PREPARATION, SOLUBILITY, INFRARED SPECTRA AND RADIOLYSIS OF TETRAMETHYLAMMONIUM HYDROGENSELENATE MONOHYDRATE AND LITHIUM TETRAMETHYLAMMONIUM SELENATE TETRAHYDRATE

David Havlíček[a1],*, Libor Turek[a], Jiří Plocek[a,b] and Zdeněk Mička[a2]

[a] Department of Inorganic Chemistry, Faculty of Science, Charles University,
Albertov 2030, 128 43 Prague 2, Czech Republic; e-mail: [1] havlicek@natur.cuni.cz,
[2] micka@natur.cuni.cz

[b] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic,
250 68 Řež near Prague, Czech Republic; e-mail: plocek@iic.cas.cz

Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Solubility in the $(Me_4N)_2SeO_4$–H_2SeO_4–H_2O and $(Me_4N)_2SeO_4$–Li_2SeO_4–H_2O systems were studied. The new compounds, tetramethylammonium hydrogenselenate monohydrate ($(Me_4N)HSeO_4 \cdot H_2O$) and lithium tetramethylammonium selenate tetrahydrate ($Li(Me_4N)SeO_4 \cdot 4H_2O$), have been found in these systems. Both substances were characterised by chemical analysis and IR molecular spectroscopy. Both of the title substances decompose under the influence of X-radiation and, thus, their structures cannot be determined. The radiolysis of both substances was studied in greater detail. Tetramethylammonium hydrogenselenate monohydrate is dehydrated by X-radiation to form the anhydrous salt. The reaction is controlled by first-order kinetics with a rate constant of $1.30(3) \times 10^{-3}$ s^{-1}.
Keywords: Tetramethylammonium salts; Hydrogenselenates; Selenates; Infrared spectroscopy; Radiolysis; Double salts; Solubility diagrams; Kinetics.

The alkaline selenate–selenic acid–water and alkaline selenate–lithium selenate–water systems were recently studied (refs[1,2] and references therein). These systems were studied in order to determine the crystallisation field and, thus, the conditions for the preparation of all the acidic and double salts existing in these systems (i.e. $CsHSeO_4$, $Cs_3H(SeO_4)_2$, $CsH_3(SeO_4)_2$, $CsLiSeO_4 \cdot 1/2H_2O$, $Cs_3Li(SeO_4)_2 \cdot 1/2H_2O$, $Li(NH_4)SeO_4$[1,2] and possibly also acidic double salts of the $X_4LiH_3(SeO_4)_4$ (X = K, Rb, Cs) type and to study their properties, especially in relation to possible phase transitions, leading to phases with important dielectric properties, which have been observed

in the past for some selenates (e.g. tetracesium lithium trihydrogen tetrakis-(selenate)[3]). Phases with dielectric properties, derived from the structure of β-K_2SO_4, mostly contain rubidium or cesium cations (e.g. refs[4–11]), which are usually quite expensive. This work was originally intended for replacement of the larger alkaline cation in above mentioned systems with selenic acid and lithium selenate by the tetramethylammonium cation, which is more than twice as large compared to the large cations of the alkaline metals or the ammonium cation (347 pm (ref.[12]) for the radius of Me_4N^+ compared with 148 pm for Rb^+, 165 pm for Cs^+ and 143 pm for NH_4^+ (ref.[12])).

