

**PREPARATION AND SOLUBILITY OF SODIUM HYDROGENSELENITES.
THERMOANALYTICAL PROPERTIES, INFRARED SPECTRA
AND CRYSTAL DATA OF $\text{NaH}_7(\text{SeO}_3)_4$**

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The solubility diagram was studied at 25°C for the $\text{Na}_2\text{SeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$ system. On the basis of the solubility study, the conditions for the preparation of the hydrogenselenites, NaHSeO_3 , $\text{NaH}_3(\text{SeO}_3)_2$ and $\text{NaH}_7(\text{SeO}_3)_4$, were refined. For the compound, $\text{NaH}_7(\text{SeO}_3)_4$, the infrared spectrum was measured, the crystal data were determined and a mechanism of thermal decomposition was proposed on the basis of the results of the study of the thermoanalytical properties of the compound.

Among the sodium hydrogenselenites that are dealt with in the present paper, the compounds NaHSeO_3 , $\text{NaH}_3(\text{SeO}_3)_2$ and $\text{NaH}_7(\text{SeO}_3)_4$ have been described¹⁻³ and their solubility diagrams studied⁴. The powder X-ray patterns of these compounds have been described⁵ and the crystal structures of NaHSeO_3 and $\text{NaH}_3(\text{SeO}_3)_2$ have been found⁶⁻¹⁴. The compounds have also been studied by the thermal analysis^{4,15-18}. On the basis of a study of the infrared and Raman spectra, the constitution and the symmetry (C_s) of the HSeO_3^- anion have been determined^{19,20} and the behaviour of protons during ferroelectric transition of the studied compounds has been described²¹⁻²⁷.

In the framework of a systematic study of hydrogenselenites, as substances with pronounced dielectric properties, this work deals with sodium selenites. Our attention has been focused on the refinement of the conditions for the preparation of all hydrogen salts that are formed in the $\text{Na}_2\text{SeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$ system at 25°C. As the behaviour of the protons in the hydrogen bonds of the compound, $\text{NaH}_7(\text{SeO}_3)_4$, has not yet been described in the literature on the isolated compounds, the infrared spectra and the crystal structure of this compound were studied. To elucidate the decomposition of $\text{NaH}_7(\text{SeO}_3)_4$ occurring during X-ray measurements, the thermoanalytical properties of this substance were studied.

EXPERIMENTAL

Sodium selenite (Lachema, Brno; *p.a.*) and recrystallized selenious acid (Lachema, Brno; pure) were used in the study of the solubility diagram. The $\text{NaH}_7(\text{SeO}_3)_4$ compound was prepared by the heterogeneous reaction of 1.5 g Na_2SeO_3 , 15.2 g H_2SeO_3 , and 3.4 g H_2O . After equilibration, the colourless crystalline substance was filtered off on an S2 frit, washed with chloroform and, because of its weakly hygroscopic properties, dried over P_2O_5 . A single crystal was selected for the X-ray study from the crystals thus obtained. The deuterated salt, $\text{NaD}_7(\text{SeO}_3)_4$, was prepared analogously, using Na_2SeO_3 , SeO_2 and D_2O as the reactants.

The reactants and the compounds obtained were analyzed gravimetrically. Selenium was determined by the modified Bode method²⁸ and sodium as $\text{NaZn}(\text{UO}_2)_3(\text{CH}_3\text{COOH})_9 \cdot 6 \text{H}_2\text{O}$ (ref.²⁹), after separation of selenium. In the solubility study, selenium(IV) was determined by iodometric titration³⁰ and sodium by AAS on a Perkin-Elmer 306 instrument.

The thermoanalytical properties were studied by thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSG), and by the method of gradually increased temperature. The simultaneous recording of TG and DTA curves in a static air atmosphere was performed on a Derivatograph OD 102 instrument (MOM, Budapest) in the temperature range 25–600°C using a heating rate of 5°C min⁻¹ and 100 mg samples. In addition, TG curves were recorded with a Perkin-Elmer TGS-2 instrument using a smaller sample (3 mg) and a dynamic air atmosphere; the heating rate was 10°C min⁻¹. The DSC curves were measured on a Perkin-Elmer DSC-4 calorimeter, using a System 7/4 Thermal Analysis Controller and a TADS thermal analysis data station, over a temperature range of 25 to 250°C and at a heating rate of 10°C min⁻¹. The thermoanalytical curves measured by the method of gradually increased temperature were obtained over a range of 25 to 450°C by heating the samples in a regulated electric oven with a temperature increase of 10°C per 24 hours.

