

PREPARATION OF POTASSIUM SELENITES, THEIR SOLUBILITY AND BONDING CONDITIONS

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The solubility diagrams of a $K_2SeO_3-H_2SeO_3-H_2O$ system were studied at 293 and 303 K for the first time. The effect of temperature on the character of the studied system from the point of view of the transition from hydrogenselenite to diselenite was studied. The results were used to refine the preparation conditions for $K_5H_3(SeO_3)_4$, $KHSeO_3$, $KH_3(SeO_3)_2$, and $K_2Se_2O_5$. The compounds obtained were studied using thermoanalytical methods and infrared spectroscopy. The behaviour of protons in the hydrogen bonds of the acid salts was described.

Research on potassium selenites has so far dealt with methods of preparation¹⁻⁵, study of the solubility diagrams⁶ at 298 K and thermoanalytical properties⁶⁻⁹. $KH_3(SeO_3)_2$ was studied using structural analysis methods¹⁰⁻¹². The symmetry of the SeO_3^{2-} , $HSeO_3^-$, and $Se_2O_5^{2-}$ anions was determined from the molecular spectra¹³⁻¹⁵. The behaviour of the protons in the hydrogen bonds was studied¹⁶⁻¹⁸ for $KHSeO_3$ and $KH_3(SeO_3)_2$ from the point of view of occupation of ordered and unordered positions in the structure.

As a part of a systematic study of selenites, *i.e.* compounds with potential ferroelectric properties, this paper deals with potassium selenites. The solubility of the $K_2SeO_3-H_2SeO_3-H_2O$ system was studied and the conditions for the formation of the given salts were refined. The physicochemical properties of the compounds obtained were investigated to clarify the course of their thermal decomposition and, for the acid salts, to obtain information on the behaviour of protons in the hydrogen bonds present.

EXPERIMENTAL

Selenious acid used in the study of the solubility diagrams of the $K_2SeO_3-H_2SeO_3-H_2O$ system was prepared from sodium selenite (*p.a.* Lachema Brno) using Dowex 50 W-X8 ion exchanger (Fluka AG). Anhydrous potassium selenite was prepared by neutralization of this acid with potassium carbonate (*p.a.* Lachema Brno). Based on the solubility study, the molar ratios of the starting compounds, $K_2SeO_3 : H_2SeO_3 : H_2O$, were estimated to obtain optimum yields of the prepared substances. The ratios were 1:2.9:0.6, 1:0.9:2.5, 1:0.5:3, and 1:0.9:2.6 for $KH_3(SeO_3)_2$, $KHSeO_3$, $K_5H_3(SeO_3)_4$, and $K_2Se_2O_5$, respectively. The prepared compounds were filtered under vacuum through an S2 frit, washed with chloroform and dried in the air. Strongly

hygroscopic KHSeO_3 had to be isolated in a dry nitrogen atmosphere. All the obtained substances were colorless, crystalline and, except for KHSeO_3 , stable in the air. Calculated and found values (given in parentheses) of the K and Se contents were as follows: $\text{KH}_3(\text{SeO}_3)_2$ 13.21 (13.14) % K, 53.34 (53.20) % Se; KHSeO_3 23.40 (23.44) % K, 47.26 (47.29) % Se; $\text{K}_5\text{H}_3(\text{SeO}_3)_4$ 27.68 (27.50) % K, 44.72 (44.61) % Se; and $\text{K}_2\text{Se}_2\text{O}_5$ 24.74 (24.40) % K and 49.96 (49.90) % Se. Deuterated compounds $\text{KD}_3(\text{SeO}_3)_2$, KDSeO_3 , and $\text{K}_5\text{D}_3(\text{SeO}_3)_4$ were prepared similarly from K_2SeO_3 , SeO_2 , and D_2O and were used to study the infrared spectrum.

Potassium was determined¹⁹ as KClO_4 and selenium by a modified Bode method²⁰. In the solubility study, the selenium content was determined iodometrically²¹ and potassium by an AAS method using a Perkin-Elmer 306 apparatus.

Thermoanalytical properties of the substances were studied by thermogravimetry and differential thermal analysis using a Derivatograph (MON, Budapest). The heating rate was 5 K min^{-1} in a temperature interval of 298–873 K. Some of the measurements were performed using a method of gradually increasing temperature. The samples were heated in a regulated electric furnace with a temperature increased by 10 K in the range 298–625 K.