Tetramethylammonium selenate was first described in the literature as octahydrate and tetrahydrate[13]. The tetrahydrate is isostructural with the corresponding sulfate, which solid-state structure is known[14]. Its lattice parameters were determined from powder data. The lattice parameters of the octahydrate[13] were determined by single crystal X-ray diffraction. Sato et al.[15] studied anhydrous tetramethylammonium selenate in terms of the "proton spin-relaxation time" based on the temperature dependence of the solid-state ^{1}H NMR spectra and its phase transitions through a combination of differential thermal analysis with powder X-ray diffraction. Malchus and Jansen[16] solved the structure of this substance and, in the same work, studied the infrared and Raman spectra and thermal analysis in combination with mass spectroscopy. Anhydrous tetramethylammonium hydrogenselenate was described by Zakharov et al.[17] in three crystalline forms. Structures and phase transitions of all the modifications were described. Hydrated tetramethylammonium hydrogenselenates and double lithium tetramethylammonium selenates have been mentioned in the literature only in our preliminary communication[18]. Of analogous sulfur compounds, only anhydrous tetramethylammonium hydrogensulfate has been described[19–21].

This work describes the results of a study of the solubility in the $(Me_4N)_2SeO_4$–H_2SeO_4–H_2O and $(Me_4N)_2SeO_4$–Li_2SeO_4–H_2O systems and a study of the two substances formed in these systems that have previously not been described, $(Me_4N)HSeO_4·H_2O$ and $Li(Me_4N)SeO_4·4H_2O$, using infrared molecular spectroscopy and powder X-ray diffraction. It was found that both substances undergo decomposition under X-radiation. Thus, a special chapter is devoted to the kinetics of radiolysis of tetramethylammonium hydrogenselenate monohydrate.

EXPERIMENTAL

Chemicals. Hydrated tetramethylammonium selenate was obtained by neutralisation of a solution of tetramethylammonium hydroxide (Aldrich) using dilute selenic acid (BDH,

England). The dilute solution was reduced to a minimal volume in a vacuum evaporator. The white amorphous material was recrystallised from a minimum amount of water at ca. 50 °C. Crystallisation proceeded in a desiccator over P_2O_5. The separated crystals were filtered off on a glass filter and washed with diethyl ether. According to elemental analysis, the composition did not correspond exactly to the octahydrate, because of partial spontaneous dehydration to the tetrahydrate (as demonstrated by powder diffraction)[13]. The fresh and analysed samples have been used for all further experiments.

Lithium selenate was prepared by neutralisation of a lithium hydroxide (Lachema) solution with dilute selenic acid, with potentiometric indication of the equivalence point. The solution formed was filtered and concentrated on a water bath for crystallisation. The precipitated monohydrate was dehydrated for 1.5 h at 160 °C to form anhydrous salt (for Li_2SeO_4 calculated: 50.3% Se, 4.4% Li; found: 49.8% Se, 4.2% Li).

All other used chemicals employed in this work were of p.a. purity.

Solubility diagrams. Solubility was studied by analysis of the liquid phase in samples of the system with a selected overall composition. The samples were thermostatted at 30 °C and shaken occasionally. Establishing of equilibrium was monitored by measuring the refractive index and required ca. 20 days. The composition of the equilibrium solid phase was calculated from the known overall composition of the sample and the determined composition of the liquid phase.

Powder X-ray diffractograms. The X-ray diffractograms were measured on a URD-6 diffractometer (Freiberg, Germany) in the range 2θ 10–50° using CuKα radiation to identify the solid phases formed in the studied systems. For this purpose, recordings were made in the continuous regime (sample irradiation time up to 20 min). Attempts to obtain good recordings in the stepwise regime (irradiation time of several hours) were accompanied by gradual decomposition of the samples. The experimental details of this decomposition are described below.

Infrared spectra. Infrared spectra were measured using an ATI Mattson Genesis FTIR spectrometer with AgCl windows in Nujol (400–4000 cm^{-1}) and Fluorolube (1300–4000 cm^{-1}) suspensions.

Analytical methods. The content of selenic acid in the samples was determined alkalimetrically using 0.05 M NaOH with potentiometric indication of the equivalence point. Selenium was determined by the modified method according to Blanka[22] by titration of bromine released in the reaction of Se^{VI} with KBr using 0.05 M hydrazine sulfate with potentiometric indication of the equivalence point. Lithium was determined by AAS method on a Varian SpectrAA 300/400 instrument at a wavelength of 670.8 nm. Tetramethylammonium was determined gravimetrically using Reinecke salt[23]. The content of water of crystallisation was determined from the curves.

