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Thermochimica Acta 342 (1999) 89–95

thermochimica acta

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DTA, DSC and X-ray studies on copper and manganese selenate hydrates

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Received 5 May 1999; received in revised form 15 July 1999; accepted 18 July 1999

Abstract

The thermal dehydration of copper and manganese selenate hydrates has been studied by TG, DTA and DSC. The enthalpies of dehydration stages as well as the enthalpies of formation of $CuSeO_4{\cdot}5H_2O$, $CuSeO_4{\cdot}H_2O$, $MnSeO_4{\cdot}5H_2O$, $MnSeO_4{\cdot}2H_2O$ and $MnSeO_4{\cdot}H_2O$ have been determined. The comparatively lower temperature of $CuSeO_4{\cdot}H_2O$ dehydration as compared to the kieserite-type compounds $MeSeO_4{\cdot}H_2O$ (Mg, Mn, Co, Ni, Zn) and the formation of $CuSeO_4{\cdot}0.5H_2O$ have been discussed in terms of the crystal structures. The dehydration of copper and manganese selenate hydrates has been studied in aqueous and aqueous-acid solutions. A crystallization field of $MnSeO_4{\cdot}4H_2O$ is observed in the ternary $MnSeO_4$–H_2SeO_4–H_2O system at 20°C. The strength of the hydrogen bonds in $MnSeO_4{\cdot}2H_2O$ and $CuSeO_4{\cdot}H_2O$ has been studied by FTIR spectroscopy. Two crystallographically unequivalent water molecules asymmetrically bonded to the metal ions are assumed to exist in $MnSeO_4{\cdot}2H_2O$. The oxygen atoms from water molecules in an almost square planar structure of $Cu(H_2O)_2(SeO_4)_2$ complex form strong hydrogen bonds due to the strong Cu–H_2O interaction (synergetic effect). Lattice parameters of $CuSeO_4{\cdot}3H_2O$ have been calculated: $a = 5.720(2)$ Å, $b = 13.437(4)$ Å, $c = 7.475(2)$ Å, $\beta = 97.25(2)°$, $V = 570.0(2)$ Å^3, SG Cc.

Keywords: Copper and manganese selenate hydrates; Heat of dehydration; Heat of formation; Lattice parameters; Hydrogen bond strength

1. Introduction

This paper aims at studying the thermal dehydration of some manganese and copper selenate hydrates by the methods of DTA and DSC. Based on the DSC measurements both the enthalpies of dehydration for the observed stages and the enthalpies of formation of some manganese and copper selenate hydrates have been calculated. Our previous investigations of the thermal dehydration of divalent metal selenate hydrates (Mg, Co, Ni, Zn) are discussed elsewhere [1–5].

The dehydration of the copper selenate hydrates in air (TG and DTA) and in solutions is reported in [6]. The following scheme of the dehydration of $CuSeO_4{\cdot}5H_2O$ was proposed:

$$CuSeO_4\cdot 5H_2O \overset{125°C}{\rightarrow} CuSeO_4\cdot 3H_2O \overset{147°C}{\rightarrow} CuSeO_4\cdot H_2O \overset{225°C}{\rightarrow} CuSeO_4\cdot 0.5H_2O \overset{270°C}{\rightarrow} CuSeO_4$$

The thermal dehydration of $MnSeO_4{\cdot}5H_2O$ and $MnSeO_4{\cdot}2H_2O$ is commented in [7,8].

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PII: S0040-6031(99)00238-5

2. Experimental

Manganese and copper selenates were prepared by neutralization of the corresponding hydroxide carbonates with aqueous solutions of selenic acid at 50°C. Then the solutions were filtered and concentrated. The crystals of $MnSeO_4{\cdot}xH_2O$ were obtained either by concentration of the solution under vacuum (in order to avoid the oxidation of the Mn^{2+} ions) or by salting out with ethyl alcohol. $MnSeO_4{\cdot}5H_2O$ and $MnSeO_4{\cdot}2H_2O$ were prepared by recrystallization from aqueous solutions at 25 and 50°C, respectively, and $MnSeO_4{\cdot}H_2O$ – from solutions containing about 50–60% selenic acid at room temperature. $CuSeO_4{\cdot}5H_2O$ crystallizes from an aqueous solution at room temperature; $CuSeO_4{\cdot}3H_2O$ – from the $CuSeO_4$–H_2SeO_4–H_2O system at 60°C in the concentration range of 35–45% selenic acid, and $CuSeO_4{\cdot}H_2O$ – from a solution containing about 60% selenic acid at 25°C. All the reagents used were 'p.a.' (Merck).