The X-ray patterns of the $\text{NaH}_7(\text{SeO}_3)_4$ crystal were obtained on a Weissenberg goniometer in the air at 23°C, using CuK_α radiation with a Ni filter. Preliminary values of the lattice parameters were calculated from the rotation and Weissenberg photographs of the h0l, 0kl and h1l layers. The systematic absences of the reflections (for hCl, $l = 2n + 1$, and for 0k0, $k = 2n + 1$) indicate the space group $\text{P2}_1/c$. The powder data were obtained on a Chirana diffractometer and published elsewhere³¹. The lattice parameters were refined by the least squares method using the MPIN program³² from a set of 40 indexed reflections. The intensities of 2 175 reflections in the h0l–h7l layers were measured using a single-crystal two-circle Super-Pace diffractometer. The SHELX 76 program³³ was used in an attempt to solve the phase problem of $\text{NaH}_7(\text{SeO}_3)_4$.

The infrared spectra were obtained on a UR 20 instrument (Zeiss, Jena) from 4 000 to 400 cm⁻¹, using the nujol mull method and potassium bromide cells. The measurements in the region from 4 000 to 1 600 cm⁻¹ were also carried out by the tripene suspension method.

The density of $\text{NaH}_7(\text{SeO}_3)_4$ was determined pycnometrically under xylene, at a temperature of 23 C.

RESULTS

Solubility Study in the Na_2SeO_3 – H_2SeO_3 – H_2O System at 25°C

The Schreinemakers method was used to study the solubility. The equilibration time for the samples was 3 to 4 weeks. The diagram obtained (Fig. 1) indicates that, in addition to the initial compounds (crystallization fields I and IX) and sodium

selenite pentahydrate (crystallization field XI), three hydrogen salts are formed in the system, namely $\text{NaH}_7(\text{SeO}_3)_4$ (crystallization field III), $\text{NaH}_3(\text{SeO}_3)_2$ (crystallization field V), and NaHSeO_3 (crystallization field VII). The equilibrium between two solid phases and solution with compositions given by invariant points A, B, C, D, and E is represented by field II, IV, VI, VIII and X. The liquid phase compositions at the invariant points of the system are given in Table I.

From the solubility diagram, the molar ratios of the initial compounds, Na_2SeO_3 : H_2SeO_3 : H_2O , were determined that lead to maximal yield of hydrogenselenites: 2.25 : 2.25 : 17.9 for NaHSeO_3 , 1.1 : 3.5 : 20 for $\text{NaH}_3(\text{SeO}_3)_2$ and 0.45 : 5.9 : 9.2 for $\text{NaH}_7(\text{SeO}_3)_4$.

TABLE I
Liquid phase composition (wt %) at the invariant points of the system

| Inv. point | Na_2SeO_3 | H_2SeO_3 | H_2O |
|------------|---------------------------|--------------------------|----------------------|
| A | 4.1 | 79.6 | 16.3 |
| B | 7.8 | 70.9 | 21.3 |
| C | 35.2 | 31.2 | 33.6 |
| D | 49.1 | 18.1 | 32.8 |

