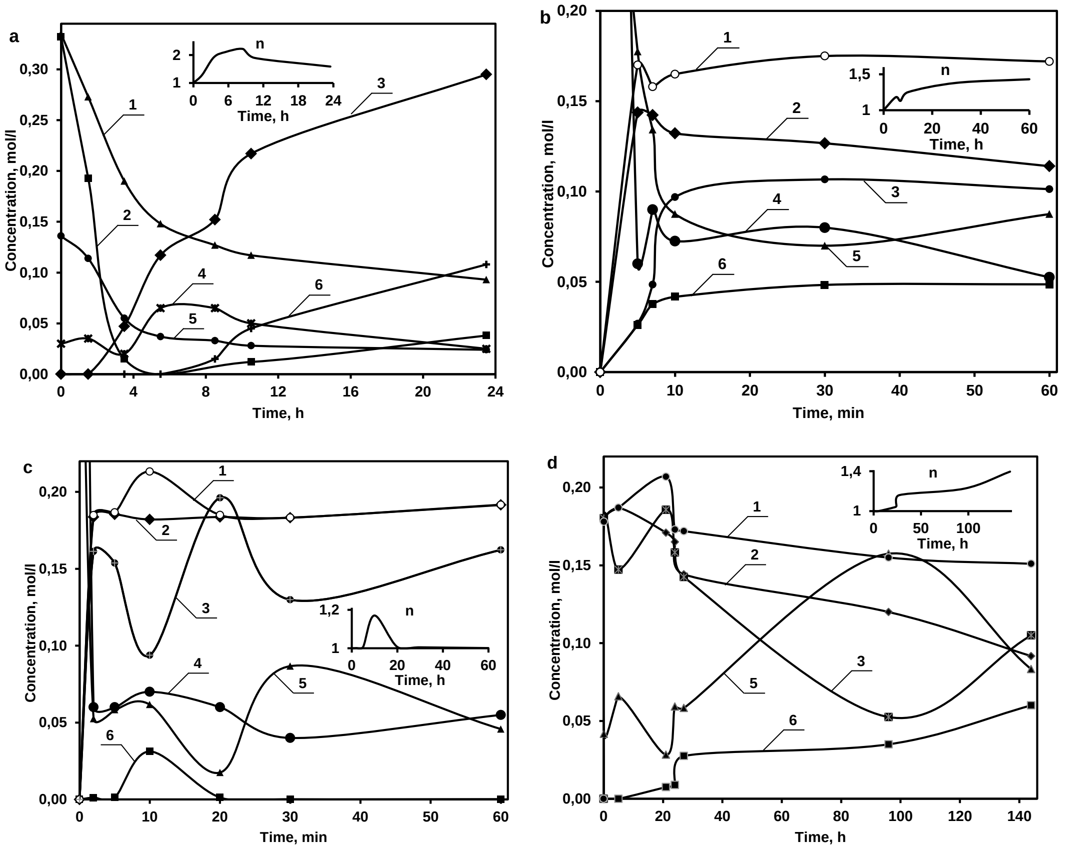

Fig. 1. Kinetics of reaction of H_2SeO_3 and H_2SO_3: (a) 1.4 mol/1 H_2SO_3 addition to suspension of $CaCO_3$ in 8 mol·dm^{-3} H_2SeO_3: 1 – m, 2 – $H_2SeS_2O_6$, 3 – Se_{el}, 4 – H_2SO_3, 5 – H_2SeO_3, 6 – H_2SO_4. (b) 1 mol·dm^{-3} $KHSO_3$ addition to 0.4 mol·dm^{-3} H_2SeO_3; (c) 0.4 mol·dm^{-3} H_2SeO_3 addition to 1 mol·dm^{-3} $KHSO_3$ at 0°C; (d) 0.4 mol·dm^{-3} H_2SeO_3 addition to 1 mol·dm^{-3} $KHSO_3$ at 25°C; (d) 1 – m, 2 – $H_2SeS_2O_6$, 3 – Se_{el}, 4 – H_2SO_3, 5 – H_2SeO_3, 6 – $H_2Se_2S_2O_6$. Inset: n – number of Se atoms in $H_2Se_nS_2O_6$.