The infrared spectra were measured in the region $400\text{--}4\,000 \text{ cm}^{-1}$ with a UR-20 (Zeiss, Jena) device employing the Nujol suspension method and KBr cells. The triprene suspension method was also used in the $1\,600\text{--}4\,000 \text{ cm}^{-1}$ region.

RESULTS AND DISCUSSION

The solubility diagrams of the $\text{K}_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$ system at 293 and 303 K obtained by Schreinemakers method are in Figs 1 and 2. The composition of the liquid phase in the invariant points of the system are given in Table I. Comparison of the diagrams shows that the main difference appears in the region of KHSeO_3 and $\text{K}_2\text{Se}_2\text{O}_5$ crystallization. The formation of hydrogenselenite was observed at a lower temperature (293 K) whereas at a higher temperature (303 K) diselenite was found. The system described previously⁶, $\text{K}_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$ at 298 K, is similar

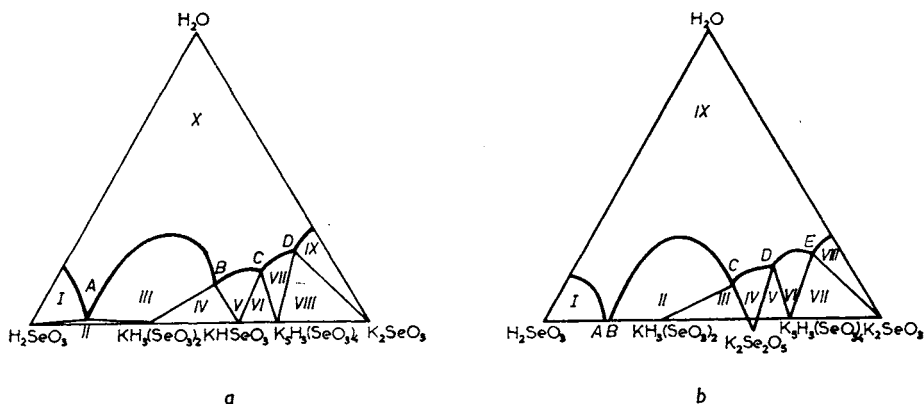


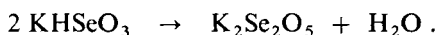
FIG. 1

Solubility diagram of the $\text{K}_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$ system at: a 293 K, b 303 K

to our solubility study at 293 K in the formation of KHSeO_3 . Nevertheless, the former temperature corresponds to the temperature of transition and the published curve did not attain the shape predicted by thermodynamics.

The results of study of the thermoanalytical properties of K_2SeO_3 , KHSeO_3 , $\text{KH}_3(\text{SeO}_3)_2$, $\text{K}_5\text{H}_3(\text{SeO}_3)_4$, and $\text{K}_2\text{Se}_2\text{O}_5$ are given in Tables II and III. Study of the thermoanalytical properties of K_2SeO_3 revealed that, at temperatures up to 875 K, only evaporation of dampness (the compound is strongly hygroscopic) and a polymorphous change occurred. In contrast to some studies^{8,9}, neither decomposition nor successive oxidation of the sample to selenate was observed.

The evaluation of the thermoanalytical curves for KHSeO_3 demonstrated that the thermal decomposition is characterized by the transition of the substance to diselenite:



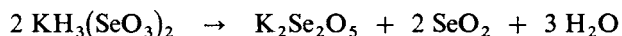
Similar process, connected with incongruent melting for hygroscopic substances, was observed²² for all acid alkali metal selenites of the MHSeO_3 type. The effect of the hydrogen bond strength on the decomposition temperatures can be followed if the behaviour of the deformation vibrations of the hydroxyl groups, $\delta(\text{OH})$ is used as a criterion of the strength of the hydrogen bond system. The lowest wave number found in the KHSeO_3 spectrum for alkali metals corresponded to the longest hydrogen bond²³ and to the lowest temperature of decomposition of the compound to diselenite. Thus, the lowest temperature of the transition of hydrogenselenite to diselenite for heterogenous $\text{M}_2\text{SeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$ systems was found for potassium compounds.

