

Temperature Effect on the Sulfur Adsorption-Diffusion Processes from Potassium Pentathionate Solutions by Polycaproatamide Film

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The temperature effect on the sulfur adsorption-diffusion processes by polycaproatamide film to 4 h exposed in the acidified $0.15 \text{ mol} \cdot \text{dm}^{-3}$ water solutions of potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6$, is investigated by methods of UV, IR absorption spectroscopy and chemical analysis. The pentathionate anions $\text{S}_5\text{O}_6^{2-}$ were found to sorb into a polymer. IR absorption spectra were investigated in the region of the wavenumbers $200 \text{ cm}^{-1} - 1400 \text{ cm}^{-1}$. The characteristic absorption peaks were found in the regions $240 - 245$, $337 - 385$, $416 - 470$, $523 - 538$, $580 - 611$, $1020 - 1022$, $1170 - 1268 \text{ cm}^{-1}$ and assigned, respectively, to $\delta(\text{SSS})$, $\gamma_t(\text{SO}_3)$, $\nu(\text{S-S})$, $\delta_{\text{as}}(\text{O-S-O})$, $\delta_s(\text{O-S-O})$, $\nu_s(\text{S-O})$ and $\nu_{\text{as}}(\text{S-O})$. The kinetic study of sulfur adsorption-diffusion processes showed that sorbed pentathionate ions concentration in a polymers film sample increases with increasing temperature of the $\text{K}_2\text{S}_5\text{O}_6$ solution and the duration of treatment. Sulfur concentration in the polymer, depends on the conditions for the process of sorption and it varies from $0.94 \text{ mg} \cdot \text{cm}^{-3}$ to $7.64 \text{ mg} \cdot \text{cm}^{-3}$. The estimated apparent sulfur diffusion coefficients in polycaproatamide increase with increasing temperature of the potassium pentathionate solution. The concentration of sulfur in a polymer film is no limited by the stage of pentathionate decomposition, since the apparent activation energy of pentathionate diffusion in polycaproatamide is four times smaller than that needed for the polythionate decomposition.

Keywords: polycaproatamide, potassium pentathionate, sulfuration, diffusion.

INTRODUCTION

The modification of polymers by formation on their surface of thin layers of sulfides with important physical properties leads to obtaining of new class of materials – composites with different properties. Metal sulfide thin films have number of applications in various devices such as solar cells, super ionic conductors and as semiconductors, photo-detectors, photo-thermal conversion, electro conductive electrodes, microwave shielding coating [1–4], as polarizers of infrared radiation [5], as active absorbents of radio waves [6].

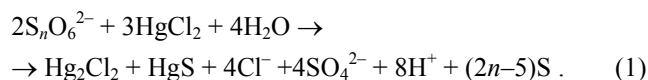
Various methods were used for the formation of metal sulfides layers on various dielectrics and on the polymers: vacuum evaporation [7, 8], activated reactive evaporation, spray pyrolysis, electroless deposition, successive ionic layer adsorption and reaction, chemical bath deposition [9]. Adsorption-diffusion method [10] is one of the simple and promising methods. Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various sulfuration agents, *e.g.*, sulfur solutions in organic solvents [11], sodium polysulfide (Na_2S_n , $n = 4.8$) aqueous solutions [12], polythionic acid ($\text{H}_2\text{S}_n\text{O}_6$, $n = 9 - 45$) aqueous solutions [13]. To prevent environmental pollution with vapours of toxic solvents and to avoid swelling of some polymers in organic solvents, the use of sulfides solutions is limited due to their high alkalinity. The synthesis of sulfurous polythionic acids appears to fairly complicated and prolonged (to 2 days), and it is based on the reaction of interaction of toxic hydrogen sulfide and thiosulfurous acid. The aqueous solutions of polythionic acids are unstable and they rapidly decompose with the

isolation of elemental sulfur. Recently, an adsorption-diffusion method for the formation of thin metal sulfide layers on the surface of polycaproatamide (PKA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $\text{S}_n\text{O}_6^{2-}$, ($n \leq 6$) has been under extensive investigation [14–16]. However, in the solutions of lower polythionates, *i.e.*, trithionate, $\text{S}_3\text{O}_6^{2-}$, and tetrathionate, $\text{S}_4\text{O}_6^{2-}$, an insufficient quantity of sulfur in the film is obtained, in order to form the sufficiently electro-conductive layers of metal sulfide [16].