Small amount of triselenopentathionic acid $H_2Se_3S_2O_6$ also forms, which quickly decomposes. 0.2 - 0.3 mol·dm^{-3} diselenotetrathionic acid together with $H_2Se_3S_2O_6$ (n = 1.9 – 2.1) were found in the reaction solution at 3.5 to 8.5 h from the beginning of the reaction. Decomposition of formed $H_2Se_2S_2O_6$ to $H_2SeS_2O_6$ with release of elemental Se starts after 10 h from the beginning of reaction.

Further we tried to study in more detail the reaction of selenous acid with potassium hydrogen sulfite [11] (Fig. 1, b):

$$2H_2SeO_3 + 5KHSO_3 \rightarrow H_2Se_2S_2O_6 + 3K_2SO_4 + KHSO_4 + 3H_2O$$

$H_2SeS_2O_6$ forms in a first preparation at the beginning of the reaction, together with significant amount (0.03 – 0.05 mol·dm^{-3}) of $H_2Se_2S_2O_6$. Number of selenium atoms n in molecule of $H_2Se_nS_2O_6$ increases continuously from 1.0 to 1.43 with release of el. Se (Fig. 1, b) during the initial fast stage of reaction.

Further solution change color to orange then to red with the formation of colloidal amorphous selenium. Solution can be stable for weeks, if refrigerated.

$H_2SeS_2O_6$ forms in a second preparation at the beginning of the reaction, together with small amount ($1.25\cdot10^{-3}$-$3.1\cdot10^{-2}$ mol·dm^{-3}) of $H_2Se_2S_2O_6$. Average number of atoms of selenium n in molecule of $H_2Se_nS_2O_6$ during the initial fast stage (one hour from the mixing of reagents) of reaction remains ~ 1.0 (1.00 – 1.17), e.g. the second preparation allow us to prepare almost 99.3% of $H_2SeS_2O_6$ (Fig. 1, c) only with insignificant release of el. Se. Further reaction kinetics was investigated at 25°C using thermostatic arrangement. Monoselenotrithionic acid $H_2SeS_2O_6$ only after 20 h starts to decompose to $H_2Se_2S_2O_6$ (n = 1.04 – 1.40) with release of el. Se (Fig. 1, d).

Reaction rate depends on temperature and initial solutions' concentration. According the kinetics curves some characteristics of three types of reaction were calculated (Table 1). As a reaction is very complicated we tried to apply the isolation method in conjunction with the method of initial rates [13]. The method of initial rates might not reveal the entire rate law, for in a complex reaction the products themselves might affect the rate. That is in the case for formation of monoselenotrithionic $H_2SeS_2O_6$ and diselenotetrathionic $H_2Se_2S_2O_6$ acids which decomposition through unstable intermediate product H_2SeSO_3 or known [8] sulfurous decomposition of diselenotetrathionic acid leads to regeneration of initial reagents such as H_2SO_3:

$2H_2SeS_2O_6 + H_2O \rightarrow H_2Se_2S_2O_6 + H_2SO_4 + H_2SO_3$
$H_2Se_2S_2O_6 + H_2SO_3 \rightarrow H_2SeSO_3 + H_2SeS_2O_6$
$H_2SeSO_3 \rightarrow H_2SO_3 + Se$

or as final common process:

$H_2Se_nS_2O_6 + H_2O \rightarrow n\,Se + H_2SO_4 + H_2SO_3$

The kinetics of three types of $H_2Se_nS_2O_6$ formation process were studied and analyzed by three mechanisms. The first-order rate expression by plotting ln c_{H2SeO3} against time, a plot of $1/c_{H2SeO3}$ against time, based on the assumption of a second-order mechanism, and a plot of $1/c^2_{H2SeO3}$ against time were tested for all three types of reaction. Our calculations show that the correlation coefficients, R^2, for the first-order rate law (0.9724 - 0.9984) are much greater than the correlation coefficients of other plots, respectively, 0.9133 – 0.9603 and 0.8238 – 0.9164 for all three types of studied reactions. The data of the reaction with addition of $KHSO_3$ to an excess of H_2SeO_3 show a best compliance with the first - order equation and the regression coefficients for the linear plots were highest (R^2 = 0.9984) among all type of reactions in this study. It suggests that preferred mechanism of the first stage of reaction is first - order rather than a second order. In addition, the data for the first - order rate law were only analyzed for the 10 – 20 min or five first hours of $H_2Se_nS_2O_6$ formation reactions. After this the deviation from linear curve increased rapidly, e.g., the linearity of the first-order plots are only valid for the very fast first stage of $H_2Se_nS_2O_6$ formation process. Our kinetic calculations allow us to decide that the reaction with the rate law of the form $v = k_t\,[H_2SeO_3]$ corresponds to first-order reaction and the integrated rate law of a reaction might be expressed as following:

