

Sorption of potassium selenopentathionate by the polyamide PA 6

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The sorption of potassium selenopentathionate, $K_2SeS_4O_6$, from its aqueous solution by the polyamide PA 6 has been studied. It has been shown that the chemical stability of sorbed $K_2SeS_4O_6$ is far less than of that in water solution. The stability of the sorbed salt increases with decreasing the solution pH value. Apart the mentioned salt, non-mobile products of its decomposition such as elemental sulfur and selenium are accumulated in the polymer. By the chemical analysis and modeling of the decomposition process the dependencies of concentrations of undecomposed sorbed selenopentathionate ions on the $K_2SeS_4O_6$ solution pH, concentration and temperature are determined. The sorption mechanism is discussed. The importance of the results obtained for the production of the polymer–metal chalcogenide composites is shown.

Key words: potassium selenopentathionate, polyamide PA 6, sorption

INTRODUCTION

The polymeric materials exhibit a variety of properties; for example, they are elastic, light, environmentally resistant, non-electrically conductive, etc. The modification of polymers by forming on their surface thin layers of inorganic compounds results in composites having new important physical properties, for example, optical, of electrical conductivity, etc. The interest in thin films of copper sulfides, Cu_xS , and copper selenides, Cu_xSe , was previously focused mostly on their possible use in solar cells [1–7]. Chemically deposited CuS thin films have been found to possess near-ideal solar control characteristics: transmittance in the visible region 20–50%, low transmittance (10–20%) in the infrared region, low reflectance (< 10%) in the visible region so as to avoid glare, and relatively high reflectance (> 15%) in the near-infrared region [8]. $Cu_{2-x}Se$ films are typically *p*-type, highly conducting, semitransparent, semiconductors with the band gap varying between 1.1 and 1.4 eV, suitable for solar energy conversion and as a semitransparent layer in high speed detectors working in the visible range [9, 10]. More recently their application in solar control coatings for architectural and automobile glazings [11,

12], in transparent and conductive coatings on glass, polymers [13–15], and as elastic thin film Cu sensor electrodes [16–20], in the production of electronic and optical devices [21, 22], thermoelectric converters [23, 24] has been discovered.

A number of methods for the deposition of thin films of copper sulfide and copper selenide on various dielectrics have been reported: vacuum evaporation [25, 26], activated reactive evaporation [27], spray pyrolysis [28], electroless deposition [14, 29], successive ionic layer adsorption and reaction (SILAR) [30, 31], chemical bath deposition [13, 32–42]. Methods of copper sulfide coatings were reviewed in the works of [32–37, 39–42].

The sorption–diffusion methods for the formation of thin semiconductive and electrically conductive layers of copper sulfide and copper selenide in the surface of polyamide (PA 6), on the basis of experience gained in earlier decades in the chemistry of polythionates and selenopolythionates [43–47], over the last years at the Department of Inorganic Chemistry of KTU were studied. Using these methods, a PA 6 film is first treated with a solution of polythionic acids, $H_2S_nO_6$ (*n* – an average number of sulfur atoms in the molecule), containing chains of divalent sulfur atoms of low oxidation state in the molecule, $^-O_3S-S-S-.....-S-S-SO_3^-$ [48, 49], when looking for the formation of sulfide layers [50–52]. When the goal is the formation of copper selenide layers in the surface of PA 6 [53–55], the latter is treated with the solution of potassium selenotriothionate, $K_2SeS_2O_6$, containing one divalent selenium

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atom in low oxidation state $^{-}\text{O}_3\text{S}-\text{Se}-\text{SO}_3^{-}$ [56] in the first stage of the process. However, the formation of mixed copper sulfide–copper selenide layers in the surface of PA 6 at the beginning of our studies in this direction [57] was not studied, although the similarity of sulfur and selenium atoms and their ability to interchange each other in various molecules was obvious [58].

A mixed chain of three divalent chalcogen atoms $^{-}\text{O}_3\text{S}-\text{S}-\text{Se}-\text{S}-\text{SO}_3^{-}$ of low oxidation state is present in the anion of salts of monoselenopentathionic acid, $\text{H}_2\text{SeS}_4\text{O}_6$, [48–59]. Thus it was reasonable to apply these compounds for the formation of mixed copper sulfide–copper selenide layers in the surface of PA 6 films.

The aim of the present work was to investigate the regularities and mechanism of the sorption–diffusion of selenopentathionate ions into a polyamide PA 6 film from water solutions of potassium selenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6$.

EXPERIMENTAL

Samples of polyamide PA 6 (specification TY 6-05-1775-76, grade PK-4) films 15×70 mm in size and 70 μm thick were used. Before chalcogenation they had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried first on filter paper and then over CaCl_2 for 24 h. Distilled water, reagents of the grades “especially pure”, “chemically pure” and “analytically pure” were used in the experiments.

The salt of potassium selenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6 \cdot 1.5\text{H}_2\text{O}$, was prepared and chemically analyzed according to published procedures [60].