The salts obtained were identified by chemical analysis (the metal ion concentrations were determined compelexometrically) and by X-ray powder diffraction method. The X-ray patterns were obtained at a scanning speed of $1^\circ\ min^{-1}$ with a DRON-3 powder diffractometer using Cu Kα radiation. The lattice parameters were calculated using LSUCR program. The DSC measurements were recorded with a Perkin Elmer DSC-4 instrument up to 400°C using standard aluminium pans with pin holes at heating rates of 5 and $2.5^\circ C\ min^{-1}$ (sample mass 5–6 mg). The temperature and sensitivity were carefully calibrated before the experiments. Indium (purity > 99.9%) was used as a standard substance. The experimental error in $\Delta_{deh}H$ is about 2–2.5%. The enthalpy values were obtained as mean values from three measurements. TG, DTG and DTA curves were obtained using derivatograph Paulik-Paulik-Erdey MOM OD-102 in the temperature range up to 450°C at a heating rate of $5^\circ C\ min^{-1}$ and sample mass 250 mg. The IR spectra of the isotopically dilute samples (5–7% D_2O) were recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution < $2\ cm^{-1}$) at ambient temperature using KBr discs (manganese selenate hydrates) and paraffin mulls (copper selenate hydrates).

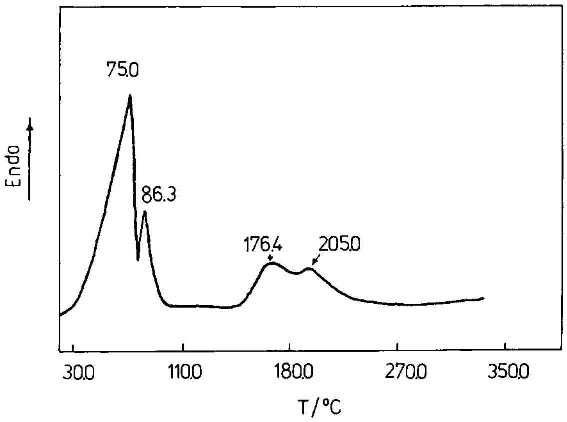

Fig. 1. DSC curve of $CuSeO_4{\cdot}5H_2O$.

The solubilities in the $MnSeO_4$–H_2O system in the temperature interval of 20–60°C as well as in the ternary system $MnSeO_4$–H_2SeO_4–H_2O at 20°C were studied using the method of isothermal decrease of supersaturation. The equilibrium was reached in about 10–12 h. The experiments were carried out in the presence of argon to prevent the oxidation of Mn^{2+}ions and at a slight excess of selenic acid (2–3%) for $MnSeO_4$–H_2O system to suppress the hydrolysis of the salt.

3. Results and discussion

3.1. Copper selenate hydrates

The TG and DTA data of the copper selenate hydrates coincide with those reported in [6] and are not given in the paper. The DSC curve of $CuSeO_4{\cdot}5H_2O$ (Fig. 1, Table 1) exhibits strong endothermic effect with two maxima in the temperature interval of 30–100°C, which corresponds to the stepwise separation of four water molecules, thus forming $CuSeO_4{\cdot}H_2O$. The maximum at 75°C is attributed to the formation $CuSeO_4{\cdot}3H_2O$, in agreement with the DTA and TG measurements. However, the lower heating rate ($2.5^\circ C\ min^{-1}$) does not lead to the resolution of the two dehydration stages. The dehydration of $CuSeO_4{\cdot}H_2O$ occurs also stepwise – two maxima at 176 and 205°C are observed in the temperature interval of 130–270°C. Based on the DTA