The aim of present work was to put in the whole and to discuss the results received by us during studies of the adsorption-diffusion of pentathionate ions containing a chain of divalent sulfur atoms of low oxidation state $^-\text{O}_3\text{S-S-S-SO}_3^-$ [17], into PKA films and to create conditions for the formation of Me_nS layers on the surface of this polymer by a sulfured PKA treatment with the metal salt solution.

EXPERIMENTAL

In searching for new sulfur precursor we have chosen the potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6$, as a source of sulfur for its inclusion into polycaproatamide. Potassium pentathionate hemitrihydrate, $\text{K}_2\text{S}_5\text{O}_6 \cdot 1.5 \text{ H}_2\text{O}$, was prepared from the As_2O_3 and potassium thiosulfate [18, 19] and chemically analyzed according to equation (1) [20]:



The obtained solution was titrated by $0.1 \text{ mol} \cdot \text{dm}^{-3}$ solution of KOH. Four hydrogen ions are fallen to one mole of polythionate. The purity of obtained potassium pentathionate was 99.3 %. The salt was stored in the desiccators over sulfuric acid.

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The layers of chalcogens were deposited on PKA film (specification TY 6-05-1775-76, grade PK-4, Russia) tape 70 μm thick. This film is close to a nonporous material, because the pores of PKA are much less than 1.5 nm. The porosity was measured by the BET method using a Quantasorb (USA). Prior to the experiments, samples of the PKA film of 15 mm $\times$ 70 mm in the size were boiled in distilled water for two hours to remove the remainder of the monomer. After that they have been dried by filter paper and than in the desiccators over CaCl_2 for 24 h.

PKA films were sulfured in a thermostatic vessel using a continually stirred acidified ($0.1 \text{ mol} \cdot \text{dm}^{-3}$ HCl , $\text{pH} \sim 1.5$) freshly prepared $0.15 \text{ mol} \cdot \text{dm}^{-3}$ $\text{K}_2\text{S}_5\text{O}_6$ solutions up to 4 h at a temperature of $0^\circ\text{C} - 20^\circ\text{C}$ (at a temperature of 0°C – in the refrigerator). Such interval of temperature was chosen because of the stability of potassium pentathionate in a solution.

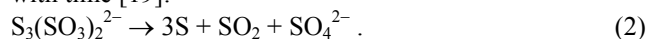
After a certain time of exposure (15 minutes to 4 hours) in the solution of $\text{K}_2\text{S}_5\text{O}_6$, the PKA film samples were removed, rinsed with distilled water, dried with filter paper, left over CaCl_2 for 24 h and then used in further experiments and analysis.

The UV spectra (200 nm – 400 nm) were recorded on a Spectronic^R GenesysTM 8 UV/Visible spectrophotometer with compensation of the absorbion of PKA. IR spectra ($200 \text{ cm}^{-1} - 1300 \text{ cm}^{-1}$) were recorded on a Perkin-Elmer FT-IR Spectrum GX spectrophotometer by the compensation method.