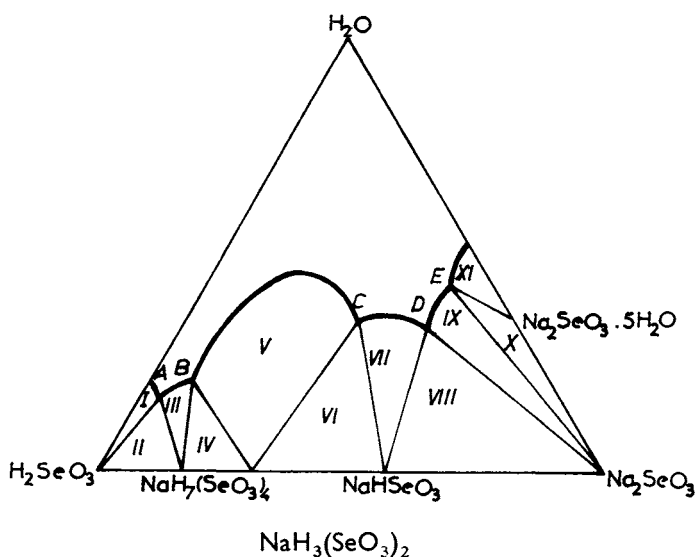


FIG. 1
Solubility diagram for the Na_2SeO_3 - H_2SeO_3 - H_2O system at 25°C

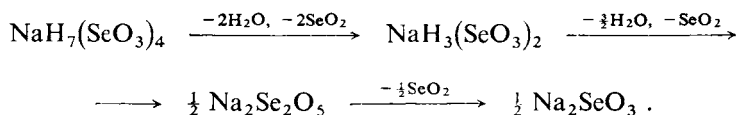
Thermoanalytical Properties, Infrared Spectra and Crystal Data

The results of the study of the thermoanalytical properties of $\text{NaH}_7(\text{SeO}_3)_4$ by the TG, DTA and DSC methods are given in Table II and those obtained by the method of gradually increased temperature in Table III. The intermediates and the final products of the thermal decomposition were characterized analytically, by X-ray measurement, and by infrared spectroscopy. The infrared spectra of $\text{NaH}_7(\text{SeO}_3)_4$ and $\text{NaD}_7(\text{SeO}_3)_4$ are described in Table IV. The absorption bands were assigned according to the literature¹⁹⁻²⁷. The basic crystal data of $\text{NaH}_7(\text{SeO}_3)_4$ are given in Table V.

DISCUSSION

In the $\text{Na}_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$ system at 25°C, congruently soluble hydrogen-selenites NaHSeO_3 and $\text{NaH}_3(\text{SeO}_3)_2$, and incongruently soluble salt $\text{NaH}_7(\text{SeO}_3)_4$ were found. These compounds were identified by comparing the X-ray powder patterns and the infrared spectra with the published data^{5,19-27}. Hydrogenselenites NaHSeO_3 , $\text{NaH}_3(\text{SeO}_3)_2$, and $\text{NaH}_7(\text{SeO}_3)_4$ were found earlier by Sabbah and Perinet⁴ in the solubility study of this system. It follows from the comparison of the two solubility diagrams that our study permitted refinement of the liquid phase composition in the invariant points of the system (Table I) and clarification of the shape of the solubility curve which, in work⁴, does not fully correspond to the shape expected from thermodynamics.

The study of the thermoanalytical properties of $\text{NaH}_7(\text{SeO}_3)_4$ by the TG, DTA and DSC methods indicates decomposition of the compound within a temperature range of 45–75°C to $\text{NaH}_3(\text{SeO}_3)_2$ with the liberation of selenium dioxide and water. The $\text{NaH}_3(\text{SeO}_3)_2$ intermediate is decomposed in a temperature range of 105 to 180°C, with a further release of selenium dioxide and water, to sodium diselenite. The further decomposition of diselenite to selenite (390 to 450°C) is preceded by sublimation of selenium dioxide (200 to 280°C) formed during the preceding decomposition stages. The overall mechanism of the $\text{NaH}_7(\text{SeO}_3)_4$ decomposition can be represented as follows,



This mechanism was clarified mainly on the basis of the results of thermal analysis using the gradually increased temperature method with a very slow heating rate. While some decomposition stages merge when using the normal dynamic TG method, the method of gradually increased temperature permits differentiation of all inter-

mediate phases and, due to the relatively large sample size, their characterization by chemical analysis, X-ray powder diffraction, and IR spectroscopy. The existence

TABLE II

The results of the thermal analysis of $\text{NaH}_7(\text{SeO}_3)_4$ obtained by the TG, DTA and DSC methods

| TG <i>m</i> , % wt. °C | DTA effect °C | DSC effect °C | Assignment |
|------------------------------|---------------------|----------------------|---|
| 11·40 45–180 | endo 40–60 | endo 58–62, 65–70 | decomp. to $\text{NaH}_3(\text{SeO}_3)_2$, SeO_2 , and H_2O ($m_{\text{calc}} = 6\cdot69\%$ wt.) |
| 60·90 200–280 | endo 110–165 | endo 125–160 | decomp. to $\text{Na}_2\text{Se}_2\text{O}_5$, SeO_2 , and H_2O and H_2O evaporation ($m_{\text{calc}} = 11\cdot71\%$ wt.) |
| 84·15 390–450 | endo 205–265 | endo 165–240 | SeO_2 sublimation and a polymorphous transition of $\text{Na}_2\text{Se}_2\text{O}_5$ decomp. to Na_2SeO_3 and SeO_2 ($m_{\text{calc}} = 83\cdot92\%$ wt.) |

