

Magnesium selenites

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The solubility diagram in the $\text{MgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system at 298 K was studied and on this basis the magnesium hydrogenselenite tetrahydrate $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ was prepared. Selenites $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ were studied by thermal analysis, X-ray powder analysis, and infrared spectroscopy. Magnesium diselenite MgSe_2O_5 was prepared on the basis of the thermal decomposition of $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$; this substance was studied in the same manner as the other selenites. The infrared spectra yielded the force constants for the bonds between selenium and oxygen: 498 N m^{-1} for $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$, 532 N m^{-1} for the SeO_2 group and 333 N m^{-1} for the SeOH group for $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ and for MgSe_2O_5 , 541 N m^{-1} for the SeO_2 group and 266 N m^{-1} for the selenium—oxygen—selenium bridge bonds. Analysis of the spectra yielded values for the energy of the hydrogen bonds in selenites in the range $20\text{—}39 \text{ kJ mol}^{-1}$ and hydrogen bond lengths in the range $269\text{—}289 \text{ pm}$.

Была изучена диаграмма растворимости при 298 в системе $\text{MgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ и на ее основании был впервые приготовлен $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$. Селениты $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ и $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ были изучены при помощи термического анализа, рентгенографии в порошках и инфракрасной спектроскопии. На основании термического разложения $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ был приготовлен селенит магния состава MgSe_2O_5 , который был изучен таким же способом, как и остальные селениты. По ИК спектрам были определены силовые константы связей Se—O : 498 Н м^{-1} для $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$, 532 Н м^{-1} в группе SeO_2 и 333 Н м^{-1} в группе SeOH для $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$, 541 Н м^{-1} в группе SeO_2 и 266 Н м^{-1} в мостиковых связях Se—O—Se для MgSe_2O_5 . Энергии водородных связей в селенитах были по спектрам найдены в интервале $20\text{—}39 \text{ кДж моль}^{-1}$ и длины связей порядка $269\text{—}289 \text{ пм}$.

The study of selenites has recently received increased attention because of the ferroelectric properties which have been observed for these substances. Thus we also began a systematic study of selenites; this work will deal with magnesium selenites.

The preparation of the hexahydrate of magnesium selenite consists of precipitation of a magnesium chloride solution with a sodium selenite solution as described by Nilson [1]. The thermodynamic properties (ΔH_{298}^0 , ΔG_{298}^0 , ΔS_{298}^0) for the formation of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ were found by Leshchinskaya [2] on the basis of calorimetric measurements; Chukhlantsev [3] found the solubility product (1.29×10^{-5}). Leshchinskaya [2] studied the thermal decomposition and at 473 K obtained the anhydrous amorphous selenite MgSeO_3 , which yielded crystalline anhydrous MgSeO_3 after boiling for 2 h in water and drying for 12 h at 463–473 K in the air. The crystal structure of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ was found by Weiss [4]. Paetzold [5–7] systematically measured the infrared spectra of the selenites and, from the spectra of alkali selenites, determined the approximate constitution and symmetry of selenite, hydrogenselenite, and diselenite ions and calculated the force constants of the selenium—oxygen bonds. For the SeO_3^{2-} anion he proposed the symmetry point group C_{3v} and for the HSeO_3^- anion the point group C_s with a hydroxyl group bonded to the SeO_2 group; for the $\text{Se}_2\text{O}_5^{2-}$ anion he proposed a point group of symmetry C_{2v} with two SeO_2 groups joined by an oxygen bridge. Rocchiccioli [8] measured the infrared spectrum of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$.

Salts with magnesium to selenium ratios other than 1 : 1 have been studied much less. The first mention of a substance corresponding to the formula MgSe_2O_5 appeared in the work by Berzelius [9]; neither the preparation nor the analysis is, however, described.