The concentration of sulfur in PKA film samples in the form of sulfates was determined turbidimetrically [21]. Before the analysis, samples of PKA strips with sulfur containing thin films have been mineralized. Samples were treated under heating with concentrated HNO_3 to destroy PKA and to oxidize sulfur compounds to sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. Sulfate ions in the range $1 \text{ mg} \cdot \text{dm}^{-3} - 15 \text{ mg} \cdot \text{dm}^{-3}$ may be readily determined by utilising the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium sulfate. A glycerol-ethanol solution helped to stabilise the turbidity of the barium sulfate suspension. The measurement of the intensity of the transmitted light as a function of the concentration of the suspension of BaSO_4 was carried out photometrically with a KFK-4 (Russia) photoelectric colorimeter at a wavelength $\lambda = 400 \text{ nm}$. The standard deviation of the method with the photometric procedure in the range of concentrations from $5 \text{ mg SO}_4^{2-} \cdot \text{dm}^{-3}$ to $10 \text{ mg SO}_4^{2-} \cdot \text{dm}^{-3}$ is $\pm 8\%$.

ANALYSIS AND RESULTS

Previous experiments [14] have shown that the sorption from the solutions of a lower concentration was too slow and insufficient, and at the higher temperatures (higher 30°C) the stability of pentathionate solution was insufficient, since, gradual spontaneous decomposition of polythionate with the liberation of elemental sulfur occurs with time [19]:



The nature of sulfur-containing particles adsorbed by a PKA film at temperature $0^\circ\text{C} - 20^\circ\text{C}$ was studied by means of UV and IR absorption spectroscopy of the

polymer films treated in an aqueous potassium pentathionate solution. A chain of three divalent sulfur atoms $\text{O}_3\text{S}-\text{S}-\text{S}-\text{SO}_3^-$ of low oxidation state is present in the anion of potassium pentathionate. Optical absorption spectra of sulfides thin films on PKA revealed that films have high absorbance (10^4 cm^{-1}) indicating direct band gap transition. However, percentage transmission (90 %) is maximum at $\lambda = 250 \text{ nm}$. According to the data of a study of the UV absorption spectra of lower potassium polythionates [22, 23] the absorption peaks of polythionate ions are most intensive at 256 nm ($\log E = 3.15$) and 295 nm ($\log E = 2.45$; E – molar extinction coefficient). In addition, the UV absorption spectra of nanofilms, formed using single precursor $\text{K}_2\text{S}_5\text{O}_6$ are very closely identical. The UV absorption spectra of PKA samples sulfured for different periods of time in a solution of $\text{K}_2\text{S}_5\text{O}_6$ at 20°C temperature are presented in Figure 1, a, where the spectrum of PKA substrate is added for comparison. Two absorption peaks are observed in these spectra: at 250 nm as a peak, and as less intense and shallower band is present at $\lambda = 295 \text{ nm}$. Thus UV absorption spectra recorded by us confirm again that sulfur is adsorbed by PKA films in the form of pentathionate ions. The intensity of peak of absorption spectra increases with an increase of the exposure time. The UV absorption spectra of PKA samples sulfured for periods of 4h time in a solution of $\text{K}_2\text{S}_5\text{O}_6$ at different temperature $0^\circ\text{C} - 20^\circ\text{C}$ are presented in Figure 2, a, where the spectrum of PKA substrate is added for comparison. The intensity of absorption peaks in the spectra increases with an increase of temperature of a polymer treatment with a solution of potassium pentathionate. With a decrease temperature of the solution, absorption peaks in the spectra it is moved to the side of smaller values $\lambda = 240 \text{ nm}$.

The IR spectra of PKA surface before and after sulfuration process shows that, a new material formed or bonded on the surface of PKA after sulfuration. In particular, IR spectra of all prepared samples showed the following common features (Fig. 1, b, Fig. 2, b). It was found that the peaks of most intensive bands in the IR spectra of PKA samples, sulfured in a $\text{K}_2\text{S}_5\text{O}_6$ solution, recorded by the compensation method (with PKA absorption eliminated) were present in the intervals of the wavenumber 240 – 245, 337 – 385, 416 – 470, 523 – 538, 580 – 611, 1020 – 1022, 1170 – 1268 cm^{-1} . For identification of characteristic vibration frequencies IR spectra were compared with the IR spectra of $\text{K}_2\text{S}_5\text{O}_6 \cdot 1.5 \text{ H}_2\text{O}$ [24].