$[H_2Se_nS_2O_6] = [H_2SeO_3]_0\,(1-e^{-kt})$
where $[H_2Se_nS_2O_6]$ – the concentration of formed selenopolythionic acid at time t;
$[H_2SeO_3]_0$ – the initial concentration of selenous acid; k_t – rate constant.

Table 1.Kinetic characteristics for $H_2Se_nS_2O_6$ (n = 1-2) formation at 0° and 25°C

Reaction type	Ratio of concentrations mol·dm^{-3} H_2SeO_3:H_2SO_3	Temperature, °C	Rate law	Average rate constant k 10^3, s^{-1}
Addition of H_2SO_3 to the suspension of $CaSeO_3$	0.081:0.21	0	$V = k_t\,[H_2SeO_3]$	4,6 10^{-2}
Addition of $KHSO_3$, to an excess of H_2SeO_3	0.02:0.05	25	$v = k_t\,[H_2SeO_3]$	1,85
Addition of H_2SeO_3 to an excess of $KHSO_3$	0.02:0.05	0	$v = k_t\,[H_2SeO_3]$	5,09

The mechanism and kinetic characteristics of this reaction were compared with already investigated and known properties of stability of monoselenotrithionic $H_2SeS_2O_6$ and diselenotetrathionic $H_2Se_2S_2O_6$ isolated from their potassium salts [5] (Fig. 2, a and b).

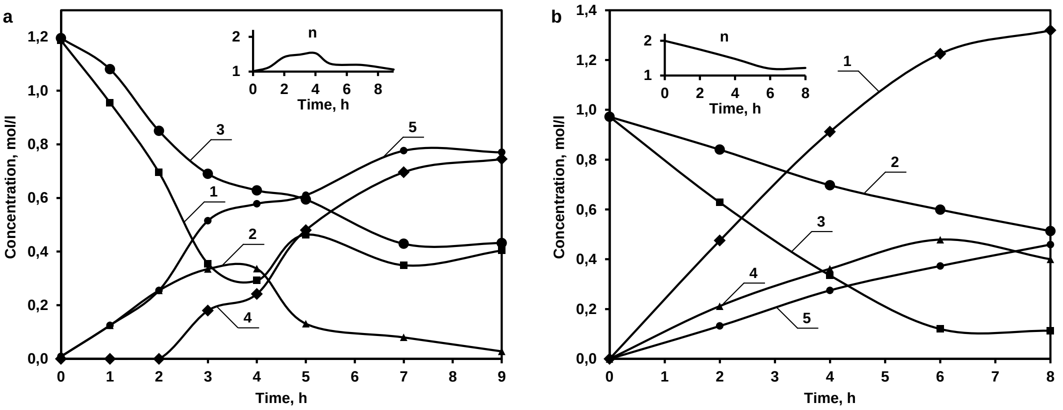

Fig. 2. Kinetics of decomposition of $H_2Se_nS_2O_6$ acids at 25 °C: (a) 1. 02 M $H_2SeS_2O_6$; (b) 0. 97 M $H_2Se_2S_2O_6$. 1 – $H_2SeS_2O_6$, 2 – $H_2Se_2S_2O_6$, 3 – m, 4 – Se_{el}, 5 – H_2SO_4. Inset: n – number of Se atoms in $H_2Se_nS_2O_6$.

Table 2 summarizes the known kinetic characteristics of selenopolythionic acids and its potassium salts. Selenopolythionic acid's stability decreases with increasing number of selenium atoms in acid molecule. Table 2 shows the values of the first-order rate constant, k, were found to increase for $H_2Se_2S_2O_6$ y four-fold in comparison with $H_2SeS_2O_6$ from 2.98 10^{-6} s^{-1} to 10.6 10^{-6} s^{-1}, approximately for the same initial concentration, respectively, 0.190 mol·dm^{-3} and 0.247 mol·dm^{-3}.