Kinetic measurements. We found in diffractometric study of the newly prepared substances that, as the time of irradiation of the sample is prolonged, the intensities of the original diffractions decrease and new peaks appear, whose intensity gradually increases. Following irradiation of the sample for several tens of minutes, the appearance of the diffractogram was completely different from the original diffractogram (Fig. 1). The following experiment was carried out to compare the rate of dehydration by X-rays and through the effect of weathering: a sample of tetramethylammonium hydrogenselenate monohydrate was ground to a fine powder in an agate mortar. One part of the sample was irradiated in a diffractometer cuvette for 30 min (CuKα, 40 kV, 30 mA, 2θ 17–23°) and the appearance of the diffractogram was regularly checked. The other part of the sample was left standing for the same

period of time in an agate mortar in the diffractometer area, but with no contact with X-radiation, and then its diffraction pattern was recorded in the same 2θ interval as in the previous case. The X-radiation caused complete disintegration of the first part of the sample at the impact site, while decomposition of the other part of the sample could not be observed in the given time interval and its diffraction record was identical with that of the first part of the sample at the beginning of the irradiation.

A narrow interval of 17–23° (2θ) was chosen for kinetic measurements for $(Me_4N)HSeO_4\cdot H_2O$; this interval contains both the diffraction of the original substance and that of the decomposition product. Decreasing diffraction intensity was monitored at 17.8, 19.9 and 21.8° (2θ), while increasing diffraction intensity was measured at 21.0, 20.5 and 19.1° (2θ). The 18–24° interval was selected for $Li(Me_4N)SeO_4\cdot 4H_2O$ and decreasing diffraction intensity was monitored for 18.3° and increasing diffraction intensity for 22.4°. The samples were placed in the diffractometer holder and the measurements started at time t_0 in the above 2θ interval at 6°/min, with graphical recording. The paper speed was 6 cm/min. The recorder was not turned off from this moment, so that the time axis could be determined from the paper speed. The 2θ interval was again measured under the same conditions, where the X-radiation also impinged on the sample at the time when the arm of the diffractometer was not moving, so that time information could be assigned to each repeated measured diffraction. The measurement of each sample in this way took ca. 1 h.

RESULTS AND DISCUSSION

Study of Solubility

A part of the solubility diagram in the H_2SeO_4–$(Me_4N)_2SeO_4$–H_2O system at 30 °C is depicted in Fig. 2. The figure involves the crystallisation field of tetramethylammonium selenate tetrahydrate (A, field 1) and the crystal-
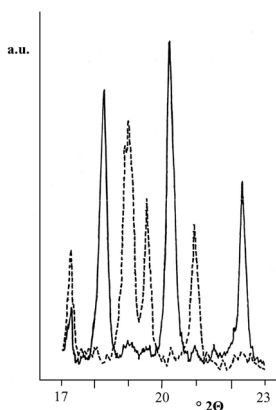

FIG. 1

Selected area of diffraction pattern of tetramethylammonium hydrogenselenate monohydrate before (full line) and after (dashed line) irradiation (see text)

lisation field of tetramethylammonium hydrogenselenate monohydrate (B, field 3). Field 2 corresponds to the equilibrium between two solid phases and a solution with composition corresponding to eutonic point E (62.98% $(Me_4N)_2SeO_4$, 16.38% H_2SeO_4, 20.64% H_2O). The area of the diagram from ca. 50% H_2SeO_4 towards its projection point was not studied experimentally. In this region, supersaturated viscous solutions are formed which do not permit adequate separation of the liquid and solid phases. Tetramethylammonium hydrogenselenate monohydrate is congruently soluble. For further study, this substance was prepared by mixing the starting substances (tetramethylammonium selenate hydrate and selenic acid) in the stoichiometric ratio with addition of a small amount of water (according to the solubility diagram). The solution was filtered into a crystallisation dish and concentrated in a desiccator over P_2O_5. The obtained crystals were separated from mother liquor, washed with a small amount of Et_2O and vacuum-dried for a short time in air (for $(Me_4N)HSeO_4$ calculated: 33.44% Se, 0.43% H^+, 31.40% Me_4N^+, 7.63% H_2O; found: 33.28% Se, 0.43% H^+, 32.33% Me_4N^+, 7.58% H_2O).