TABLE III

The results of the thermal analysis of $\text{NaH}_7(\text{SeO}_3)_4$ obtained by the gradually increased temperature method

| <i>t</i> , °C | <i>m</i> , % wt. | Assignment |
|---------------|------------------|--|
| 40–70 | 6·45 | decomp. to $\text{NaH}_3(\text{SeO}_3)_2$, SeO_2 , and H_2O and H_2O evaporation ($m_{\text{calc}} = 6\cdot69\%$ wt.) |
| 85–150 | 11·45 | decomp. to $\text{Na}_2\text{Se}_2\text{O}_5$, SeO_2 , and H_2O and H_2O evaporation ($m_{\text{calc}} = 11\cdot71\%$ wt.) |
| 180–250 | 70·15 | SeO_2 sublimation ($m_{\text{calc}} = 61\cdot89\%$ wt.) |
| 350–420 | 84·15 | decomp. to Na_2SeO_3 and SeO_2 ($m_{\text{calc}} = 83\cdot92\%$ wt.) |

of the individual intermediates corresponds to the temperature ranges of their stability and the proposed mechanism is in agreement with the thermoanalytical properties of $\text{NaH}_3(\text{SeO}_3)_2$, NaHSeO_3 and $\text{Na}_2\text{Se}_2\text{O}_5$ (ref. ^{4,15-18,34}).

TABLE IV
Infrared spectra^a of $\text{NaH}_7(\text{SeO}_3)_4$ and $\text{NaD}_7(\text{SeO}_3)_4$

| $\tilde{\nu}(\text{NaH}_7(\text{SeO}_3)_4)$ | $\tilde{\nu}(\text{NaD}_7(\text{SeO}_3)_4)$ | $\frac{\tilde{\nu}(\text{NaH}_7(\text{SeO}_3)_4)}{\tilde{\nu}(\text{NaD}_7(\text{SeO}_3)_4)}$ | Assignment ^b |
|---|---|---|---|
| 412 s | 418 s | 0.99 | $\delta(\text{SeO}_2)(\text{X}_2\text{SeO}_3)$ |
| 450 w | 455 w | 0.99 | $\delta(\text{SeO}_2)(\text{XSeO}_3^-)$ |
| | 530 m | | |
| 642 s | 625 s | 1.03 | $\nu(\text{SeOX})(\text{XSeO}_3^-)$ |
| 690 s | 680 s | 1.01 | $\nu_{\text{as}}(\text{SeO}_2)(\text{X}_2\text{SeO}_3)$ |
| | | | $\nu_{\text{s}}(\text{SeO}_2)(\text{XSeO}_3^-)$ |
| 760 s | 758 s | 1.00 | $\nu_{\text{as}}(\text{SeO}_2)(\text{XSeO}_3^-)$ |
| 810 w | 815 s | 0.99 | $\nu_{\text{s}}(\text{SeO})(\text{X}_2\text{SeO}_3)$ |
| 868 s | 875 s | 0.99 | $\nu_{\text{s}}(\text{SeO}_2)(\text{XSeO}_3^-)$ |
| 893 s | 895 sh | 1.00 | |
| 1 130 m | | | |
| 1 242 m | 958 m | 1.30 | $\delta(\text{OX})(\text{SeOX})$ |
| 1 302 m | 980 m | 1.33 | |
| 1 600 wb | 1 220 wb | 1.31–1.33 | $\nu(\text{OX})(\text{SeOX})$ |
| 2 500–2 100 sb | 1 900–1 600 sb | | |
| (max. 2 570, 2 270) | (max. 1 770) | | |
| 3 300–2 600 sb | 2 500–1 900 sb | | |
| (max. 2 800, 2 700) | (max. 2 100) | | |

^a The relative intensities and shapes of the bands: vs very strong, s strong, m medium, w weak, vw very weak, b broad, sh shoulder. Notation of vibrations: ν_{s} and ν_{as} symmetrical and anti-symmetrical stretching, respectively, δ deformation. Band positions ($\tilde{\nu}$) in cm^{-1} ; ^b X denotes H or D.