Table 2. Rates of decomposition for $H_2Se_nS_2O_6$ (n = 1-2) at 25°C [5], *$K_2SeS_2O_6$ at 20° C and 30°C* [12, 14]

Selenopolythionic compound	Concentration, mol·dm^{-3}	Half – life, $\tau_{½}$, h	Average rate constant k 10^6, s^{-1}
$H_2SeS_2O_6$	1.02	2.6	63.5
	0.375		6.38
	0.190	42	2.98
$H_2Se_2S_2O_6$	0.972	3	76.6
	0.603		25.7
	0.247	16	10.6
$K_2SeS_2O_6^{*}$	0.0488	112	1.64
$K_2SeS_2O_6^{**}$	0.0452	22	7.88
$K_2SeS_2O_6^{***}$	0.0396	75	2.70

[*] in distilled water at 30°C

[**] in 0.1 mol·dm^{-3} HCl at 30°C; [***] in 0.1 mol·dm^{-3} HCl at 20°C

The comparison of data for potassium selenotrithionate decomposition (Table 2) shows that decomposition rate and isolation of elemental Se depends on the acidity of solution. In acidified solutions (pH = 1.1) isolation of Se starts after 45 h from the beginning of decomposition at 30°C, in distilled water (pH = 7.0), respectively, after 120 h. First –order decomposition rate constants calculated for the first stage of decomposition show that $K_2SeS_2O_6$ decomposes approximately fivefold faster in acidic solution than in distilled water at 30°C. The data also [9, 14] show an increase of decomposition rate of $K_2SeS_2O_6$ in acidified solutions with temperature. Table 2 shows the values of the first-order rate constant, k, were found to increase from 2.70 10^{-6} s^{-1} to 7.88 10^{-6} s^{-1}, for an increase in the solution temperature from 20°C to 30°C. Again the average value of the temperature coefficients of $K_2SeS_2O_6$ decomposition is 2.90 to 3.06, e.g., corresponds to first-order reactions [9].

Quantitative data on potassium diselenotetrathionate's decomposition kinetics are not available. According [14], $K_2Se_2S_2O_6$ more stable is in slightly acidified solutions, but in acidic solutions completely decomposes as following:

$$Se_2S_2O_6^{2-} + H_2O \rightarrow 2Se + SO_4^{2-} + H_2SO_3$$

Some difficulties occur in comparison of kinetic data for decomposition of selenopolythionic acids and its potassium salts due to differences in concentrations and temperature. However, it might be stated that the stability of selenopolythionic acids is significantly higher than the stability of its potassium salts even at higher concentrations (Table 2). This feature shows that selenopoplythionic acids are more convenient in longer selenization processes despite the fact that both, acids and salts, possess almost the same purity and decomposition products. Nevertheless, the elemental composition of acids (32.75 – 49.36 % of Se in acids against 24.73 – 39.66 % of Se in its potassium salts) helps to increase an amount of Se in selenized surface layer of the substrate.

Direct reactions of isolation of selenopolythionic compounds showed the strong dependence upon the conditions of reactions: temperature, admixtures and duration. According [6], in usual conditions 0.02 mol·dm^{-3} $H_2Se_2S_2O_6$ solutions with triple amount of H_2SO_4 produce. An addition of $CaCO_3$ allows increasing the concentration of diselenotetrathionic acid ten-fold and significantly decreasing amount Using of $KHSO_3$ instead of H_2SO_3, allows increasing the concentration of resulting solution of selenotrithionic and of diselenotetrathionic acids to ~ 0.2 mol·dm^{-3} and its stability as H_2SO_4 was eliminated.

An amount of elemental Se, respectively, 33.64, 40.54 and 49.65 % in synthesized using three types of direct reactions precursors $H_2Se_nS_2O_6$ (n = 1.04, 1.40 and 2.1) shows similar enrichment with Se compared to selenotrithionic and diselenotetrathionic acids (10% increase compared to potassium salts).

An estimation of direct experiments' reaction rates and the calculation of reactions rate' constants showed us that the most suitable for selenization process, especially for CBD procedure on flexible polymeric or glass substrates is fast reaction of selenous acid and $KHSO_3$. The superior of easy selenopolythionate anion $Se_nS_2O_6^{2-}$ produce in direct experiments compared to its preparation in the form of potassium salts or even longer isolation from potassium salts in the form of selenopolythionic acids makes this type of selenopolythionic precursor preparation especially attractive for selenization.