According to the literature data [24 – 27] the bands in the range of the wavenumbers $1000 \text{ cm}^{-1} - 1250 \text{ cm}^{-1}$ correspond to vibration frequencies of the SO band: in the range of $1170 \text{ cm}^{-1} - 1268 \text{ cm}^{-1}$ they correspond to the asymmetric valence S–O vibrations, $\nu_{\text{as}}(\text{S}-\text{O})$. The peak of $\sim 1021 \text{ cm}^{-1}$ corresponds to the symmetric valence S–O vibrations, $\nu_{\text{s}}(\text{S}-\text{O})$. That the absorption bands the symmetric valence vibrations of the S–O band not split shows, that the symmetry of the pentathionate ion is not disrupted.

The vibration modes (the scissoring mode) of the O–S–O group occur as a strong band between $400 - 650 \text{ cm}^{-1}$ [28]. Therefore the peak of $\sim 610 \text{ cm}^{-1}$ corresponds to the

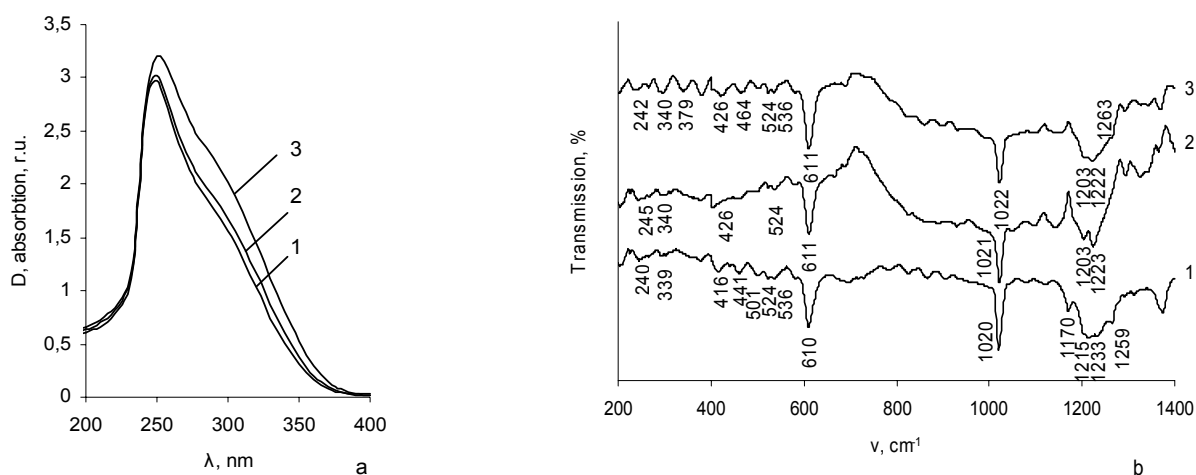


Fig. 1. UV (a) and IR (b) absorption spectra of PKA films sulfured in $0.15 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$ solution in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ (pH 1.5) at 20°C temperature of different time. Time of duration, h: 1 – 2; 2 – 3; 3 – 4