It is further mentioned that MgSeO_3 is soluble in selenous acid to give a salt which can be precipitated by ethanol from the solution [10]. Again neither the composition nor the analysis is described. Somewhat more concrete data on hydrogenselenites or diselenites are given in the works by Nilson [1] and by Boutzoureano [11], which describe the preparation of substances in aqueous solution at laboratory temperature with compositions corresponding to the formulae $\text{Mg}(\text{HSeO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{MgH}_4(\text{SeO}_3)_3$. The preparation of anhydrous diselenite MgSe_2O_5 in a sealed tube at 473 K is also described. All these works were carried out in the last century and since then no one has studied magnesium hydrogenselenites and diselenites.

This work was carried out in order to prepare all the selenites in the $\text{MgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system at 298 K and to study their bonding conditions.

Experimental

Chemicals and methods

Magnesium selenite $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ was prepared by precipitating a 0.2 M aqueous solution of sodium selenite (Lachema, Brno; anal. grade) with a 0.2 M aqueous solution of magnesium(II) perchlorate (Xenon, Łódź; anal. grade). The deuterated derivative

$\text{MgSeO}_3 \cdot 6\text{D}_2\text{O}$ for infrared spectroscopy was prepared from anhydrous, amorphous MgSeO_3 by shaking for several hours with deuterium oxide. The deuterated derivative $\text{Mg}(\text{DSeO}_3)_2 \cdot 4\text{D}_2\text{O}$ for infrared spectroscopy was prepared from $\text{MgSeO}_3 \cdot 6\text{D}_2\text{O}$, SeO_2 , and D_2O according to the solubility diagram. Selenium dioxide was the product of Lachema, Brno (anal. grade).

The initial substances and final products were analyzed gravimetrically. Selenium was determined by an adjusted method according to Bode [12]: selenite was reduced to grey selenium in a 6 M-HCl medium at the boiling point with sulfur dioxide. After 12 h the mixture was filtered on an S3 frit, washed with water and acetone, dried for 3 h at 333 K and weighed. Magnesium was determined as $\text{Mg}_2\text{P}_2\text{O}_7$ [13]. Titrimetric analysis was used to determine the solubility. Selenium(IV) was determined iodometrically by the method described by Ganitskii [14]; magnesium was titrated complexometrically using Eriochrome Black in a Schwarzenbach buffer medium [15].

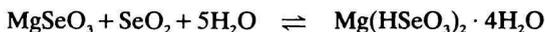
Thermal decomposition with increasing temperature was studied on a Derivatograph instrument (MOM, Budapest) over the range 293—873 K with a temperature program of 5 K min^{-1} . X-ray powder diffraction patterns were measured on an instrument from Chirana, Czechoslovakia, using cells from Siemens or Chirana with a diameter of 57.3 mm. The sample was placed on a rod or, with anhydrous substances, in a Lindenmann glass capillary with a diameter of 0.3—0.5 mm. The average exposure time was 45 min at a voltage of 35 kV and a current of 20 mA. The diffractograms were measured on a Diffractograph from Chirana, Czechoslovakia, at a voltage of 35 kV and a current of 15 mA.

The infrared spectra were obtained on a UR-20 instrument (Zeiss, Jena) in the range 400—4000 cm^{-1} . The spectra were measured in a nujol mull using potassium bromide cells. The region of stretching vibrations of the hydroxyl group was also measured in a tripene mull.

Study of solubility in the MgSeO_3 — SeO_2 — H_2O system at 298 K

The solubility in the MgSeO_3 — SeO_2 — H_2O system was studied using the method of determining solubility in ternary systems based on the Schreinemakers method. The time required for equilibration differed for individual samples of the system. If a solid phase remained after mixing the initial components of the system, then the time required for attainment of equilibrium was not greater than several days. If, however, a supersaturated solution was formed, from which a solid phase slowly crystallized out, then the equilibrium formation lasted up to several weeks.