Table 1
DSC data for copper and manganese selenate hydrates

Dehydration processes	T_{onset} (°C)	T_{max} (°C)	$\Delta_{deh}H$ (kJ mol^{-1})
$CuSeO_4 \cdot 5H_2O \rightarrow CuSeO_4 \cdot 3H_2O + 2H_2O$	53.1	75.0	
$CuSeO_4 \cdot 3H_2O \rightarrow CuSeO_4 \cdot H_2O + 2H_2O$		86.3	203.6
$CuSeO_4 \cdot H_2O \rightarrow CuSeO_4 \cdot 0.5H_2O + 0.5H_2O$	156.8	176.4	
$CuSeO_4 \cdot 0.5H_2O \rightarrow CuSeO_4 + 0.5H_2O$		205.0	77.9
$CuSeO_4 \cdot 5H_2O \rightarrow CuSeO_4 + 5H_2O$			281.5
$CuSeO_4 \cdot H_2O \rightarrow CuSeO_4 + H_2O$			77.9
$MnSeO_4 \cdot 5H_2O \rightarrow MnSeO_4 \cdot 4H_2O + H_2O$	41.1	58.5	
$MnSeO_4 \cdot 4H_2O \rightarrow MnSeO_4 \cdot 2H_2O + 2H_2O$		64.5	154.9
$MnSeO_4 \cdot 2H_2O \rightarrow MnSeO_4 + 2H_2O$	143.7	163.1; 185.8	
		237.2	112.6
$MnSeO_4 \cdot 5H_2O \rightarrow MnSeO_4 + 5H_2O$			267.5
$MnSeO_4 \cdot 2H_2O \rightarrow MnSeO_4 \cdot H_2O + H_2O$	172.6	174.6	48.1
$MnSeO_4 \cdot H_2O \rightarrow MnSeO_4 + H_2O$	247.0	262.2	84.9
$MnSeO_4 \cdot 2H_2O \rightarrow MnSeO_4 + 2H_2O$			133.0
$MnSeO_4 \cdot H_2O \rightarrow MnSeO_4 + H_2O$	208.5	243.8	68.9

and TG measurements $CuSeO_4 \cdot 0.5H_2O$ is assumed to be formed as an intermediate product.

In the literature there are no crystallographic data of $CuSeO_4 \cdot 3H_2O$. It is unstable in air and transforms rapidly into $CuSeO_4 \cdot 5H_2O$. The X-ray powder diffraction measurements were carried out using a paraffin thin film (parafilm ‘M’ – American Can Company). $CuSeO_4 \cdot 3H_2O$ is isostructural with $CuSO_4 \cdot 3H_2O$ and crystallizes in the monoclinic system with lattice constants: $a = 5.720(2)$ Å, $b =$ 13.437(4) Å, $c = 7.475(2)$ Å, $\beta = 97.25(2)°$, $V =$ 570.0(2) Å^3, SG Cc (h k l and d-spacings are given in Table 2).

The formation of $CuSeO_4 \cdot 0.5H_2O$ as well as the comparatively lower temperature of $CuSeO_4 \cdot H_2O$ dehydration as compared to those in the kieserite-type compounds $MeSeO_4 \cdot H_2O$ (Mg, Mn, Co, Ni, Zn) need some additional comments. In $CuSeO_4 \cdot H_2O$ crystal structure the water molecule is bridging bonded to two crystallographically unequivalent copper ions and exhibits two different Cu–O_w bond lengths (Cu(1)–O_w is 2.434 Å and Cu(2)–O_w is 2.020 Å) [9]. As a result of the different coordination environments of the two copper ions in the squares ([Cu(1)O_4] and [Cu(2)$O_2(O_w)_2$]) the water molecule is strongly distorted and forms two different hydrogen bonds (2.812 and 2.723 Å). The strong distortion of the water molecule in $CuSeO_4 \cdot H_2O$ crystal structure reflects in the appearance of two bands at 2460 and 2318 cm^{-1} in the IR spectrum of the isotopically dilute sample, corresponding to two O–D distances (Fig. 2(a)). The stronger hydrogen bond (band at 2318 cm^{-1}) than as is expected from the O...O_w distance (2.723 Å) in the kieserite-type selenates [10,11] is due to the strong Cu–H_2O interaction (synergetic effect) in the Cu(2)-octahedra. The large Cu(1)–H_2O distance and the weaker hydrogen bond (band at 2460 cm^{-1}) explain the formation of $CuSeO_4 \cdot 0.5H_2O$. Contrarily, a symmetrical water molecule (site symmetry C_2) exists in the crystal structure of the kieserite-type compounds [10], which form comparatively strong hydrogen bonds (see Fig. 2(b)) and as a result the formation of semihydrates is not observed.