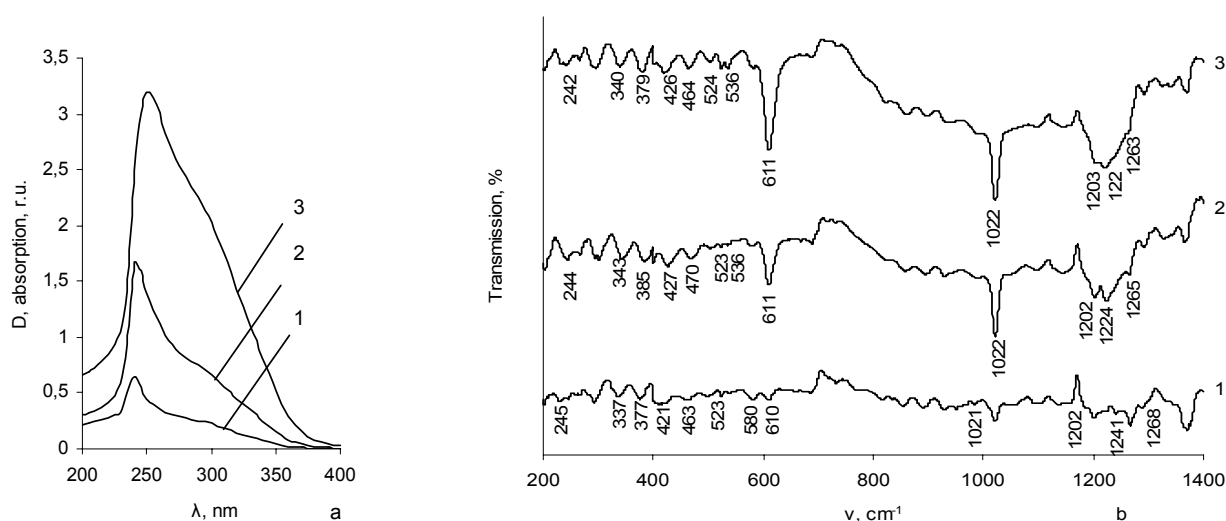


Fig. 2. UV (a) and IR (b) absorption spectra of PKA films sulfured in $0.15 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$ solution in $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ (pH 1.5) at time of 4 h of different temperature. The temperature of PKA sulfuration, $^\circ \text{C}$: 1 – 0; 2 – 10; 3 – 20

symmetric deformation of O–S–O vibrations, $\delta_s(\text{O–S–O})$, and the peak in the $498 \text{ cm}^{-1} - 538 \text{ cm}^{-1}$ interval corresponds to the asymmetric deformation of O–S–O vibrations, $\delta_{as}(\text{O–S–O})$. Comparing the frequencies of the corresponding absorption bands of the recorded spectra with the spectrum of pure salt, it was observed the tendency of their displacement to the side of smaller values. Authors of work [29] explain the displacement of the spectra of the absorption to the side of smaller frequencies in comparison with their position in the pure salt, as following. Polycapromamide by their SO_3^{2-} group forms hydrogenous bond with the chains of polymer, and as a energy S–O the connection in $\text{S}_3(\text{SO}_3)_2^{2-}$ ion becomes weaker and the peaks of absorption of fluctuations in the spectrum are moved to the side of lower energy – lower frequencies.

The IR absorption spectra of PKA samples sulfured for different periods of time in a solution of $\text{K}_2\text{S}_5\text{O}_6$ at 20°C temperature are presented in Figure 1, b. It is shown, that the intensity of the peaks of IR spectra increases with an increase of the treatment time. From Figure 2, b, evidently, that the intensity of absorption peaks in the spectra increases with an increase of temperature because at the

higher temperature the polymer sorbs more sulfur from the precursor solution potassium pentathionate.

A variety of new effects become important as the interactions of inorganic sorbates with PKA surface is concerned, e.g. the electrostatic interaction of sorbate ions, namely $\text{S}_3(\text{SO}_3)_2^{2-}$ with charged sites of the sorbent, such as the ionized polyamide functional groups $-\text{CO}-\text{NH}-$ and $-\text{NH}_2$, and exchange reactions of these ions with ligands previously bonded to the polymer surface or their ionized functional groups. Probably, the surface reaction forms a second adsorbed species, which is different from inorganic ions dissolved near the surface.