Samples of PA 6 film were chalcogenized in 0.025, 0.05, 0.1 and 0.2 $\text{mol} \cdot \text{dm}^{-3}$ solutions of $\text{K}_2\text{SeS}_4\text{O}_6$ acidified with the addition of HCl (0.1 $\text{mol} \cdot \text{dm}^{-3}$ HCl, pH ~ 1.5) and without acid addition at temperatures of 30, 40 and 50 $^{\circ}\text{C}$. The total duration of experiments was 4.5 h.

The concentration of selenium in a PA 6 sample was determined using the analytical method of atomic absorption spectrophotometry [61]: a PA 6 sample treated in a solution of potassium selenopentathionate was dissolved in concentrated nitric acid, and selenium present in the resulting solution was determined with an Perkin–Elmer-503 the atomic absorption spectrometer wavelength $\lambda = 196$ nm, diffractive gap 5 (2.0 nm), electrodeless discharge lamp, air-acetylene flame. For the standard conditions described above, the sensitivity is about 0.5 $\mu\text{g}/\text{ml}$ Se for 1% absorption.

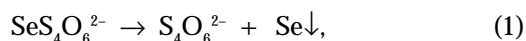
The concentration of sulfur in PA 6 was determined nephelometrically as described in [62]. A K \times K-3 photometer (Russia) was used for determination of the optical density of the solution at a wavelength 405.0 nm. For the preparation of this

solution the chalcogenized PA 6 film sample was treated similarly as for the preparation of selenium determination by atomic absorption spectrometry. 10 cm^3 of the solution was diluted to 50 cm^3 . Then to 20 cm^3 of resulting solution 5 cm^3 of 0.1 N HCl solution was added and evaporated to dryness. This procedure for was repeated several times a complete elimination of NO_3^{-} anions which interfered the further analysis. Then the residual precipitate was dissolved in water, 5 cm^3 of 0.1 $\text{mol} \cdot \text{dm}^{-3}$ BaCl_2 solution was added and the mixture diluted to 25 cm^3 . If sulfur was present in the solution, the resulting mixture became turbid (BaSO_4). Using the data on solution optical density measurements and the calibration curve, the concentration of sulphate ions in the solution and finally the concentration of sulfur in the initial chalcogenized PA 6 film sample were calculated.

ANALYSIS AND RESULTS

The PA 6 sorption capacity depends on the pH value of the solution. In this work, the sorption by polyamide PA 6 of potassium selenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6$, was studied from water solutions with pH 5.6 (the amide groups of polyamide are not protonized, – the isoelectric point of the PA 6) and from the acidified solutions (pH 1.5), when the protonized amide groups are the sorption centres of a polymer.

The low stability of potassium selenopentathionate solutions made some difficulties for the study of sorption–diffusion processes. $\text{K}_2\text{SeS}_4\text{O}_6$ slowly decomposes in the solution with the pH < 5 , but its stability increases with decreasing the solution pH, concentration and temperature [63]. Therefore, using an acidified $\text{K}_2\text{SeS}_4\text{O}_6$ solution we could expect to obtain results of better reliability and to achieve a significantly more intensive sorption of $\text{SeS}_4\text{O}_6^{2-}$ anions into the PA 6 film. The selenopentathionate decomposition reactions had been determined earlier [63]:



The beginning of the $\text{K}_2\text{SeS}_4\text{O}_6$ solution decomposition can be easily detected visually because of the start of the red colloidal selenium liberation.

$\text{K}_2\text{SeS}_4\text{O}_6$ sorbed into PA 6 is even more unstable. This may be seen from the change of PA 6 film colour during the sorption process. PA 6 film samples treated with $\text{K}_2\text{SeS}_4\text{O}_6$ solution of low concentration and at a lower (30 $^{\circ}\text{C}$) temperature were actually colourless. However, when the $\text{K}_2\text{SeS}_4\text{O}_6$ solution concentration, temperature and treatment duration were increased, partial decomposition of sorbed $\text{SeS}_4\text{O}_6^{2-}$ ions could be detected by the changed slightly yellow colour of the polymer film. If the

PA 6 film was treated with the 0.2 M $K_2SeS_4O_6$ solution at a temperature of 50 °C for 10 min, the colour of the film was orange and after 4.5 h of treatment even dark red.

The study was complicated also by the problem that it was difficult to distinguish the amounts of elemental sulfur and selenium liberated during the partial decomposition of $K_2SeS_4O_6$ diffused into PA 6 and the amount of not decomposed $SeS_4O_6^{2-}$ ions present in the polymer. Chemical analysis could give only the overall amount of sorbed $SeS_4O_6^{2-}$ anions and of liberated sulfur and selenium concentrations, c_s and c_{se} respectively. However, the concentration of not decomposed sorbed selenopentathionate ions, as will be shown later, could be calculated using other indirect measurements which unfortunately reduced the accuracy of results.

0.025–0.2 mol · dm⁻³ $K_2SeS_4O_6$ solutions were used in a series of experiments for determining the influence of solution concentration on sorption kinetics: sorption from solutions of lower concentration was too slow, and at a higher $K_2SeS_4O_6$ concentrations the stability of the latter was insufficient. Solutions at a temperature of 50 °C were used for a more efficient selenopentathionate sorption-diffusion in this study.