The solubility diagram for the Li_2SeO_4–$(Me_4N)_2SeO_4$–H_2O system at 30 °C is depicted in Fig. 3. The figure shows the crystallisation field of tetramethylammonium selenate tetrahydrate (A, field 2), of lithium selenate monohydrate (C, field 6) and the crystallisation field of lithium tetra-
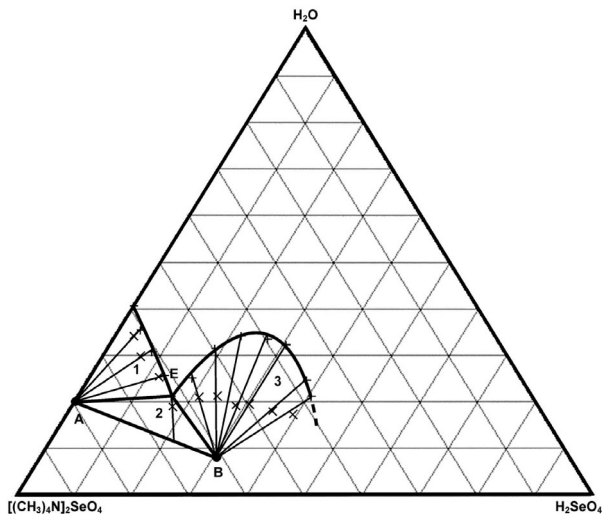

FIG. 2
Solubility diagram in the $(Me_4N)_2SeO_4$–H_2SeO_4–H_2O system at 303 K (in wt.%)

methylammonium selenate tetrahydrate (B, field 4). Fields 3 and 5 correspond to equilibrium between the two solid phases and solutions with a composition corresponding to the eutonic points E_1 (58.81% $(Me_4N)_2SeO_4$, 2.18% Li_2SeO_4, 39.01% H_2O) and E_2 (17.06% $(Me_4N)_2SeO_4$, 31.93% Li_2SeO_4, 51.01% H_2O). Field 1 is the area of unsaturated solutions. Lithium tetramethylammonium selenate tetrahydrate is congruently soluble. For further study, this substance was prepared by dissolving the starting substances $Li_2SeO_4 \cdot H_2O$ and hydrated tetramethylammonium selenate in the stoichiometric ratio in a small amount of water. The solution was evaporated in a desiccator over P_2O_5 to crystallisation. The crystals were filtered off, washed with Et_2O and vacuum dried for a short time in air (for $Li(Me_4N)SeO_4$ calculated: 26.67% Se, 2.34% Li, 25.04% Me_4N^+, 24.34% H_2O; found: 24.55% Se, 2.06% Li, 25.27% Me_4N^+, 24.38% H_2O).