The S–S stretching frequency gives rise only to a rather weak absorption in the infrared region, probably because the symmetrical vibration of the bond involves little change of dipole moment. It is strong and easily detected in the Raman spectrum, and usually occurs between 440 cm^{-1} and 510 cm^{-1} . The vibration frequencies are consistent with an unbranched, nonplanar structure. The fact that the S–S stretching frequency, although weak, occurs in the infrared, excludes a planar, centrosymmetric trans form for disulfides. The S–S vibration frequency in the spectrum occurs at about $421 \text{ cm}^{-1} - 470 \text{ cm}^{-1}$.

The S–S linkage absorption is unlikely to be of any value in infrared analysis except in a very few special instances. It occurs as a very weak band in the 500 cm^{-1} – 400 cm^{-1} region and is identifiable only because the corresponding Raman line is very strong.

The low intensity peaks at 422 cm^{-1} and 463 cm^{-1} can be attributed to $\nu(\text{SS})$ vibrations.

The band in the range 242 cm^{-1} – 245 cm^{-1} corresponds to S–S–S vibrations, $\delta(\text{SSS})$, the peak of 337 cm^{-1} – 385 cm^{-1} corresponds to vibrations of $\gamma_r(\text{SO}_3)$ [28].

These results confirm that the sorption of pentathionate ions by a PKA occurs during the polymer treatment with an acidified solution of $\text{K}_2\text{S}_5\text{O}_6$.

From point of view of the mechanism of formation of nanofilms on PKA surface, the key problem is that the nanofilms obtained are coated with a film of chalcogens that blocks the surface sites, modifying their surface properties and particularly their electrical properties. These, in turn, are responsible for the network formation.

The kinetics of sulfur containing particles adsorption-diffusion process from potassium pentathionate solution of 0.15 mol dm^{-3} into PKA films was investigated. Chemical analysis of PKA samples sulfured in a $\text{K}_2\text{S}_5\text{O}_6$ solution showed that the concentration of sulfur adsorbed by a polymer depended at the temperature of the sulfuration solution and exposure time.

Figure 3 shows the sulfur concentration in the PKA films investigated as a function of exposure time. It was found, that the sulfur concentration (c_s , $\text{mg}\cdot\text{cm}^{-3}$) in the samples, kept in potassium pentathionate solution at 0, 10 and 20°C , increases with time. Moreover, the adsorption-diffusion process becomes faster with increasing temperature resulting in higher sulfur concentration in the film. The sulfur concentrations close to saturation ($c_{s\infty}$, $\text{mg}\cdot\text{cm}^{-3}$) of all films are shown in Table 1. The highest values of $c_{s\infty}$ were obtained in samples treated in potassium pentathionate solution at 20°C . The sulfur concentrations found in samples treated at 20°C are twofold or five fold higher, than those found in samples treated at 10°C and 0°C .

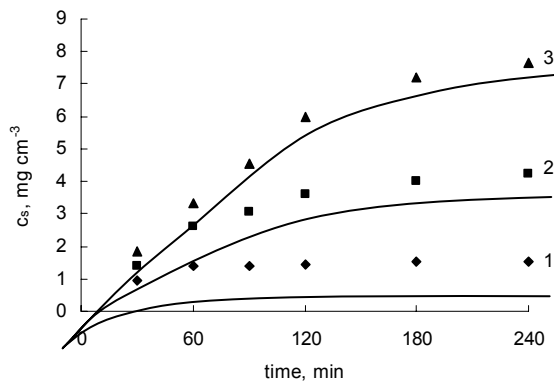


Fig. 3. Dependence of sulfur concentration (c_s) in polycapraamide on its exposure time in 0.15 mol dm^{-3} solution of $\text{K}_2\text{S}_5\text{O}_6$ in $0.1\text{ mol}\cdot\text{dm}^{-3}$ HCl at different temperatures. Temperature, $^\circ\text{C}$: 1 – 0; 2 – 10; 3 – 20

The concentration of sulfur sorbed at a temperature of 10°C and 20°C increases significantly with increasing the temperature of potassium pentathionate solution (Fig. 3).