The temperature of $K_2SeS_4O_6$ solution was another parameter of selenopentathionate sorption into PA 6 film. The experiments were carried out at a solution temperature in the interval 30–50 °C. Such interval was imposed by the very slow diffusion at a lower temperature and a more intensive decomposition of $K_2SeS_4O_6$ solution at a higher temperature. A sufficiently stable optimal 0.05 mol · dm⁻³ concentration of $K_2SeS_4O_6$ solution was used when the influence of the solution temperature was studied.

The diffusion kinetics at the different pH values of $K_2SeS_4O_6$ solution on the basis of data on c_{se} change with the sorption duration is shown in Figs. 1, 3 and on the basis of data on c_s change in Figs. 2 and 4.

Changes of selenium and sulfur concentrations in the polymer with time (Figs. 1–4) when the concentration of $K_2SeS_4O_6$ solution was $c^{sol}_{SPT} > 0.05M$ (the upper index shows the $K_2SeS_4O_6$ concentration in the solution) show that the equilibrium values of c_{se} and c_s were not reached even during all the treatment time, $\tau \leq 4.5$ h, *i.e.* the diffusion does not follow Fick's law.

The deviation from Fick's diffusion may be explained by the accumulation of selenopentathionate decomposition products in the matrix of the polymer. One can see from equations 1 and 2 that the equivalent amounts of elemental selenium and sulfur are products of selenopentathionate decomposition. As is seen from equation (1), elemental selenium and a tetrathionate ion are formed in the first

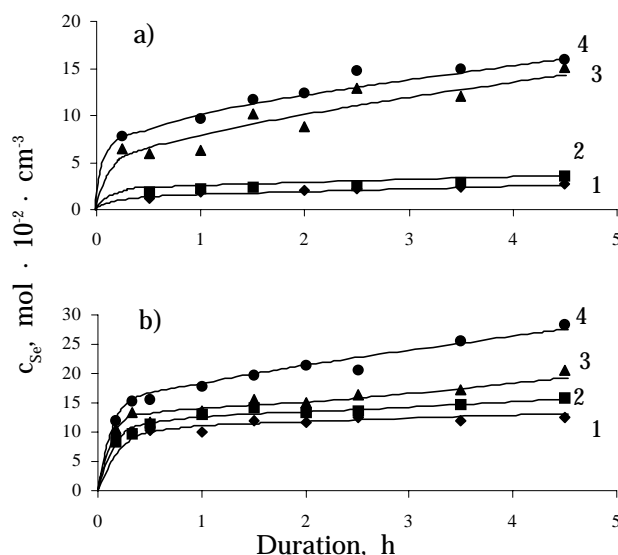


Fig. 1. Dependence of the kinetics of selenium concentration in the PA 6 film on the concentration of $K_2SeS_4O_6$ solution. The conditions of sorption: the temperature of solution 50 °C, pH 5.6 (a) or pH 1.5 (b); the concentration of solution, mol · dm⁻³: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

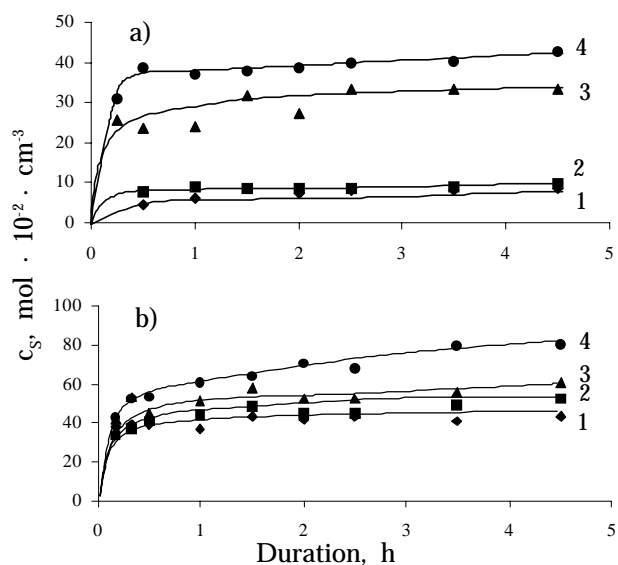


Fig. 2. Dependence of the kinetics of sulfur concentration in the PA 6 film on the concentration of $K_2SeS_4O_6$ solution. Conditions of sorption: the temperature of solution 50 °C, pH 5.6 (a) or pH 1.5 (b); the concentration of solution, mol · dm⁻³: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

stage of decomposition. The formation of selenium can be observed visually. Nonpolar molecules of it cannot be sorbed by the polar amide groups, and being insoluble in water Se will remain not moveable in the matrix of PA 6. If the decomposition would proceed only to elemental selenium (which would accumulate in the polymer) and tetrathionate (which would desorb into solution), positions of the latter would be occupied by the diffusing seleno-