3.2. *Manganese selenate hydrates*

The derivatogram of $MnSeO_4 \cdot 5H_2O$ (Fig. 3) exhibits four endothermic peaks at 70, 105, 160 and 260°C on the DTA and DTG curves, indicating that the dehydration of the pentahydrate occurs in four steps. The mass losses calculated show that the first peak at

Table 2
X-ray powder diffraction data for $CuSeO_4 \cdot 3H_2O$

d_{obs} (Å)	h k l	I/I_0	d_{obs} (Å)	h k l	I/I_0
5.24	1 1 0	80	2.347	$\bar{1}$ 5 1	10
4.97	0 2 1	15	2.319	0 2 3	7
4.54	$\bar{1}$ 1 1	100	2.264	$\bar{2}$ 2 2	7
4.05	1 1 1	50	2.168	2 4 0	<5
3.71	0 0 2	70	2.143	0 6 1	5
3.51	1 3 0	40	2.101	$\bar{1}$ 3 3	5
3.36	0 4 0	60	2.085	$\bar{1}$ 5 2	5
3.28	$\bar{1}$ 3 1	40	1.983	1 5 2	10
3.20	$\bar{1}$ 1 2	7	1.950	1 3 3	5
3.08	1 3 1	60	1.911	$\bar{2}$ 2 3	<5
2.869	1 1 2	50	1.871	$\bar{3}$ 1 1	25
2.840	2 0 0	7	1.819	1 7 0	5
2.658	$\bar{1}$ 3 2	<5	1.762	$\bar{3}$ 1 2	30
2.612	2 2 0	5	1.742	$\bar{2}$ 6 1	50
2.558	$\bar{2}$ 2 1	70	1.686	1 1 4	10
2.489	0 4 2	20	1.682	2 6 1	10
2.458	1 3 2	5	1.659	$\bar{1}$ 7 2	10
2.406	$\bar{2}$ 0 2	5	1.653	$\bar{3}$ 3 2	40
2.380	2 2 1	10	1.650	$\bar{2}$ 0 4	20

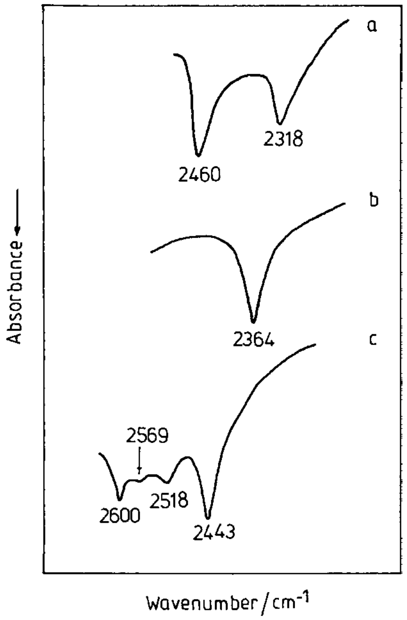

Fig. 2. IR spectra of isotopically dilute samples (5/7% D_2O) of $CuSeO_4 \cdot H_2O$ (a); $MnSeO_4 \cdot H_2O$ (b) and $MnSeO_4 \cdot 2H_2O$ (c).

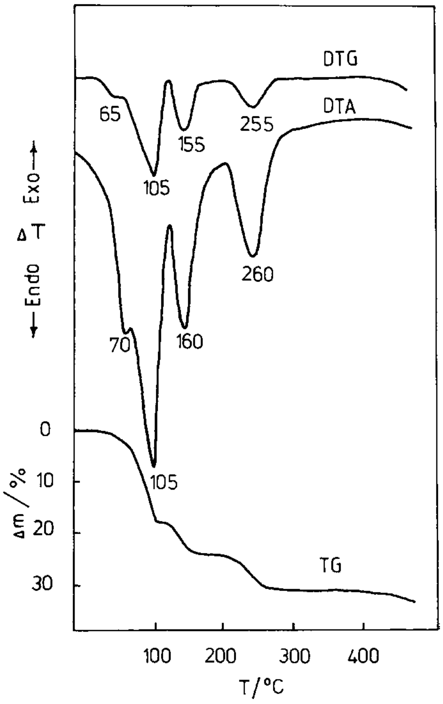

Fig. 3. TG, DTG and DTA curves of $MnSeO_4 \cdot 5H_2O$.