The $(Me_4N)HSeO_4$–$Li(Me_4N)SeO_4$–H_2O cross-section of the H_2SeO_4–$(Me_4N)_2SeO_4$–Li_2SeO_4–H_2O quaternary system was studied to gain information on the existence of acid double selenate $Li(Me_4N)_4H_3(SeO_4)_4$, the K, Rb and Cs analogs (alkali metal instead of Me_4N) of which were isolated[2,3]. Samples designated 1–6 (Table I) correspond to molar ratios of $Li(Me_4N)SeO_4$:$(Me_4N)HSeO_4$ = 1:5, 1:4, 1:3, 1:2, 1:1 and 2:1, respectively; they were obtained by mixing the initial components of the quaternary system. Establishment of equilibrium was monitored as described in the Experimental. Equilibrium solid phases were identified by X-ray powder
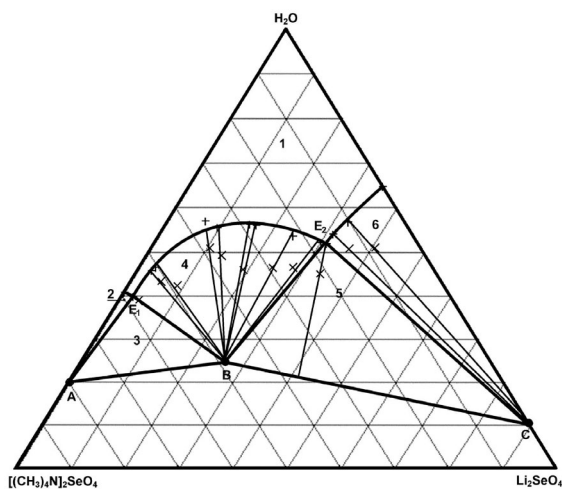

FIG. 3
Solubility diagram in the $(Me_4N)_2SeO_4$–Li_2SeO_4–H_2O system at 303 K (in wt.%)

diffraction (quick scan). It is apparent from the table that this cross-section is not a stable diagonal and that the crystallisation fields of $Li(Me_4N)_4H_3(SeO_4)_4$ apparently do not lie in this cross-section. A mixture of $Li(Me_4N)SeO_4 \cdot 4H_2O$ and $(Me_4N)HSeO_4 \cdot H_2O$ was found in the vicinity of the projection point of this substance.

Vibrational Spectra

Tables II and III depict the infrared spectra of the two substances prepared on the basis of study of the solubility diagrams. As Nujol or Fluorolube suspensions of these two substances are very difficult to obtain, the two spectra are of rather low intensity. The measurement (see Experimental) was carried out in AgCl windows, as both these substances corrode KBr windows. The spectra were interpreted on the basis of literature data[16,24,25]. In the infrared spectra of tetramethylammonium selenate monohydrate, the measured wavenumbers of the vibrations of $HSeO_4^-$ correspond in general to the data published, e.g. for $KHSeO_4$ or NH_4HSeO_4 (ref.[23]) (δ_{OH} at 1287 cm^{-1}, $\nu_{s(Se-OH)}$ at 734 cm^{-1}), confirming the correct formulation of the studied substance. The spectrum of lithium tetramethylammonium selenate tetrahydrate also corresponds to the substances that we have formerly studied ($Li(NH_4)SeO_4$ and $CsLiSeO_4 \cdot 1/2H_2O$ (ref.[2])). However, the spectrum is less easily interpreted, as the symmetrical valence vibration of Me_4N^+ extends into the area of valence vibrations of the selenate ion and the bands of SeO_4^{2-} are highly splitted as a consequence of the decreased symmetry.

TABLE I
$(Me_4N)HSeO_4$–$Li(Me_4N)SeO_4$–H_2O cross-section of the H_2SeO_4–$(Me_4N)_2SeO_4$–Li_2SeO_4–H_2O quaternary system

Sample	Molar ratio $Li(Me_4N)SeO_4:(Me_4N)HSeO_4$	Identified solid phases[a]
1	1:5	$(Me_4N)HSeO_4 \cdot H_2O$
2	1:4	$(Me_4N)HSeO_4 \cdot H_2O$
3	1:3	$(Me_4N)HSeO_4 \cdot H_2O$, $Li(Me_4N)SeO_4 \cdot 4H_2O$
4	1:2	$(Me_4N)HSeO_4 \cdot H_2O$, $Li(Me_4N)SeO_4 \cdot 4H_2O$
5	1:1	$(Me_4N)HSeO_4 \cdot H_2O$, $Li(Me_4N)SeO_4 \cdot 4H_2O$
6	2:1	$(Me_4N)_2SeO_4 \cdot 8H_2O$, $Li(Me_4N)SeO_4 \cdot 4H_2O$

[a] X-ray powder diffraction.