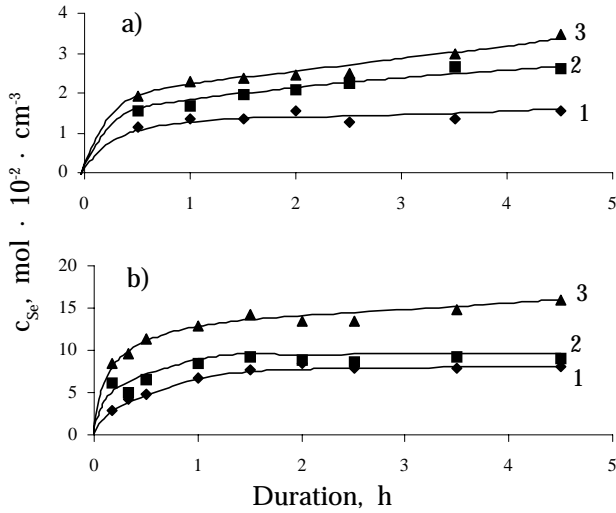


Fig. 3. Dependence of kinetics of selenium concentration in PA 6 film with time on the temperature of $K_2SeS_4O_6$ solution. The conditions of sorption: the concentration of solution $0.05 \text{ mol} \cdot \text{dm}^{-3}$, pH = 5.6 (a) or pH = 1.5 (b); the temperature of solution, °C: 1 – 30; 2 – 40; 3 – 50

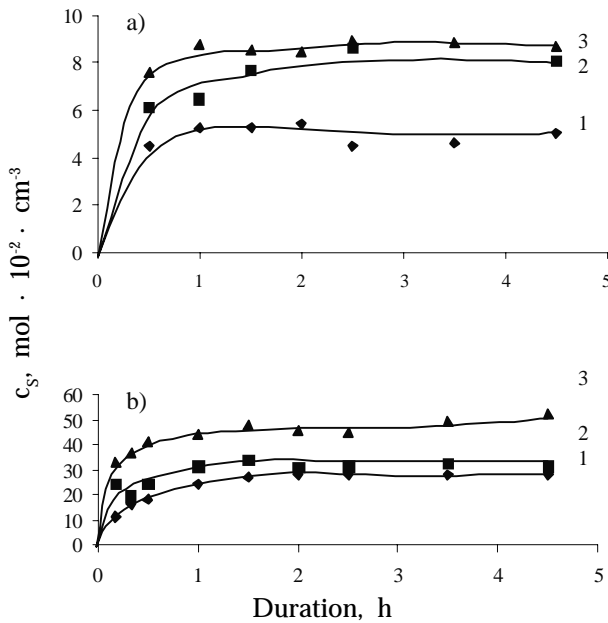


Fig. 4. Dependence of kinetics of sulfur concentration in PA 6 film with time on the temperature of $K_2SeS_4O_6$ solution. Conditions of sorption: the concentration of solution $0.05 \text{ mol} \cdot \text{dm}^{-3}$, pH 5.6 (a) or pH = 1.5 (b); the temperature of solution, °C: 1 – 30; 2 – 40; 3 – 50

pentathionate ions. In this case, the overall amount of selenium would increase and the overall amount of sulfur in the polymer would quickly reach the equilibrium value. But the data presented in Figs. 1–4 show that the values of c_{Se} and of c_S increase throughout the 4.5 h duration of PA 6 treatment in the $K_2SeS_4O_6$ solution. Therefore, we can state that the decomposition proceeds into the final products. The elemental sulfur and selenium are not moveable in a PA 6. It was confirmed by a control exper-

iment. The analysis of PA 6 sample placed in sulfur powder and heated for 4.5 h at a temperature of 50 °C showed no presence of sorbed sulfur. Therefore the sulfur not moveable in the PA 6 matrix will accumulate as a fine-grained filler. The other products of decomposition, sulfate and sulfite ions (formed from SO_2 and sorbed water) are moveable and gradually desorb into the solution.

The selenopentathionate ion sorption centres released from the decomposed selenopentathionate ions will be occupied by the others diffusing from the solution selenopentathionate ions. Thus, selenopentathionate diffusion may be expressed by the equation

$$\frac{\partial C^p_{SPT}}{\partial \tau} = \frac{\partial}{\partial x} \left(D \frac{\partial C^p_{SPT}}{\partial x} \right) - k(C^p_{SPT})^\alpha, \quad (3)$$

where c^p_{SPT} is the concentration of selenopentathionate sorbed by PA 6 (the upper index means the concentration in the polymer), x is the diffusion coordinate, k and α are the constants describing the kinetics of selenopentathionate decomposition in the polymer matrix. If the selenopentathionate diffusion coefficient $D = \text{const}$ and the concentration of $K_2SeS_4O_6$ solution $c^{sol}_{SPT} = \text{const}$, then

$$\frac{\partial C^p_{SPT}}{\partial \tau} D \frac{\partial^2 C^p_{SPT}}{\partial x^2} - kC^\alpha. \quad (4)$$

The first member of equation (4) describes the stream of diffusion which follows Fick's law, and the second member shows the reduction of selenopentathionate concentration because of decomposition. A fast increase of selenopentathionate concentration diffused into the polymer is observed at the beginning of the sorption because of the domination of the first member in the last equation. But later the increase of the concentration of diffused selenopentathionate becomes slow since the accumulation of selenopentathionate decomposition products and an additional selenopentathionate diffusion start.