The values of sulfur concentration obtained in PKA (up to $\sim 7.64\text{ mg}\cdot\text{cm}^{-3}$) thus, the results received in the present describe the conditions for the formation of metal sulfide layers on a surface of polycapraamide PKA.

Table 1. Dependence of sulfur concentration close to saturation $c_{s\infty}$ in polycapraamide treated in $\text{K}_2\text{S}_5\text{O}_6$ solution at different temperatures, apparent $\text{S}_5\text{O}_6^{2-}$ ions diffusion coefficient D and apparent adsorption heat $-\Delta H_{\text{ads}}$

Temperature, $^\circ\text{C}$	$c_{s\infty}$, $\text{mg}\cdot\text{cm}^{-3}$	$D\cdot 10^{-11}$, $\text{cm}^2\cdot\text{s}^{-1}$	$-\Delta H_{\text{ads}}$, $\text{kJ}\cdot\text{mol}^{-1}$
0	1.52	2.2	
10	4.25	3.3	66.64
20	7.64	4.7	47.01

After lowering the temperature of the sulfuration solution from 20°C to 0°C , $c_{s\infty}$ in polycapraamide film samples decreases clearly: from 20°C to 10°C by a factor of 1.8, from 10°C to 0°C – 2.8 times. As it is evident from the values presented, sulfur adsorption-diffusion in polycapraamide is less affected by the solution temperature. This is shown by the lowest value of the apparent adsorption heat $|\Delta H_{\text{ads}}|$ (Table 1) obtained. We calculated the apparent adsorption heat by the Langmuir equation [30]. Examples representing the sulfur adsorption for the determination $|\Delta H_{\text{ads}}|$ are shown in Figure 4. The apparent adsorption heat was negative, because the adsorption of a molecule on a surface was an exothermic process [30]. We found that $|\Delta H_{\text{ads}}|$ increases at lower solution temperatures: it is almost 1.4 times smaller for temperature interval from 10°C to 0°C below temperature interval from 20°C to 0°C .

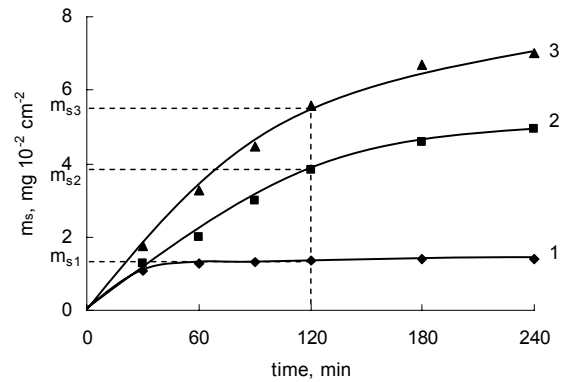


Fig. 4. The dependence of adsorbed sulfur amount in polycapraamide on exposure time in solution of $\text{K}_2\text{S}_5\text{O}_6$ ($c = 0.15\text{ mol}\cdot\text{dm}^{-3}$) at temperatures. Temperature, $^\circ\text{C}$: 1 – 0; 2 – 10; 3 – 20

To characterize the process kinetically, an apparent diffusion coefficient (D , $\text{cm}^2\cdot\text{s}^{-1}$) of sulfur diffusion into polycapraamide was calculated. Since the diffusible substance seeks to get uniformly distributed, D becomes a measure of the rate at which the system manages to reduce the difference in concentrations. This rate is related to certain system parameters, characterizing the thermal mobility of diffusible particle, as a part of the diffusion environment [31, 32].

Calculations of diffusion process parameters are based on Fick's second law [30, 31]. Until the front of the diffusate has not reached the centres of the film, thus, when $c_{s\tau}/c_{s\infty} > 0.5$, the apparent coefficients of sulfur diffusion in polycapraamide are calculated according to the inclination angle [33] of the curves $1 - c_{s\tau}/c_{s\infty} = f(\tau^{0.5})$ by means of Boltzmann resolution for semi-infinite environment as expressed by

$$1 - c_{s\tau}/c_{s\infty} = \frac{\pi}{l} \sqrt{\frac{D\tau}{8.2}}, \quad (3)$$

where: l is the thickness of the film, $c_{s\tau}$ is the concentration of sulfur in the sample in period τ , and $c_{s\infty}$ is the sulfur concentration close to saturation in the sample. The calculated error in D is in the range of $\pm 10\%$.