Kinetic Measurements

Figure 4 depicts the time dependence of the intensity (peak height) of the diffraction at 2θ 21.8° (diffraction with decreasing intensity) and the same dependence of the intensity (peak height) of the diffraction at 2θ 21.0° (diffraction with increasing intensity) for irradiation of tetramethylammonium selenate monohydrate by CuKα X-radiation (40 kV, 30 mA). Assuming that the ratio of the intensity (peak height) of the diffracted radiation of the

TABLE II
Infrared spectra[a] of $(Me_4N)HSeO_4 \cdot H_2O$

Wavenumber, cm^{-1}		Assignment
Nujol	Fluorolube	
402 m, sp		$\delta(OSeO_3)$ $(A_1 + E)$
459 w, sp		$\delta_{as}[(CH_3)_4N]$ (F_2)
607 sh, b		$\nu_R(H_2O)$
734 s		$\nu_s(Se–OH)$ (A_1)
862 s, sp		$\nu_s(SeO_3)$ (A_1)
902 s		$\nu_{as}(SeO_3)$ (E)
953 m, sp		$\rho(CH_3)$, $\nu_{as}[(CH_3)_4N]$ (F_2)
1287 m		$\delta(OH)$
1411 m, sp	1404, 1418 m	$\delta_s(CH_3)$
1485 s, sp	1488 s, sp	$\delta_{as}(CH_3)$
	1540 w, sp	–
	1558 w, sp	–
1680 m, b	1647 m, b	$\delta(H_2O)$
2424 m, b	2384 m, b	$\nu(OH)$
2584 vw	2767 vw	combination bands H_2O?
	2870 w, b	$\nu(OH)$
	2929 m	$\nu_s(CH_3)$
2959 m	2960 m	$\nu_s(CH_3)$
3033 m	3032 s	$\nu_{as}(CH_3)$
3297 s, b	3395 s, b	$\nu(H_2O)$

[a] vw, very weak, w, weak; m, middle; s, strong; sh, shoulder; b, broad; sp, sharp.

substance at the site of X-radiation impact and its weight fraction are constant, the following kinetic equation (*1*) holds for diffraction with decreasing intensity

$$I = I_0 \exp(-kt) \tag{1}$$

where I is the intensity of the diffraction at time t, I_0 is the intensity of the diffraction at time $t_0 = 0$ and k is the rate constant. As the value of I_0 cannot

TABLE III
Infrared spectra^a of $Li(Me_4N)SeO_4 \cdot 4H_2O$

Wavenumber, cm^{-1}		Assignment
Nujol	Fluorolube	
411 s		$\nu_4(SeO_4)$ (F_2)
467 sh, m		$\delta_{as}[(CH_3)_4N]$ (F_2)
610 s, b		$\nu_R(H_2O)$
767 sh, w		$\nu_s[(CH_3)_4N]$ (A_1)
868 s		$\nu_3(SeO_4)$ (F_2)
891 s		$\nu_3(SeO_4)$ (F_2)
916 s		$\nu_3(SeO_4)$ (F_2)
954 s, sp		$\rho(CH_3)$, $\nu_{as}[(CH_3)_4N]$ (F_2)
	1416 s, sp	$\delta_s(CH_3)$
	1454 m, sp	$\delta_s(CH_3)$
	1486 s, sp	$\delta_{as}(CH_3)$
	1540 w, sp	–
	1574 w, sp	–
1666 m, b	1660 s, b	$\delta(H_2O)$
2290 w, b	2256, 2484 w	combination bands?
	2586 vw	H_2O?
	2959 s	$\nu_s(CH_3)$
	3043 s	$\nu_{as}(CH_3)$
3180, 3450 s, b	3250, 3380 s, b	$\nu(H_2O)$