70°C is due to the separation of one water molecule thus forming $MnSeO_4 \cdot 4H_2O$. However, no temperature interval of stability of the tetrahydrate could be seen on the TG curve. The transformation of $MnSeO_4 \cdot 4H_2O$ into $MnSeO_4 \cdot 2H_2O$ is registered on the DTA and DTG curves with a peak at 105°C. At higher temperatures the dehydration proceeds with the formation of $MnSeO_4 \cdot H_2O$ (160°C) and $MnSeO_4$ (260°C). On the basis of the experimental results we propose the following scheme of the thermal dehydration of $MnSeO_4 \cdot 5H_2O$:

$$MnSeO_4 \cdot 5H_2O$$

$$\underset{\Delta m_{exp}=5.8\%, \Delta m_{th}=6.2\%}{\overset{70^\circ C}{\longrightarrow}} MnSeO_4 \cdot 4H_2O$$

$$\underset{\Delta m_{exp}=18.4\%, \Delta m_{th}=18.7\%}{\overset{105^\circ C}{\longrightarrow}} MnSeO_4 \cdot 2H_2O$$

$$\underset{\Delta m_{exp}=24.8\%, \Delta m_{th}=25.0\%}{\overset{160^\circ C}{\longrightarrow}} MnSeO_4 \cdot H_2O$$

$$\underset{\Delta m_{exp}=31.2\%, \Delta m_{th}=31.3\%}{\overset{260^\circ C}{\longrightarrow}} MnSeO_4$$

The strong endothermic peak with maxima at 58 and 64°C in the DSC curve of $MnSeO_4 \cdot 5H_2O$ (Fig. 4(a), Table 1) corresponds to the separation of three water molecules. As TG and DTA experiments show

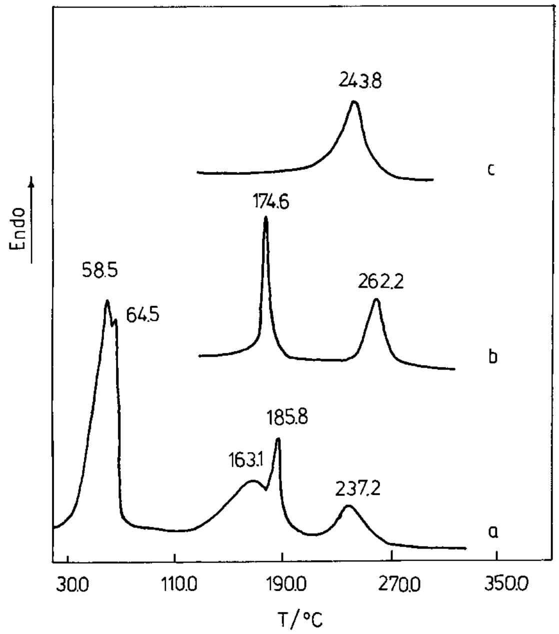

Fig. 4. DSC curves of $MnSeO_4{\cdot}5H_2O$ (a); $MnSeO_4{\cdot}2H_2O$ (b) and $MnSeO_4{\cdot}H_2O$ (c).

Table 3
Solubility in the $MnSeO_4$–H_2O system

Temperature (°C)	Liquid phase (mass%)	Composition of the solid phase
20	35.08	$MnSeO_4{\cdot}5H_2O$
25	35.54	–
30	36.05	–
35	36.71	–
38	37.12	–
40	37.51	$MnSeO_4{\cdot}2H_2O$
45	37.08	–
50	36.35	–
60	35.80	–

Table 4
X-ray powder diffraction data for $MnSeO_4{\cdot}5H_2O$

d_{obs} (Å)	h k l	I/I_0	d_{obs} (Å)	h k l	I/I_0
10.40	0 1 0	25	3.26	$\bar{1}\ \bar{3}\ 1$	10
5.94	1 0 0	60	3.11	1 2 1	15
5.70	1 1 0	60	2.971	2 0 0	80
5.29	$0\ \bar{1}\ 1$	15	2.862	$\bar{1}\ \bar{2}\ 2$	20
5.02	$\bar{1}\ 0\ 1$	100	2.776	$\bar{1}\ 1\ 2$; 0 1 2	30
4.73	$\bar{1}\ 1\ 0$	8	2.550	2 3 0	8
4.42	1 2 0	50	2.515	$\bar{2}\ 0\ 2$	20
4.17	$\bar{1}\ \bar{2}\ 1$	5	2.327	0 4 1; $\bar{2}\ \bar{3}\ 2$	10
4.04	$0\ \bar{2}\ 1$	30	2.219	1 4 1	15
3.77	0 2 1	60	2.129	$\bar{3}\ \bar{2}\ 1$	20
3.49	0 3 0	60	2.102	2 3 1; $\bar{1}\ 3\ 2$	20
3.35	$1\ \bar{1}\ 1$	15			