Fig. 1 depicts the solubility diagram obtained according to Gibbs—Roozeboom. It follows from the diagram that the incongruently soluble compound $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ is formed in crystallization field III and that crystallization fields I and V correspond to the original substances. Equilibrium between two solid phases and the solution corresponding to point P or E corresponds to fields II and IV. Peritonic point P corresponds to composition 17.6% MgSeO_3 , 13.4% SeO_2 , and 69.0% H_2O and eutonic point E to composition 13.5% MgSeO_3 , 56.5% SeO_2 , and 30.0% H_2O . In field II at a composition of the liquid phase corresponding to point P the phase reaction leading to formation of hydrogenselenite can be described



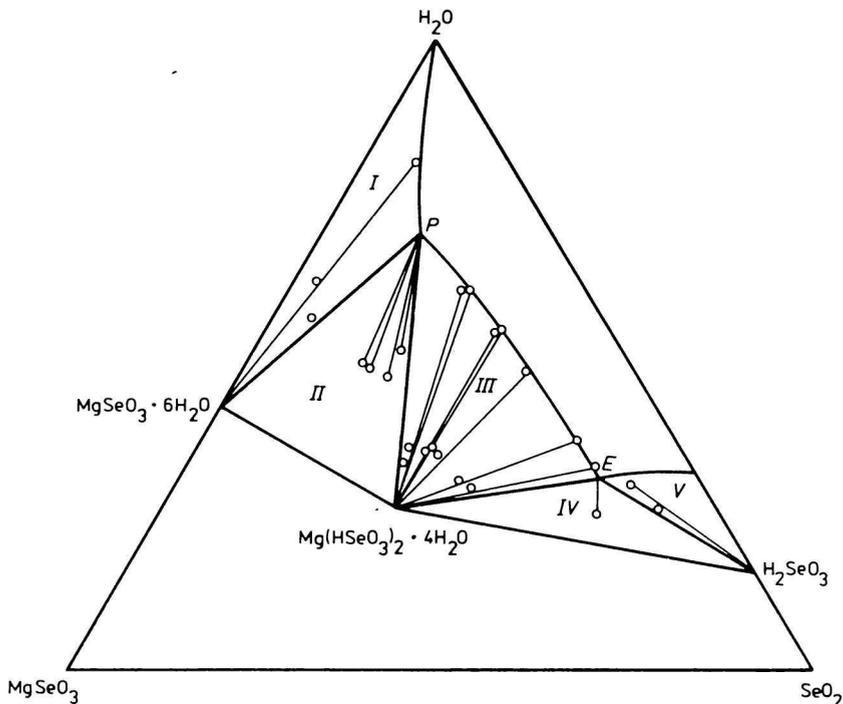


Fig. 1. Solubility diagram of the MgSeO₃—SeO₂—H₂O system.

On the basis of this solubility diagram the magnesium hydrogenselenite tetrahydrate was isolated. The material was collected on an S3 frit, rinsed with ethanol and ether and dried in the air at laboratory temperature. The results of gravimetric analysis corresponded well to the calculated data (found: 6.92% Mg and 44.1% Se; calculated 6.89% Mg and 44.7% Se). The isolated substance is fine, crystalline, and colourless and is stable in the air at laboratory temperature.

Thermal analysis, X-ray powder analysis, and molecular infrared spectroscopy

The results of thermal decomposition of MgSeO₃ · 6H₂O are given in Table 1. The initial substances and products of thermal decomposition were studied by X-ray diffraction. The hexahydrate of magnesium selenite yields the X-ray powder diffraction pattern given in Table 8. Heating of this substance yields anhydrous amorphous MgSeO₃, which, at higher temperatures (Table 1), crystallizes to anhydrous crystalline MgSeO₃, and yields the X-ray powder diffraction pattern given in Table 8.

The results of thermal decomposition of Mg(HSeO₃)₂ · 4H₂O are given in Table 2. The initial substances and products of thermal decomposition were studied by X-ray diffraction. The magnesium hydrogenselenite tetrahydrate yields the X-ray powder diffraction pattern given in Table 8. Heating yields MgSe₂O₃ (Table 2), which yields the X-ray powder diffraction pattern given in Table 8. Further heating converts the diselenite to anhydrous

Table 1

Thermal decomposition of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$

T/K	GTA	DTA	Assignment
328—388 468 and higher	Decrease -42.9% delayed	endo —	Dehydration MgSeO_3 , anhydrous, amorphous
673—693	—	exo	Recrystallization to MgSeO_3 , anhydrous, crystalline