^{a} vw, very weak; w, weak; m, middle; s, strong; sh, shoulder; b, broad; sp, sharp.

be measured directly (in our measurements, the first measured intensity corresponds to $t = 48$ s), after taking logarithms

$$\ln I_0 - \ln I = kt \qquad (2)$$

the average I_0 and k values were calculated from all 37 measurements. The resulting value of k was then equal to $1.30(3) \times 10^{-3}$ s^{-1}. Analogous calculations were carried out for diffraction with decreasing intensity at 2θ 17.8 and 19.9°, with an average result of $k = 1.34(4) \times 10^{-3}$ s^{-1}.

Similarly, for diffraction with increasing intensity, the kinetic equation

$$I_K - I = I_K \exp(-kt) \qquad (3)$$

was obtained, where the symbols have the same meaning as in the previous equation, and I_K is the final intensity of the increasing diffraction. Similarly as for diffraction with decreasing intensity for I_0, this value was calculated for all 27 measurements after taking logarithms

$$\ln I_K - \ln(I_K - I) = kt. \qquad (4)$$

The resulting value equalled $1.07(8) \times 10^{-3}$ s^{-1}. Analogous calculations were carried out for diffraction with increasing intensity at 2θ 19.1 and 20.5°, with an average result of $k = 1.06(5) \times 10^{-3}$ s^{-1}.
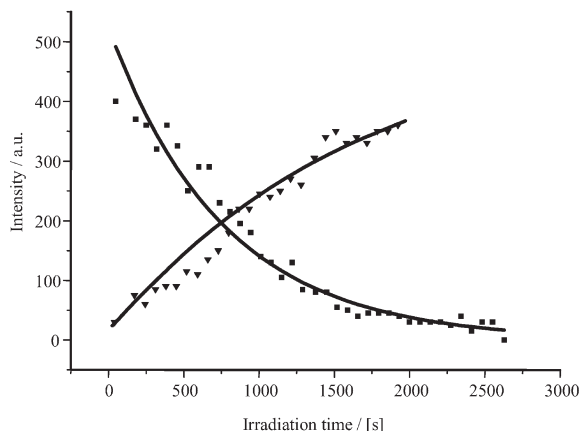

F$_{IG}$. 4

Dependence of intensity of the diffraction at 2θ 21.8° (■) and at 2θ 21.0° (▼) on irradiation time (see text)

Comparison of the rate constant values obtained from the data for diffraction with decreasing intensity with the values obtained from data for diffraction with increasing intensity indicates that the former are somewhat larger than the latter. This can be explained by the fact that the decomposition of the hydrate is accompanied by the formation of the anhydrous salt in amorphous form, followed by its crystallisation. However, only the crystalline form of the product is recorded by powder diffraction, which leads to a lower apparent reaction rate. However, as follows from the above discussion, the obtained data correspond satisfactorily to the first-order kinetic reaction.

An orientation study was also carried out on the effect of the X-radiation intensity on the rate of decomposition. It was found that even decreasing the values of the current and voltage in the generator to approx. one half has practically no effect on the reaction rate. Apparently, only the initial impulse of the ionising radiation is important and the reaction then occurs spontaneously, similar to radioactive decomposition.

In an attempt to carry out the same interpretation of data for radiolysis of lithium tetramethylammonium selenate tetrahydrate that the data can be processed as a first-order reaction only for diffraction of decreasing intensity (2θ 18.3°). The corresponding rate constant then equalled $5.4(1) \times 10^{-4}$ s^{-1}. The analogous dependence for diffraction of increasing intensity at 2θ 22.4° is far more complex. The higher degree of hydration of this substance may mean that the studied diffraction of increasing intensity could correspond to a crystalline intermediate of the decomposition (with lower water content), which further decomposes under the action of the radiation. It is very difficult to consider the kinetics related to the time dependence of the intensity of such diffraction. Here, a consecutive reaction with much more complex kinetics probably occurs.