these peaks are attributed to the formation of $MnSeO_4{\cdot}4H_2O$ and $MnSeO_4{\cdot}2H_2O$, respectively. The comparison of the DSC curves of $MnSeO_4{\cdot}5H_2O$, $MnSeO_4{\cdot}2H_2O$ and $MnSeO_4{\cdot}H_2O$ (Fig. 4(a), (b) and (c)) shows that the endothermic effects in the temperature interval of 110–270°C are due to the formation of an anhydrous salt. $MnSeO_4{\cdot}2H_2O$ prepared by crystallization from an aqueous solution at 40°C dehydrates in two steps forming $MnSeO_4{\cdot}H_2O$ and $MnSeO_4$ (174 and 262°C) (see Fig. 4(b)). However, the DSC curve of $MnSeO_4{\cdot}2H_2O$ obtained as a result of the thermal dehydration of $MnSeO_4{\cdot}5H_2O$ is more complicated and consists of three maxima at 163, 185 and 237°C, respectively (see Fig. 4(a)).

The dehydration of $MnSeO_4{\cdot}5H_2O$ was studied in the $MnSeO_4$–H_2O system. It is known that $MnSeO_4{\cdot}5H_2O$ and $MnSeO_4{\cdot}2H_2O$ crystallize from aqueous solutions at 30 and 60°C, respectively [12]. The experimental results for the $MnSeO_4$–H_2O system (Table 3 and the X-ray powder diffraction study) show that $MnSeO_4{\cdot}5H_2O$ crystallizes in the temperature interval of 20–38°C and $MnSeO_4{\cdot}2H_2O$ – at temperatures higher than 38°C. $MnSeO_4{\cdot}5H_2O$ forms triclinic crystals with lattice parameters: $a = 6.456(6)$ Å, $b = 10.83(1)$ Å, $c = 6.241(9)$ Å, $\alpha = 98.7(1)^\circ$, $\beta = 109.67(8)^\circ$, $\gamma = 75.4(1)^\circ$, $V = 396.6(5)$ Å^3, SG $P\bar{1}$ and proves to be isomorphous with the selenate pentahydrates of magnesium, zinc and cobalt [2,3,13] (h k l and d-spacings are given in Table 4). $MnSeO_4{\cdot}2H_2O$ crystallizes in the orthorhombic system with lattice parameters: $a = 10.421(6)$ Å; $b = 10.516(4)$ Å; $c = 9.232(5)$ Å; $V = 1011.8(7)$ Å^3, close to those reported in [14]. In the literature there are no structural data of metal selenate (sulfate) dihydrates. An information about the symmetry of the water molecules could be derived from the IR spectrum of an isotopically dilute sample (Fig. 2(c)). The appearance of four well resolved bands at 2443, 2518, 2569 and 2600 cm^{-1}, corresponding to four uncoupled OD modes of HDO molecules indicates the existence of two type crystallographically unequivalent water molecules which are asymmetrically

Table 5
Solubilities in the $MnSeO_4$–H_2SeO_4–H_2O system at 20°C

Liquid phase (mass%)		Wet solid phase (mass%)	
$MnSeO_4$	H_2SeO_4	$MnSeO_4$	H_2SeO_4
35.08	–	–	–
33.52	2.51	55.01	1.00
29.96	7.89	65.62	2.03
24.80	12.93	61.50	3.00
		67.83	3.51[a]
21.03	17.92	59.51	4.96
16.42	26.51	55.80	8.00
		78.04	2.03[a]
15.33	28.50	57.82	6.83
10.51	36.77	62.50	10.53

[a] After drying in air for 40 min.

bonded to the metal ions. The positions of the bands show that comparatively weak hydrogen bonds are formed in the crystal structure.

As was mentioned above, DTA and DSC analyses show the formation of $MnSeO_4{\cdot}4H_2O$ which is unknown in the literature. An attempt was made to isolate $MnSeO_4{\cdot}4H_2O$ from the ternary $MnSeO_4$–H_2SeO_4–H_2O system at 20°C. The experimental results (Table 5) and the solubility diagram (Fig. 5) point to a crystallization field of $MnSeO_4{\cdot}4H_2O$ at concentrations of selenic acid from 7.89–28.50%. $MnSeO_4{\cdot}4H_2O$ is stable only in the saturated aqueous-acid solutions and transforms in air rapidly into $MnSeO_4{\cdot}2H_2O$ as X-ray and chemical analysis show. However, the X-ray pattern (recorded using parafilm 'M') of a freshly prepared tetrahydrate exhibits reflections due to $MnSeO_4{\cdot}5H_2O$ and $MnSeO_4{\cdot}2H_2O$.