TABLE V
Crystal data for $\text{NaH}_7(\text{SeO}_3)_4$

| | |
|---|--|
| $a = 578.4 (2) \text{ pm}$ | $Z = 2$ |
| $b = 493.8 (2) \text{ pm}$ | $D_{\text{m}} = 3.173 (3) \text{ g cm}^{-3}$ |
| $c = 2 008 (1) \text{ pm}$ | $D_{\text{x}} = 3.166$ |
| $\beta = 100.39 (3)^\circ$ | space group $\text{P}2_1/c (C_{2h}^5)$ |
| $V = 564.1 (4) \cdot 10^6 \text{ pm}^3$ | |

In the study of the infrared molecular spectra of $\text{NaH}_7(\text{SeO}_3)_4$, our attention was centred on the clarification of the behaviour of the protons in the hydrogen bonds from the point of view of their ordering, because they exert a decisive effect on the dielectric properties of hydrogenselenites. In the region of the fundamental vibrations of the anion, absorption bands were found that indicate the presence of the HSeO_3^- and H_2SeO_3 groups in the structure. Therefore, the protons are located asymmetricaly along the hydrogen bonds $(\text{Se})\text{O}-\text{H}\dots\text{O}$ in the ordered locations, *i.e.* at the lowest discrete levels of a two-minimum asymmetrical potential function, with a practically zero probability of tunneling²⁶. Analogous behaviour of protons has been found in $\text{LiH}_3(\text{SeO}_3)_2$ at room temperature²⁶; this compound is already ferroelectric under these conditions. On the other hand, the broad absorption bands (665 and 820 cm^{-1}), corresponding to the presence of the selenite anion with all the protons in non-ordered positions found for $\text{NaH}_3(\text{SeO}_3)_2$ at laboratory temperature^{23,26,27}, are absent from the spectrum.

Three absorption bands were found in the region of the deformation vibrations of the $(\text{Se})\text{OH}$ group between $1\ 300$ and $1\ 100\text{ cm}^{-1}$ and can be assigned to hydrogen bonds of different strength with the protons in the ordered positions²⁴. In the region of the stretching vibrations of the $(\text{Se})\text{OH}$ group, the number of the bands, their position and shape are very similar to all hydrogenselenites of the alkali metals and are also in agreement with the spectra of other acidic salts belonging to ferroelectrics of the potassium dihydrogen phosphate (KDP) type²⁶. The similarity of the spectra of these substances that differ in the number of the hydrogen bonds and their strength is caused by the slow inter-hydrogen bond tunneling effect^{26,27,35}.

As the crystal structure of NaHSeO_3 and $\text{NaH}_3(\text{SeO}_3)_2$ are known⁶⁻¹⁴, an attempt was made to establish the crystal structure of $\text{NaH}_7(\text{SeO}_3)_4$, in order to find the structural relationships among these compounds. The crystal data for this compound were obtained (Table V), but the determination of the crystal structure was unsuccessful. It was not possible to solve the phase problem from the data available. During measurement some extra diffraction spots appeared on the Weissenberg films which evidently did not belong to $\text{NaH}_7(\text{SeO}_3)_4$. The intensities of these spots increased during the measurement and it was found that they belonged to $\text{NaH}_3(\text{SeO}_3)_2$ ($a = 1\ 034.5$, $b = 484.4$, $c = 578.7\text{ pm}$, $\beta = 91.13^\circ$, $P2_1/n$) (ref.¹⁴). The comparison of the lattice parameters of $\text{NaH}_3(\text{SeO}_3)_2$ and $\text{NaH}_7(\text{SeO}_3)_4$ indicates similarity in their diffraction angles. Therefore, the reflection intensities of the two substances overlap and the data set on $\text{NaH}_7(\text{SeO}_3)_4$ obtained under the above conditions is thus useless.

The fact, that $\text{NaH}_7(\text{SeO}_3)_4$ crystals partially decompose to $\text{NaH}_3(\text{SeO}_3)_2$ on several-day standing in the air, is in full agreement with the results of the study of the thermoanalytical properties of these substances. The effect of prolonged action of X-radiation on the decomposition of the crystal in a diffractometer also cannot be excluded. It is, however, understandable that this decomposition has not been

observed in the measurement of the IR spectra of freshly prepared $\text{NaH}_7(\text{SeO}_3)_4$ crystals, as this measurement is much less time-consuming.

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