Table 2

Thermal decomposition of $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$

T/K	GTA	DTA	Assignment
338—378 423—623	Combined decrease -25.0% delayed	Doubled endo —	Dehydration MgSe_2O_5
583—603	—	exo (weak)	?
673—723 733 and higher	Decrease -58.8% delayed	endo —	Loss of SeO_2 MgSeO_3 , anhydrous, crystalline

Table 3

Infrared spectrum of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ and of $\text{MgSeO}_3 \cdot 6\text{D}_2\text{O}$

$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ $\tilde{\nu}/\text{cm}^{-1}$	$\text{MgSeO}_3 \cdot 6\text{D}_2\text{O}$ $\tilde{\nu}/\text{cm}^{-1}$	$\tilde{\nu}\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ — $\tilde{\nu}\text{MgSeO}_3 \cdot 6\text{D}_2\text{O}$	Assignment
420 m	410 m	1.02	} $\delta(\text{SeO}_3)$
462 m	450 m	1.02	
520 m	545 m	0.95	
683 sh	—	—	
745 s	740 s	1.01	$\nu_s(\text{SeO}_3)$
810 m	813 m	1.00	} $\nu_{as}(\text{SeO}_3)$
860 w	860 w	1.00	
930 m	—	—	?
1685 m	1230 m	1.37	$\delta(\text{OH})(\text{H}_2\text{O})$
2360 mb	—	—	?
3055 sb	2290 sb	1.33	} $\nu(\text{OH})(\text{H}_2\text{O})$
3435 sb	2555 sb	1.34	

s — strong, m — medium, w — weak, sh — shoulder, b — broad; δ — bending, ν_s — symmetric stretching, ν_{as} — antisymmetric stretching.

Table 4

Infrared spectrum of $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ and of $\text{Mg}(\text{DSeO}_3)_2 \cdot 4\text{D}_2\text{O}$

$\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$ $\tilde{\nu}/\text{cm}^{-1}$	$\text{Mg}(\text{DSeO}_3)_2 \cdot 4\text{D}_2\text{O}$ $\tilde{\nu}/\text{cm}^{-1}$	$\frac{\tilde{\nu}\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}}{\tilde{\nu}\text{Mg}(\text{DSeO}_3)_2 \cdot 4\text{D}_2\text{O}}$	Assignment
482 m	482 m	1.00	$\delta(\text{SeO}_2)$
532 sh	562 m	0.94	
635 sh	647 m	0.98	$\nu(\text{SeO})(\text{SeOH})$
668 m		1.03	
825 s	813 s	1.01	$\nu_{\text{as}}(\text{SeO}_2)$
865 s	860 s	1.01	$\nu_s(\text{SeO}_2)$
950 vw	727 w	1.31	$\gamma(\text{OH})(\text{SeOH})$
1185 w	880 sh	1.35	$\delta(\text{OH})(\text{SeOH})$
1685 w	1227 w	1.37	$\delta(\text{OH})(\text{H}_2\text{O})$
2390 wb	2168 mb	1.10	$\nu(\text{OH})(\text{SeOH})$
2950 sh	2325 sh	1.27	
3185 sb	2365 sb	1.33	$\nu(\text{OH})(\text{H}_2\text{O})$
3370 sb	2530 sb	1.33	

vw — very weak; γ — bending out-of-plane (torsion).

Table 5

Infrared spectrum of MgSe_2O_5

MgSe_2O_5 $\tilde{\nu}/\text{cm}^{-1}$	Assignment
405 m	$\delta(\text{SeO}_2)$
465 mb	
527 m	$\nu(\text{Se—O—Se})$
580 mb	
625 mb	
785 s	$\nu_{\text{as}}(\text{SeO}_2)$
850 m	$\nu_s(\text{SeO}_2)$
870 sh	
890 s	

crystalline MgSeO_3 , which yields an X-ray powder diffraction pattern identical to that of crystalline MgSeO_3 obtained from decomposition of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$. The identity of these substances was also confirmed diffractographically. The infrared spectra of the substances $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$, MgSe_2O_5 , and their deuterated derivatives are given in Tables 3—5. Band assignment in the spectra was carried out according to the works of Paetzold [5—7].