3.3. Enthalpies of formation of hydrates

Using the $\Delta_{deh}H$ data obtained from DSC measurements (Table 1), as well as the $\Delta_f H^\circ$ of $MnSeO_4$ [15]

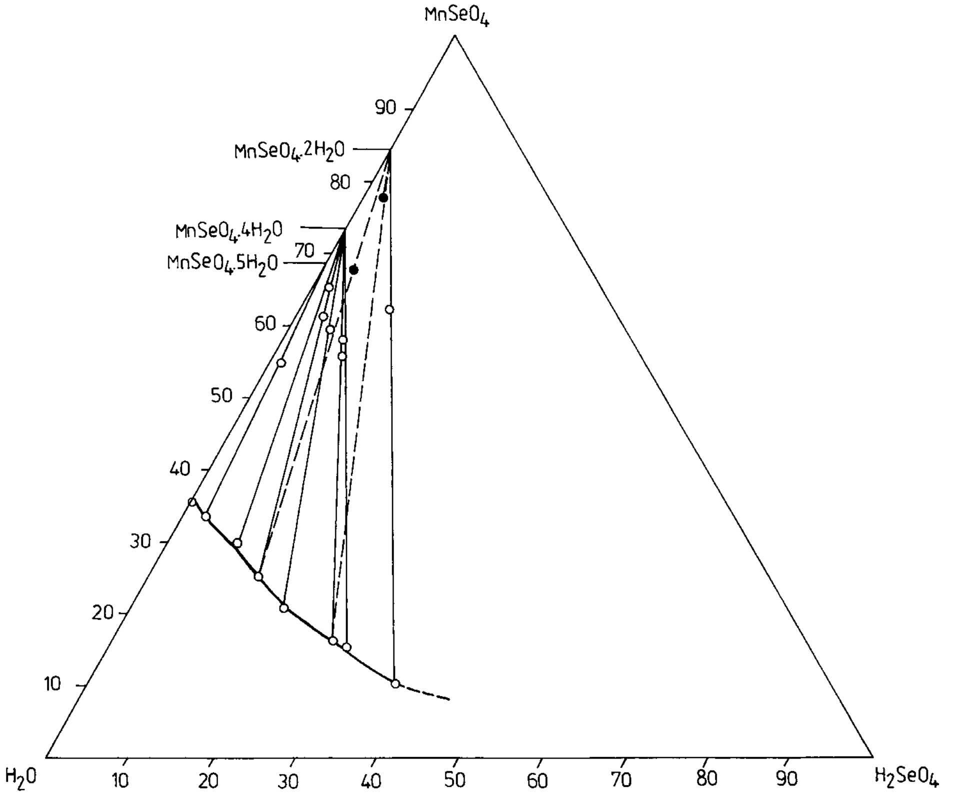

Fig. 5. Solubility diagram of the $MnSeO_4$–H_2SeO_4–H_2O system at 20°C.

and $CuSeO_4$ [16], the enthalpies of formation of manganese and copper selenate hydrates have been calculated:

$\Delta_f H^\circ$ of $MnSeO_4 \cdot 5H_2O = -2246.5$ kJ mol^{-1}

$\Delta_f H^\circ$ of $MnSeO_4 \cdot 2H_2O = -1386.5$ kJ mol^{-1}

$\Delta_f H^\circ$ of $MnSeO_4 \cdot H_2O = -1080.5$ kJ mol^{-1} (-1087.8 kJmol^{-1} according to [15])

$\Delta_f H^\circ$ of $CuSeO_4 \cdot 5H_2O = -1986.6$ kJ mol^{-1} (-1989.9 kJ mol^{-1} according to [16])

$\Delta_f H^\circ$ of $CuSeO_4 \cdot H_2O = -815.5$ kJ mol^{-1}

Acknowledgements

Dr. D. Stoilova is indebted to the Alexander von Humboldt-Foundation for a donation of Fourier transform infrared spectrometer.

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