TABLE I

Composition of the liquid phase (mass %) for the invariant points of the $\text{K}_2\text{SeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$ system in dependence on the temperature

Invariant point	K_2SeO_3		H_2SeO_3		H_2O	
	293 K	303 K	293 K	303 K	293 K	303 K
A	16.7		78.1		5.2	
B	49.3		36.4		14.3	
C	59.9	50.2	22.5	37.5	17.6	12.3
D	66.3	59.0	9.5	22.5	24.2	18.5
E		68.5		8.1		23.4

The initial process of thermal decomposition of $\text{KH}_3(\text{SeO}_3)_2$ which can be described by the equation



proceeds stepwise. The compound first melts incongruently with evaporation of the released water occurring at higher temperatures. Further decomposition of diselenite proceeds similarly as in the previous case but the effect on the DTA curve, corresponding to a polymorphic change, is overlapped by a strong endoeffect accom-

TABLE II
Thermoanalytical properties of potassium selenites studied by TG and DTA

TGA		DTA		Comments
Temperature, K	m, mass %	Temperature, K	Effect	
K_2SeO_3				
298–345	plateau			
345–385	0.40	335–385	endo	evaporation of H_2O (dampness)
385–875	plateau	545–565	endo	polymorphous change
KHSeO_3				
298–315	plateau			
315–375	0.40	315–345	endo	incongruent melting and partial evaporation of H_2O
		355–365	endo	partial evaporation of H_2O
375–420	5.45	400–415	endo	evaporation of H_2O and formation of $\text{K}_2\text{Se}_2\text{O}_5$ (s)
420–565	plateau	550–565	endo	polymorphous change
565–875	34.90	575–875	endo	decomposition to K_2SeO_3 , SeO_2 and partial oxidation to K_2SeO_4
$\text{KH}_3(\text{SeO}_3)_2$				
298–305	plateau			
305–395	0.65	335–345	endo	incongruent melting and partial evaporation of H_2O
395–465	9.60	400–435	endo	evaporation of H_2O accompanied with the formation of $\text{K}_2\text{Se}_2\text{O}_5$ (s) and SeO_2 (s)
465–525	plateau			

TABLE II
(Continued)

TGA		DTA		Comments
Temperature, K	m, mass %	Temperature, K	Effect	
$\text{KH}_3(\text{SeO}_3)_2$				
525–875	56.50	525–610	endo	sublimation of SeO_2 , decomposition to K_2SeO_3 , SeO_2 and partial oxidation to K_2SeO_4
		635–725	endo	
$\text{K}_5\text{H}_3(\text{SeO}_3)_4$				
298–325	plateau			incongruent melting and partial evaporation of H_2O evaporation of H_2O accompanied with formation of $\text{K}_2\text{SeO}_3 \cdot 3 \text{SeO}_2$ (s)
325–405	0.85	350–365	endo	
405–485	4.00	405–430	endo	
485–755	plateau			
755–875	15.40	775–785	exo	decomposition to K_2SeO_3 , SeO_2 and partial oxidation to K_2SeO_4
		805–825	exo	

panying sublimation of released SeO_2 . As the sublimation was not finished before the beginning of the diselenite decomposition, the TG curve did not exhibit a plateau for this substance alone. Nevertheless, this plateau appears on the decomposition curve obtained at gradually increasing temperatures and this demonstrates that pure diselenite can be prepared by thermal decomposition of $\text{KH}_3(\text{SeO}_3)_2$.

Thermal decomposition of $\text{K}_5\text{H}_3(\text{SeO}_3)_4$ can be described, in its initial phase, by the reaction



The loss of water proceeds, similarly to other acid salts, *via* incongruent melting with subsequent evaporation of water at higher temperatures. The intermediate product, unstable at room temperature, is decomposed during further heating to selenite and selenium(IV) oxide. This process is again accompanied by partial oxidation of selenite. The intermediate product was not characterized by physico-chemical methods.

The thermoanalytical properties of the studied potassium selenites could be explained using the method of gradually increasing temperature. In contrast to the thermogravimetric method, this procedure allows for a distinct recording of all intermediate products.