According to equations (1) and (2), the decomposition of one sorbed selenopentathionate ion produces two atoms of S and one atom of Se. When the sorption centre becomes occupied by the other selenopentathionate ion, the overall composition of these products becomes 6S and 2Se atoms, *i.e.* the stoichiometrical ratio S/Se from the value of 4 in the initial selenopentathionate reduces to a value of 3. That means that the decomposition of selenopentathionate and accumulation of decomposition products reduces the value of

$$\phi = \frac{C_S}{C_{Se}}. \quad (5)$$

The experimentally determined kinetics of the ϕ changes when the PA 6 was treated with $K_2SeS_4O_6$

solution of different concentration and at different temperature shows (Figs. 5–8) that the decomposition of diffused selenopentathionate starts already in the first stage of sorption and then $\phi < 4$, indicating a lower stability of sorbed selenopentathionate compared with the stability of $K_2SeS_4O_6$ in the solution. The 0.05 M $K_2SeS_4O_6$ solution throughout the treatment at a temperature of 30 °C remains undecomposed, but the sorbed selenopentathionate gradually decomposes and the value of ϕ reduces with time. The reason of the reduced stability of diffused selenopentathionate may be a reduced degree of ion hydration and a higher value of pH inside the polymer, since according to the data of some authors [60, 63] the degree of acids dissociation inside a polymer is decreased. As was expected, the stability of selenopentathionate sorbed from a more acidic solution was higher and the value of ϕ in these cases was higher than in the cases when $K_2SeS_4O_6$ solutions of pH 5.6 were used.

For the quantitative estimation of sorption and diffusion, determination of selenopentathionate concentrations undecomposed in the polymer was necessary. The overall amount of selenium and sulfur sorbed by the PA 6 sample – c_{Se} and c_S respectively – were determined experimentally. The sulfur concentration in the sorbed selenopentathionate ions was $c_{S\ SPT}^p = 4C_{SPT}^p$ (coefficient 4 means the number of sulfur atoms in the ion) and its overall concentration in the polymer may be expressed as:

$$c_S = 4C_{SPT}^p + c_{S\ decomp}^p \quad (6)$$

where $c_{S\ decomp}^p$ means the concentration of the selenopentathionate decomposition product – elemental sulfur in the polymer. By analogy, the concentration of selenium in the sorbed selenopentathionate ions is

$$c_{Se} = C_{SPT}^p + c_{Se\ decomp}^p \quad (7)$$

Estimating according to equations (1) and (2) the stoichiometrical ratio of the decomposition products, we obtain:

$$\phi = \frac{c_S}{c_{Se}} = \frac{4C_{SPT}^p + 2c_{S\ decomp}^p}{C_{SPT}^p + c_{Se\ decomp}^p} \quad (8)$$

Having the values of ϕ , it was possible to calculate the apparent concentrations of Se and S in undecomposed selenopentathionate ions, v_{Se} and v_S respectively:

$$v_{Se} = \frac{c_{Se\ SPT}^p}{c_{Se}} = \frac{\phi - 2}{2}, \quad (9)$$

$$v_S = \frac{c_{S\ SPT}^p}{c_S} \quad (10)$$

The latter equation does not have a convenient analytical expression, but the dependence of v_S on

ϕ obtained by the method of modelling is shown in Fig. 9, curve 1. Using the equations (9) and (10) and having the values of ϕ (Figs. 5–8), we could find the values of v at all conditions of the experiments, and to recalculate the values of c_S and c_{Se} taken from Fig. 1–4 into the concentration of undecomposed selenopentathionate in the polymer:

$$C_{SPT}^p = \frac{1}{4} v_S c_S, \quad (11)$$

$$C_{SPT}^p = v_{Se} c_{Se} \quad (12)$$

It is worthwhile to point out that the selenopentathionate concentrations in the polymer calculated by equations (11) and (12) actually coincide, indica-

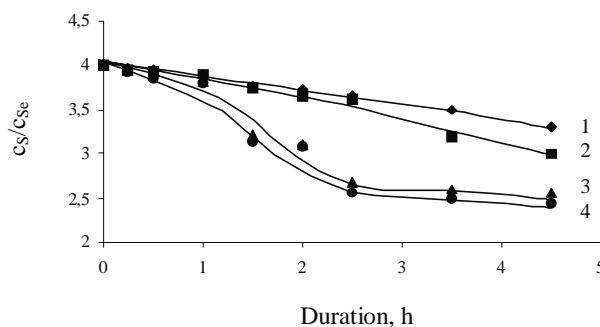


Fig. 5. The molar ratios S/Se in PA 6 films chalcogenized in $K_2SeS_4O_6$ solutions at a temperature of 50 °C. The concentration of $K_2SeS_4O_6$ solution, mol · dm⁻³: 1 – 0.025; 2 – 0.5; 3 – 0.1; 4 – 0.2