Discussion

The $\text{MgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system at 298 K was found to contain a not yet described selenite with composition $\text{Mg}:\text{Se}:\text{H}_2\text{O} = 1:2:5$. Study of similar systems with alkali metals (M^I) revealed the presence of hydrogenselenites with composition $\text{M}^I:\text{Se} 1:1, 1:2, 1:4, \text{ and } 5:4$; no hydrogen salt was found for barium, only anhydrous barium diselenite. The substance obtained here can be formulated as magnesium anhydrous hydrogenselenite tetrahydrate or as magnesium diselenite pentahydrate. Considering the presence of the bands of vibrations $\nu(\text{OH})$ (SeOH) and $\delta(\text{OH})$ (SeOH) in the infrared spectrum (Table 4), it can be regarded as unambiguously demonstrated that hydrogenselenite is present.

It follows from the thermal analysis of $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ and from the X-ray powder diffraction patterns that anhydrous selenite formed at 328—388 K, is amorphous up to 673 K and at 673—693 K crystallizes to anhydrous crystalline MgSeO_3 . Thermal decomposition of hydrogenselenite at 338—378 K yields magnesium diselenite MgSe_2O_5 , which is converted into anhydrous crystalline MgSeO_3 at 673—723 K. The double endothermic effect on the DTA curve at 338—358 and 368—378 K indicates the presence of a dehydration intermediate, which could be anhydrous $\text{Mg}(\text{HSeO}_3)_2$ or a lower hydrate.

We also studied the bonding conditions in these compounds. Table 6 lists the force constants of the Se—O bonds for the studied selenites, found from the infrared spectra. The force constants were calculated from the relationship

$$k_{\text{SeO}} = \bar{\lambda}\mu$$

If $4\pi^2\bar{\nu}^2c^2 = \lambda$, then the *Lehmann* expression [16] can be employed for averaging the wavenumbers

$$\bar{\lambda} = \frac{1}{x} [\lambda_s + \lambda_{\text{as}}(x - 1)]$$

where μ is the reduced mass of the selenium—oxygen pair of atoms, $\bar{\nu}$ is the wavenumber of the stretching vibration of the selenium—oxygen bond, c is the velocity of light, and x is the number of oxygen atoms in the SeO_x group.

Table 6

Force constants for the selenium—oxygen bonds

Substance	Group	$\bar{\nu}_s/\text{cm}^{-1}$	$\bar{\nu}_{\text{as}}/\text{cm}^{-1}$	$k_{\text{SeO}}/\text{N m}^{-1}$
$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$	SeO_3	714	835	498
$\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$	SeO_2	865	780	532
	SeOH	652	—	333
MgSe_2O_5	SeO_2	870	790	541
	Se—O—Se	577	—	266

Table 7

Energy and length of hydrogen bonds

Substance	$E/\text{kJ mol}^{-1}$ bond	O ... O Distance/pm
$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$	20 ^a	286
	39 ^a	270
$\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$	25	281
	38	269

a) Calculated from the Yuhnevich model; corresponds to energies E_1 and E_2 .

Table 8

X-ray powder diffraction patterns of magnesium selenites

$\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$		$\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$		MgSeO_3 , anhydrous, crystalline		MgSe_2O_5	
I	d	I	d	I	d	I	d
3	590	10	660	1	850	2	415
10	450	10	610	1	590	10	340
2	410	3	540	1	500	7	307
10	390	3	520	1	440	9	283
3	360	3	460	5	420	1	279
10	299	3	430	6	410	1	265
2	294	1	410	5	380	1	257
10	283	4	390	8	370	1	225
2	277	1	380	5	344	4	215
2	262	3	370	1	330	1	206
10	248	2	361	3	312	5	197
2	245	9	342	1	303	4	189
2	227	9	332	2	294	4	181
3	218	1	323	10	286	8	170
3	212	3	316	10	279	4	161.5
10	196	2	305	1	260	1	155.5
2	194	2	294	3	250	3	147.9
9	180	2	281	3	245	2	145.4
2	177	8	269	1	232	2	141.9
7	172	1	259	1	228	2	132.7
2	170	1	250	2	221	1	130.5
2	166	5	248	2	214	4	128.3
2	156	1	239	3	208	1	123.3
1	155	3	230	1	197	1	121.1
						1	118.2