The comparison of five selenopolythionic compounds of the homologous range $Se_nS_2O_6^{2-}$ (n = 1 – 3) irrespective of species of compound showed their applicability for selenization process despite the differences of its isolation duration, the stability and the purity. Their applicability as selenium single-source molecular precursor depends on the properties of substrate, required composition modulation and on applications of formed selenides layer.

The absorption spectra maximum of Se containing films on polycapramide surface was at λ = 290 nm, percentage transmission (95 %) was at λ = 400 nm (Fig. 3, a). It was clear increase in absorbance at maximum wavelength with increase of a precursor's concentration.

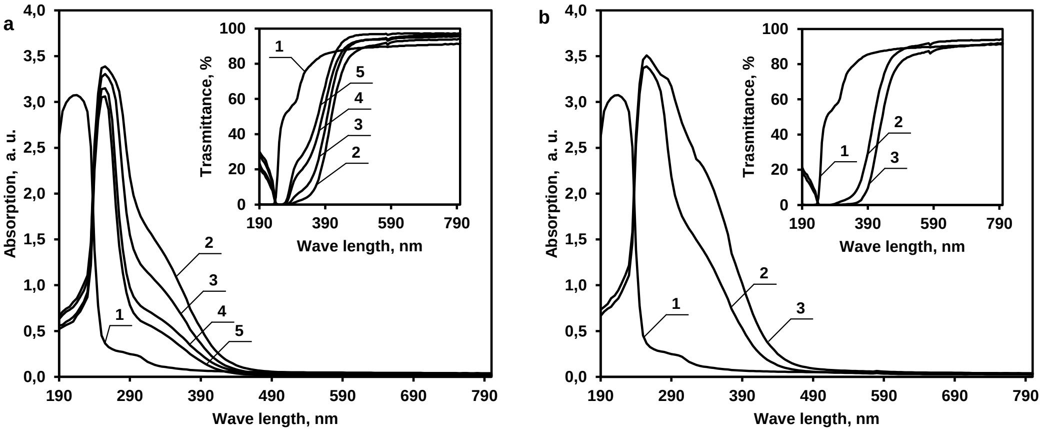

Fig. 3. Individual UV-VIS absorption spectra of PA (1) , the layers of selenium on PA surface: (a) after 48 hours of exposure in 0,2 mol·dm^{-3} *(2), 0,1 mol·dm*$^{-3}$ *(3), 0,05 mol·dm*$^{-3}$ *(4), 0,01 mol·dm*$^{-3}$ *(5); (b) after 48 hours (2) and 96 hours (3) in 0,2 mol·dm*$^{-3}$ *solution of* $H_2Se_nS_2O_6$ *at 4 °C. Inset: transmittance spectra.*

An absorbance also grows with an increase of exposure time in the solution with the same concentration (Fig. 3, b). However, percentage transmission is lower after 96 h of the selenization. The appearance of additional, unclear peak at ~ 300 nm may be explained by slight decomposition of $H_2Se_nS_2O_6$ and elemental Se release.

4. Conclusions

1. Our results show that $H_2Se_nS_2O_6$ (n = 1.04 – 2.1) might be successfully synthesized in direct reactions as the single-source selenium precursor.

2. Direct reactions of isolation of selenopolythionic compounds showed the strong dependence upon the conditions of reactions: concentration, temperature and admixtures.

3. The kinetics of direct $H_2Se_nS_2O_6$ formation ‘reactions were studied and analyzed by three mechanisms.

4. The comparison of five selenopolythionic compounds $H_2SeS_2O_6$, $H_2Se_2S_2O_6$, $K_2SeS_2O_6$, $K_2Se_2S_2O_6$ and $H_2Se_nS_2O_6$ of the homologous range $Se_nS_2O_6^{2-}$(n = 1 – 3) irrespective of species of compound showed their applicability for selenization process despite the differences of duration of its isolation, the stability and the purity.

5. Selenium layers have been deposited on polycapramide (PA) surface first time using $H_2Se_nS_2O_6$ (n = 1.18-1.27).

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