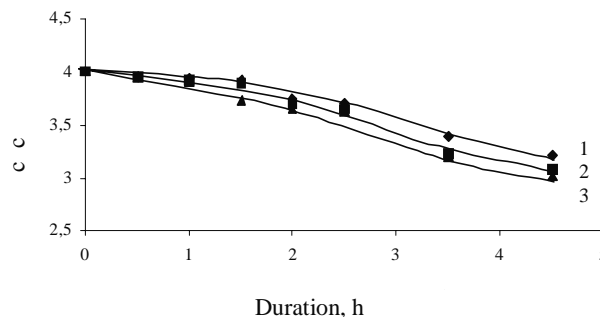


Fig. 6. The molar ratios S/Se in PA 6 films chalcogenized in $K_2SeS_4O_6$ solutions at various temperature. The temperature of $K_2SeS_4O_6$ solution, °C: 1 – 30; 2 – 40; 3 – 50

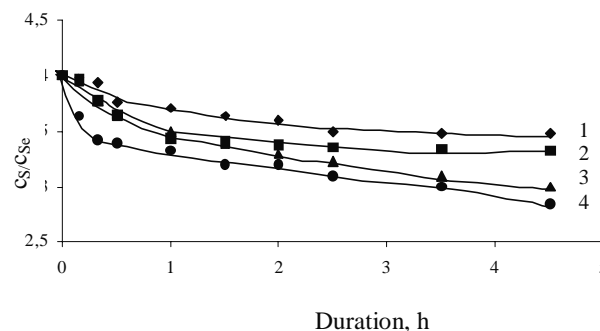


Fig. 7. The molar ratios S/Se in PA 6 films chalcogenized in $K_2SeS_4O_6$ solutions acidified with HCl at a temperature of 50 °C. The concentration of $K_2SeS_4O_6$ solution, mol · dm⁻³: 1 – 0.025; 2 – 0.5; 3 – 0.1; 4 – 0.2

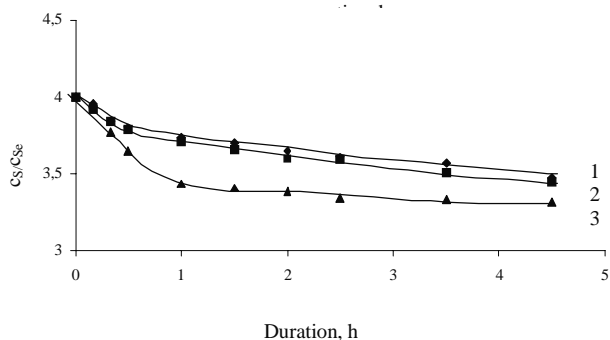


Fig. 8. The molar ratios S/Se in PA 6 films chalcogenized in $K_2SeS_4O_6$ solutions acidified with HCl at various temperature. The temperature of $K_2SeS_4O_6$ solution, °C: 1 – 30; 2 – 40; 3 – 50

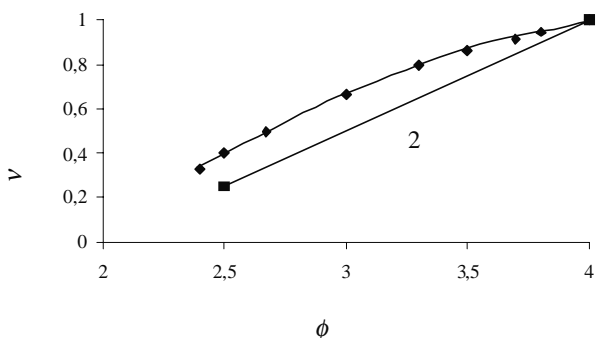


Fig. 9. Dependence of sorbed selenopentathionate selenium and sulfur concentrations (value of v) on the overall ratio of sulfur and selenium present in the polymer ϕ : 1 – v_S , 2 – v_{Se} .

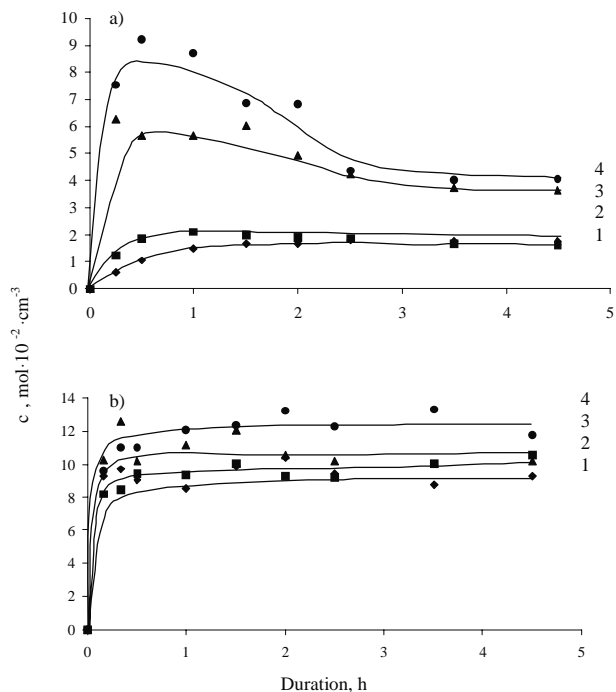


Fig. 10. Dependence of kinetics of change of undecomposed selenopentathionate concentration in PA 6 film on the concentration of $K_2SeS_4O_6$ solution. Conditions of sorption: the temperature of solution 50 °C, pH 5.6 (a) or pH 1.5 (b); the concentration of solution, mol · dm⁻³: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