TABLE III

Thermoanalytical properties of potassium selenites studied by gradually increasing temperature method

Temperature, K	m, mass %	Comments
K_2SeO_3		
298–380	0.55	evaporation of H_2O (dampness)
380–725	plateau	K_2SeO_3
$KHSeO_3$		
298–390	5.60	decomposition to $K_2Se_2O_5$ and H_2O
340–615	plateau	$K_2Se_2O_5$
615–725	34.95	decomposition to K_2SeO_3 and SeO_2 and partial oxidation to K_2SeO_4
$KH_3(SeO_3)_2$		
298–335	plateau	$KH_3(SeO_3)_2$
335–410	9.35	decomposition to $K_2Se_2O_5$ (s), SeO_2 (s) and H_2O
410–450	plateau	$K_2Se_2O_5$ (s), SeO_2 (s)
450–585	46.95	sublimation of SeO_2
585–615	plateau	$K_2Se_2O_5$
615–725	64.25	decomposition to K_2SeO_3 , SeO_2 and partial oxidation to K_2SeO_4
$K_2Se_2O_5$		
298–550	plateau	$K_2Se_2O_5$
550–655	31.20	decomposition to K_2SeO_3 and SeO_2 and partial oxidation to K_2SeO_4
655–675	plateau	mixture of K_2SeO_3 and K_2SeO_4
$K_5H_3(SeO_3)_4$		
298–320	plateau	$K_5H_3(SeO_3)_4$
320–355	4.05	decomposition to $K_2SeO_3 \cdot 3 SeO_2$ and H_2O
355–675	plateau	$K_2SeO_3 \cdot 3 SeO_2$
675–725	14.05	decomposition to $K_2SeO_3 \cdot SeO_2$ and partial oxidation to K_2SeO_4

The infrared spectra of K_2SeO_3 , $K_2Se_2O_5$, $KHSeO_3$, $KDSeO_3$, $KH_3(SeO_3)_2$, $KD_3(SeO_3)_2$, $K_5H_3(SeO_3)_4$, and $K_5D_3(SeO_3)_4$ are given in Tables IV–VII. The assignment was done according to the literature^{11–18}. Common abbreviations were used in the tables where X stands for H or D. The infrared spectra of K_2SeO_3 correspond to C_{3v} symmetry of the anion. As the compound is strongly hygroscopic

TABLE IV
Infrared spectra (cm^{-1}) of K_2SeO_3 and $K_2Se_2O_5$

K_2SeO_3		$K_2Se_2O_5$	
$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
435 m	δ_s and $\delta_{as}(SeO_3)$	419 m	$\delta(SeO_2)$
645 w	not assigned	503 m	$\nu_s(SeO)(SeOSe)$
673 w		560 s	$\nu_{as}(SeO)(SeOSe)$
780 s	$\nu_{as}(SeO_3)$	825 s	$\nu_{as}(SeO_2)$
822 s	$\nu_s(SeO_3)$	834 s	
1 340 m		868 s	$\nu_s(SeO_2)$
1 650 w	$\delta(X_2O)_{ads}$		

TABLE V
Infrared spectra (cm^{-1}) of $KHSeO_3$ and $KDSeO_3$

$KHSeO_3$ $\tilde{\nu}(I)$	$KDSeO_3$ $\tilde{\nu}(II)$	Isotopic ratio $\tilde{\nu}(I)/\tilde{\nu}(II)$	Assignment
415 m	411 m	1.01	$\delta(SeO_2)$
610 s	597 s	1.02	$\nu(SeO)(SeOX)$
780 s, b	778 s, b	1.00	$\nu_{as}(SeO_2)$
851 s, b	847 s, b	1.00	$\nu_s(SeO_2)$
1 173 m	869 sh	1.35	$\delta(OX)(SeOX)$
1 650–1 690 w	1 220–1 270 w	1.35	$\nu(OX)(SeOX)$
2 100–2 450 mb (max. 2 350)	1 550–1 850 mb (max. 1 750)	1.34	
1 600–3 200 sb (max. 3 000)	1 950–2 400 sb (max. 2 250)	1.34	

the spectra also exhibited a band corresponding to adsorbed water ($1\ 650\text{ cm}^{-1}$) as well as bands at 650 and $1\ 340\text{ cm}^{-1}$ that have been described²⁴ for other hygroscopic selenites.