The highest D value was obtained for the sample sulfured at temperature 293 K $D = 2.2 \cdot 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$. Values of D for films increase with increasing temperature of solution (Table 1).

The data in Figure 5 show, that the dependence $\ln D = f(1/T)$ on the temperature was found to be linear. Therefore, the apparent activation energy E was calculated between 273 K – 293 K by the Arrhenius equation is $25.45 \text{ kJ} \cdot \text{mol}^{-1}$. These values are nine to four times smaller than the energy needed for decomposition of polythionate ($\sim 100 \text{ kJ} \cdot \text{mol}^{-1}$) [34], thus, the amount of sulfur in polycapraamide films is no limited by the stage of pentathionate ion decomposition.

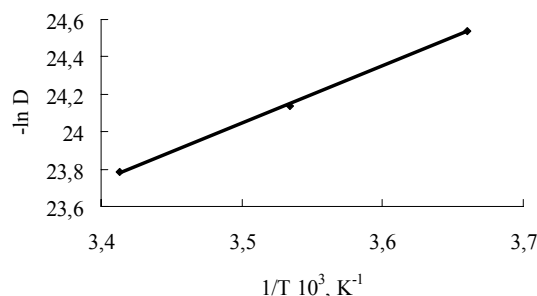


Fig. 5. Dependence of apparent coefficient (D) of sulfur diffusion into polycapraamide on the temperature of $\text{K}_2\text{S}_5\text{O}_6$ solution

The obtained results lead to the conclusion that solutions of potassium pentathionate at 20°C temperature are good sulfuring agents for polycapraamide films.

CONCLUSIONS

1. The UV (200 nm – 400 nm) absorption spectral data at 240 nm – 250 nm as a clear peak and as less intense and shallower band is present at $\lambda = 295 \text{ nm}$ confirm that sulfur is sorbed by PKA films in the form of pentathionate ions.
2. The sorption of pentathionate ions, $\text{S}_5\text{O}_6^{2-}$, from $0.15 \text{ mol} \cdot \text{dm}^{-3}$ water solutions of potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6$, in 0.1 mol dm^{-3} HCl by polycapraamide PKA films has been studied by IR ($200 \text{ cm}^{-1} - 1300 \text{ cm}^{-1}$) absorption spectra. IR spectra of modified PKA showed that the new material was chemically bonded with PKA functional groups after sulfuration. The peaks in the IR spectra of the

pentathionate anions sorbed into a polycapraamide were found in the frequency intervals 240 – 245, 337 – 385, 416 – 470, 523 – 538, 580 – 611, 1020 – 1022, $1170 - 1268 \text{ cm}^{-1}$ and assigned to the $\delta(\text{SSS})$, $\gamma_t(\text{SO}_3)$, $\nu(\text{S-S})$, $\delta_{\text{as}}(\text{O-S-O})$, $\delta_s(\text{O-S-O})$, $\nu_s(\text{S-O})$, $\nu_{\text{as}}(\text{S-O})$ respectively.

3. The sulfur concentration in polycapraamide increases with increasing the temperature of the potassium pentathionate solution and the duration of polymer treatment.
4. Apparent coefficient of sulfur diffusion in polycapraamide increases from $2.2 \cdot 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ to $4.7 \cdot 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ with increasing temperature of the potassium pentathionate solution.
5. The concentration of sulfur in a polymer film is not limited by the stage of pentathionate decomposition, since the apparent activation energy of pentathionate diffusion in polycapraamide is four times smaller than that needed for the polythionate decomposition.

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