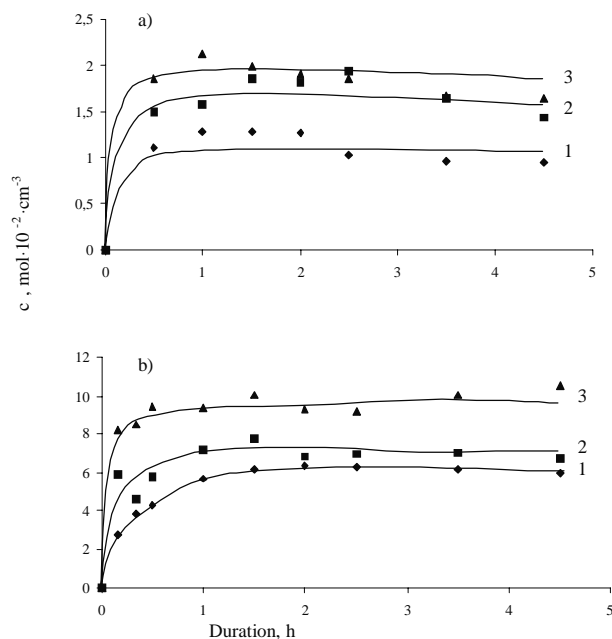
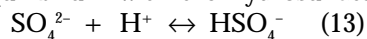


Fig. 11. Dependence of the kinetics of change of undecomposed selenopentathionate concentration in PA 6 film on the temperature of $K_2SeS_4O_6$ solution. Conditions of sorption: the concentration of solution 0.05 mol · dm⁻³, pH 5.6 (a) or pH 1.5 (b); the temperature of solution, °C: 1 – 30; 2 – 40; 3 – 50

ting that the proposed model of selenopentathionate sorption is adequate.

The curves of selenopentathionate sorption and diffusion presented in Figs. 10b and 11b are close to the Fick's diffusion, but the diffusion in the pH environment of isoelectric point of a PA 6 (Figs. 10a and 11a) does not correspond to Fick's diffusion: an increase in selenopentathionate concentration is observed at the beginning, but the decrease to a constant value was found after some duration of sorption. This phenomenon is more evident with an increase in sorption temperature and solution concentration, *i.e.* when an intensive decomposition reaction of selenopentathionate ions takes place. Such difference of sorption may be explained by the formation of a decomposition product, sulfate ion, in the centre of sorption. The sulfate ion is in equilibrium with the hydrosulfate ion:



When the solution is acidic (pH 1.5), the equilibrium of equation (13) is moved to the right and the formed moveable hydrosulfate ions, HSO_4^- , because of the concentration gradient desorbs into the solution. When the value of solution pH is increased to 5.6, the concentration of hydrogen ions in the polyamide reduces and the equilibrium of the reaction (13) moves to the left – not moveable SO_4^{2-} ions form. A low mobility of sulfate ions in polyamides was proven by our experiments and in the works of other authors. In the control experiment we kept pf PA 6 samples in a 0.2 M potas-

sium sulfate solution for 4h at the temperature of 50 °C, but no traces of sorbed sulfur were detected. Significantly, earlier sulfuric acid had been concluded to diffuse into PA 6 only in the form of hydrogen and hydrosulfate ions [64]. A great difference in the mobility of sulfate and hydrosulfate ions in the polyamide was shown in the work of J. Marshall [65].

Therefore, when the pH of solution is 5.6, the sulfate ions formed during the selenopentathionate decomposition occupy part of the sorption centers and thus reduce the sorption of undecomposed selenopentathionate ions from the solution.

The equilibrium constant of reaction (13) in the polyamide is unknown, therefore the influence of the sulfate ions in equations (5)–(12) was not taken into account, and the concentration of sorbed selenopentathionate ions calculated using these equations at the pH value 5.6 is not accurate enough. Still we can state that the concentration of selenopentathionate in the sorption process reaches its maximum and later reduces to a constant value.

The results of selenopentathionate sorption and diffusion presented in Figs. 10b, 11b correspond to Fick's diffusion and it is possible to determine the equilibrium selenopentathionate concentrations $C_{SPT\ equilibrium}^p$ in the polymer at all conditions of the experiments and using the latter to get the sorption isotherms. The

dependencies of $1/C_{SPT}^p$ on $1/c_{SPT}^{sol}$ show that the isotherms are of the Langmuir type, and they are expressed by the equation

$$C_{SPT\ equilibrium}^p = A \frac{Kc_{SPT}^t}{1 + Kc_{SPT}^t}, \quad (14)$$

where the coefficient A describes the capacity of the sorption centres of the polymer studied, and K describes the sorption system.