X-ray powder patterns of both samples after radiolysis are identical with the diffractograms obtained by dehydration of the two substances in a desiccator over P_2O_5. In the case of tetramethylammonium hydrogenselenate, this diffractogram is identical with the calculated diffractogram of anhydrous salt, phase III, the crystal structure of which was published by Zakharov et al.[17].

REFERENCES

1. Havlíček D., Mička Z., Boublíková R.: *Collect. Czech. Chem. Commun.* **1995**, *60*, 969.
2. Havlíček D., Mička Z., Barbořák V., Šmejkal P.: *Collect. Czech. Chem. Commun.* **2000**, *65*, 167.
3. Pietraszko A., Lukaszewitz K.: *Z. Kristallogr.* **1988**, *185*, 564.

 4. Zaretski V., Dempeier W.: *Seventh European Meeting on Ferroelectricity, Dijon, 1991.* Abstracts p. 207.
 5. Seifert H. J., Koknat F. W.: *Z. Anorg. Allg. Chem.* **1968**, *357*, 314.
 6. Aleksandrov K. S., Flerov I. N., Kokov I. T., Kruglig A. I., Melnikova S. V.: *Ferroelectrics* **1988**, *79*, 137.
 7. Tomaszewski P. E.: *Phase Transitions* **1992**, *B38*, 127.
 8. Altermatt D., Arend H., Niggli A., Pater W.: *Acta Crystallogr.* **1984**, *40*, 347.
 9. Kallaev S. N., Gladkij V. V., Kirikov V. A., Pakhomov V. I., Ivanova-Korfini I. N., Goryunov A. V.: *Sov. Phys. Solid State* **1989**, *31*, 1267.
10. Arend H., Muralt P., Plesko S., Altermatt D.: *Ferroelectrics* **1980**, *24*, 297.
11. Endo M., Osaka T., Makita Y.: *J. Phys. Soc. Jpn.* **1983**, *52*, 3974.
12. Robinson N. A., Stokes R. H.: *Electrolyte Solutions*, 2nd ed. Butterworths Publications Ltd., London 1959.
13. Serezhkin V. N., Tobachenko N. V., Serezhkina L. B.: *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Technol.* **1976**, *19*, 1493.
14. McLean W. J., Jeffrey G. A.: *J. Chem. Phys.* **1968**, *49*, 4556.
15. Sato S., Endo M., Hara N., Nakamura D., Ikeda R.: *J. Mol. Struct.* **1995**, *345*, 197.
16. Malchus M., Jansen M.: *Z. Naturforsch., B: Chem. Sci.* **1998**, *53*, 704.
17. Zakharov M. A., Troyanov S. I., Rybakov V. B., Aslanov L. A., Kemnitz E.: *Kristallografyia* **2001**, *46*, 1057.
18. Havlíček D., Turek L.: *Mater. Struct. Chem. Biol. Phys. Technol.* **1996**, *3*, 336.
19. Rivera J. P., Speziali N. L., Berger H., Arend H., Schmidt H.: *Ferroelectrics* **1990**, *105*, 183.
20. Sato S., Sakuma A., Furuta T., Aoyama E.: *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4139.
21. Speziali N. L., Chapuis G.: *Acta Crystallogr., Sect. B: Struct. Sci.* **1991**, *47*, 757.
22. Blanka B., Hudec P., Mošna P., Toužín J.: *Collect. Czech. Chem. Commun.* **1963**, *28*, 3434.
23. Heissigová M.: *M.S. Thesis.* Charles University, Prague 1988.
24. Horák M., Papoušek D.: *Infračervená spektra a struktura molekul.* Academia, Praha 1982.
25. Nakamoto K.: *Infrared and Raman Spectra of Inorganic and Coordination Compounds.* J. Wiley, New York 1978.