Table 8 (Continued)

MgSeO ₃ · 6H ₂ O		Mg(HSeO ₃) ₂ · 4H ₂ O		MgSeO ₃ anhydrous, crystalline	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
3	149.2	3	225	2	194
1	142.6	3	221	2	185
3	141.5	2	211	1	182
2	140.0	2	207	6	177
		3	201	4	174
		2	196	1	172
		1	191	1	168
		2	190	1	165.2
		1	185	1	160.0
		7	180	2	155.1
		4	177	4	151.4
		1	167.5	1	145.4
		5	163.5	1	143.0
		2	159.0	1	134.4
		1	145.8	1	130.8
		1	130.5	1	128.6
		1	120.4		
		1	117.9		

I — intensity 1—10, found visually; *d* — interplanar distance in pm.

It follows from the table of force constants that the force constants in the SeO₂ groups in the hydrogenselenite and diselenite anions are somewhat higher than in the SeO₃ group and, on the other hand, the force constants in the SeOH and Se—O—Se groups are much lower than for the SeO₃ group. According to Paetzold's data, the situation is analogous for alkali selenites.

Table 7 lists the energies and lengths of the hydrogen bonds in the studied selenites obtained from the infrared spectra. The energy of the hydrogen bonds was calculated for MgSeO₃ · 6H₂O from the relationship given by Yukhnevich and Karyakin [17] for coupled oscillators

$$E_1 = \frac{3780 - (v_\pi + \delta v_\pi)}{62} - e^{-\frac{3860 - (v_\pi + \delta v_\pi)}{120}}$$

$$E_2 = E_1 + 0.014\Delta v - \frac{1.8 \times 10^{-5}}{(\Delta v)^2}$$

where $\delta v_\pi = 45 \left(1 - \frac{10^4}{(\Delta v)^2} \right)$;

- ν_{π} = the value of the highest wavenumber of the OH stretching vibration region,
 $\Delta\nu$ = the difference between the wavenumbers of the absorption bands corresponding to vibrations of the hydroxyl group,
 E_1 = the energy of the hydrogen bond between the water molecules,
 E_2 = the energy of the hydrogen bonds between the water molecules and the anion.

The Yuhnevich model could not be used for $\text{Mg}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$. Thus the simple relationship [18]

$$E = \frac{\nu_0 - \nu}{0.017\nu_0}$$

was used, where 3750 is substituted for ν_0 , which is the wavenumber of the stretching vibration of the hydroxyl group in the free H_2O molecule, and ν is the wavenumber of the stretching vibration of the hydroxyl group in the hydrate.

The constants in all the formulae are calculated so that the result is in kcal mol^{-1} of bond. The lengths of the hydrogen bonds were calculated from the correlation diagrams $\nu_{\text{OH}} - R_{\text{O}\dots\text{O}}$ of *Naberukhin* [19], *Pirrene* [20], *Novak* [21], *Ratajczak* [22], and *Nakamoto* [23]. For $\text{MgSeO}_3 \cdot 6\text{H}_2\text{O}$ the spectral data can be compared with the structural data. It was found by X-ray structural analysis [4] that there are two hydrogen bonds with lengths of 291 and 270 pm, corresponding to our data. On the basis of the energy of the hydrogen bonds, the SeO_3^{2-} and HSeO_3^- anions can be classified among positively hydrated anions in which the hydrogen bond between the water molecules and the anion is stronger than that between the water molecules [17]. The hydrogen bonds in the studied selenites can be classified among weak and medium strong.

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