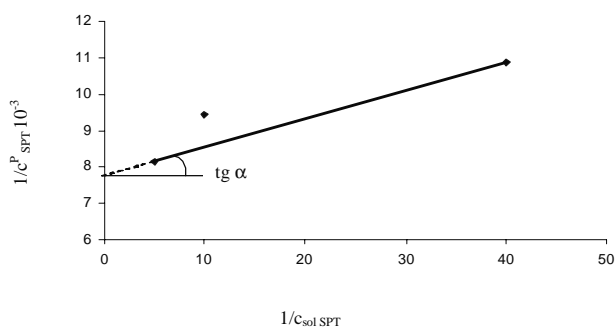


Fig. 12. The sorption isotherm

The coefficients of the sorption isotherm (from the solution with pH 1.5) calculated from the data of Fig. 12 are: $A = 0.133$ and $K = 95820.97$.

The Langmuir isotherm is characteristic of the PA 6 sorption of dyes and other electrolytes from

an acidic medium. The sorption in polyamides as a rule is an exothermic process, and it decreases with an increase of temperature. For selenopentathionate sorption the temperature dependence is principally different – the equilibrium selenopentathionate concentration increases in proportion with the increase of the temperature. Therefore, selenopentathionate sorption is an endothermic process.

The sorption of $K_2SeS_4O_6$ anions should be best at the terminal amine groups, but their content in PA 6 is not higher than $0.045 \text{ mol} \cdot \text{dm}^{-3}$ and the content accessible for the electrolytes is half as low. Therefore the amine region may sorb no more than $c_{S\ average} = 0.023 \times 4 = 0.09 \text{ mol} \cdot \text{dm}^{-3}$. The experimentally determined values of $c_{S\ average}$ (Fig. 10) show that the selenopentathionate is sorbed also by the PA 6 amide region, which is only the region of sorption from acidic solutions.

The selenopentathionate anion contains a unique chain $-O_3S-S-Se-S-SO_3^-$. Its central Se and two neighbouring S atoms are of low oxidation state and therefore can react with silver and copper cations forming the chalcogenides of these metals. On the surface of PA 6 first sorbed potassium selenopentathionate and later treated with the solutions of silver or univalent copper salts, layers of mixed sulfides and selenides of these metals are formed. The processes known before were dealing only with the individual coatings of sulfides or selenides. However, the mixed coatings may have special properties. The regularities established in this complicated system enable to regulate the composition of sorption products and the properties of coatings, as well as the technological process.

CONCLUSIONS

1. The polyamide PA 6 sorbs potassium selenopentathionate, $K_2SeS_4O_6$, from its water solutions. The sorption process is endothermic (the concentration of sorbed electrolyte increases with an increase of the temperature) and is described by the Langmuir type isotherm. The sorption increases with a decrease in the pH value of the solution.

2. The chemical stability of sorbed $K_2SeS_4O_6$ is lower compared with its stability in water solution, therefore apart the selenopentathionate, the decomposition products of this compound (elemental selenium, sulfur, sulfate and sulfite ions) are present in the polymer. The elemental selenium liberated changes colour of the polyamide sample from yellow to red. The decomposition rate decreases with a decrease in the solution concentration, temperature and pH value.

3. By means of chemical analysis and by modelling of the decomposition process it has been determined that the diffusion and sorption of undecomposed selenopentathionate ions at the pH value 1.5

is close to Fick's diffusion, but at pH 5.6 which is close to the isoelectric point of polyamide PA 6 the diffusion does not correspond to Fick's diffusion, as the concentration of undecomposed selenopentathionate reaches the maximum value but on prolongation of sorption reduces. Such difference is explained by the fact that the moveable hydrosulfate ions are the decomposition products of selenopentathionate at the high acidity of the solution and they do desorb into a solution. While increasing the pH of the solution more immobile sulfate ions are formed; they occupy the sorption centers and reduce the further sorption of selenopentathionate ions from a solution.

4. The central Se and two neighbouring S atoms of the selenopentathionate ions $^{-}O_3S-S-Se-S-SO_3^{-}$ are of a low oxidation state and do not react with the silver and copper cations forming the chalcogenides of these metals, allowing the formation of coatings of metal chalcogenides on the surface of polyamide PA 6 after the sorption of potassium selenopentathionate.

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KALIO SELENOPENTATIONATO SORBCIJA PANAUDOJUS POLIAMIDÀ PA 6

S a n t r a u k a

Buvo tirta kalio selenopentationato $K_2SeS_4O_6$ sorbcija iš jo vandens tirpalo panaudojus poliamidà PA 6. Nustatytas mažesnis poliamido sorbuotas $K_2SeS_4O_6$ nei vandens tirpale, tačiau jo cheminis stabilumas didėja mažinant tirpalo pH. Poliamide, be sorbuotos druskos, kaupiasi ir nejudrūs skilimo produktai – elementinis selenas ir siera. Chemine bandiniø analize ir skilimo proceso modeliavimu nustatyta nesuskilusio sorbuoto selenopolitionato jonø priklausomybė nuo tirpalo pH, koncentracijos ir temperatūros. Endoterminis $K_2SeS_4O_6$ sorbcijos procesas iš parūgðtinto tirpalo aprašytas Langmuir tipo izoterma. Aptartas sorbcijos mechanizmas. Parodyta gautø rezultatø svarba polimero – metalo chalkogenidø kompozitø gamybai.