TABLE VI
Infrared spectra (cm^{-1}) of $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$

$\text{KH}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{I})$	$\text{KD}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{II})$	Isotopic ratio $\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
403 m	395 m	1.02	$\delta_s(\text{SeO}_2)$
655 s	650 s	1.02	$\nu(\text{SeO})(\text{SeOX})$
	755 s		$\nu_{\text{as}}(\text{SeO}_2)$
850 s	855 s	0.99	$\nu_s(\text{SeO}_2)$
1 150 sh	920 m	1.30	$\delta(\text{OH})(\text{SeOX})$
1 250 w	930 m	1.34	
1 610 mb	1 250 mb	1.29	$\nu(\text{OX})(\text{SeOX})$
2 100—2 600 sb (max. 2 400)	1 700—1 900 sb (max. 1 800)	1.33	
2 650—3 300 sb (max. 2 850)	1 950—2 500 sb (max. 2 200)	1.30	

TABLE VII
Infrared spectra (cm^{-1}) of $\text{K}_5\text{H}_3(\text{SeO}_3)_4$ and $\text{K}_5\text{D}_3(\text{SeO}_3)_4$

$\text{K}_5\text{H}_3(\text{SeO}_3)_4$ $\tilde{\nu}(\text{I})$	$\text{K}_5\text{D}_3(\text{SeO}_3)_4$ $\tilde{\nu}(\text{II})$	Isotopic ratio $\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
418 s	420 s	1.00	$\delta_s(\text{SeO}_3^{2-})$
435 s	435 s	1.00	$\delta_s(\text{SeO}_2)(\text{XSeO}_3^-)$
637 s	625 s	1.02	$\nu(\text{SeO})(\text{SeOX})$
723 m	729 m	0.99	$\nu_{\text{as}}(\text{SeO})(\text{SeO}_3^{2-})$
810 s	815 s	0.99	$\nu_s(\text{SeO})(\text{SeO}_3^{2-})$
824 s	828 s	1.00	$\nu_{\text{as}}(\text{SeO}_2)(\text{HSeO}_3^-),$ $\nu_s(\text{SeO}_2)(\text{HSeO}_3^-)$
1 230 m	937 sh	1.31	$\delta(\text{OX})(\text{SeOX})$
1 272 w	976 w	1.30	
1 720 wb	1 300 wb	1.32	$\nu(\text{OX})(\text{SeOX})$
2 100—2 500 sb (max. 2 350)	1 550—1 800 sb (max. 1 750)	1.35	
2 600—3 100 sb (max. 2 750)	1 930—2 200 sb (max. 2 050)	1.35	

The spectrum for $K_2Se_2O_5$ indicates a decrease in the assumed anion symmetry, C_{2v} , which is demonstrated by splitting of a degenerate valence vibration $\nu_{as}(SeO_2)$. The character of the spectrum demonstrated the presence of a bridged Se—O—Se diselenite group.

The study of infrared spectra of acid potassium selenites was concerned primarily with explanation of the behaviour of protons in hydrogen bonds in terms of their ordering as they decisively affect the dielectric properties of acid selenites. The position of the bands observed in the region of fundamental vibrations for $KHSeO_3$ indicated the presence of the $HSeO_3^-$ anion. Moreover, the characteristic intense band of the deformation vibration of the HO(Se) group corresponded an asymmetric proton along the hydrogen bond in an ordered position that is at lower discrete levels of the two-minimum potential function. This arrangement suggests low probability of proton tunneling²⁵ predicted for this compound by Cody¹⁸ on the basis of the valence vibration band broadening of the SeO_2 group.

The absorption bands for $K_5H_3(SeO_3)_4$ demonstrated the presence of hydrogen-selenite anions. Thus, similarly to $KHSeO_3$, protons occupy the ordered positions in the structure with minimum possibility of tunneling. Because of the lower number of hydrogen atoms in the molecule (three hydrogen atoms per four anions), it is also necessary to consider the presence of the selenite anion. The corresponding vibrations were found in the infrared spectrum.

In agreement with the structure studies¹³⁻¹⁵ the character of the infrared spectrum for $KH_3(SeO_3)_2$ corresponded to the presence of two protons in ordered positions and one proton with a high tunneling probability.

Three broad absorption bands characterized by similar maximum wave numbers were observed in the region of the HO(Se) valence vibrations for all the acid potassium selenites. Similar spectra of compounds differing in the number and length of hydrogen bonds is caused by a slow interbonding tunnel effect^{18,26}.

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