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Thermodynamical Study of the Zinc Selenate–Cobalt Selenate–Water System at 25 °C

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Summary. The solubility in the $ZnSeO_4$–$CoSeO_4$–H_2O system has been studied at 25 °C. It has been established that the $CoSeO_4 \cdot 6H_2O$ monoclinic crystal structure is unstable and undergoes a change into a tetragonal structure due to the included zinc ions. Activity coefficients of the salt components in the saturated solutions and in the mixed crystal hexahydrates have been determined by the isopiestic method. ΔG^F of $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals shows a negative deviation from ideality.

Keywords. Zinc cobalt selenate; Activity coefficients; Free energy of mixed crystal formation; Isopiestic method.

Thermodynamische Untersuchung des Systems Zinkselenat–Kobaltselenat–Wasser bei 25 °C

Zusammenfassung. Die Löslichkeitsisotherme des Systems $ZnSeO_4$–$CoSeO_4$–H_2O wurde bei 25 °C untersucht. Es wird festgestellt, daß das monokline $CoSeO_4 \cdot 6H_2O$ unstabil ist und in tetragonale Mischkristalle übergeht. Mittels der isopiestischen Methode wurden die Aktivitätskoeffizienten der Komponenten in den gesättigten Dreistofflösungen und Mischkristallen bestimmt. ΔG^F der Mischkristallbildung weist eine negative Abweichung vom idealen Zustand auf.

Introduction

Recently, some results from the thermodynamical study of selenate systems have been reported. The water activity and the acitivity coefficients of the salts $M\text{SeO}_4 \cdot \text{nH}_2\text{O}$ (M = Mg, Co, Ni, Cu, Zn) in their binary solutions have been determined by the isopiestic method [1]. It has been established that the free energy of $(Mg_xCo_{1-x})SeO_4 \cdot 6H_2O$ and $(Zn_xNi_{1-x})SeO_4 \cdot 6H_2O$ mixed crystal formation shows a positive deviation from ideality [2, 3]. In the case of the pair $MgSeO_4 \cdot 6H_2O/ZnSeO_4 \cdot 6H_2O$, the free energy of mixed crystal formation is close to the ideality [4].

The present paper presents a study of the solubility in the $ZnSeO_4$–$CoSeO_4$–H_2O system at 25 °C; some thermodynamical characteristics of the salt components (water vapour pressure, activity coefficients of the salts in the saturated solutions and in the mixed crystal hydrates, free energy of mixed crystal formation) are determined. It is well known that the cobalt selenate hexahydrate crystallizes in the monoclinic system [2, 5] and the zinc selenate hexahydrate in the tetragonal system [6]. As a consequence of the different crystal structures of the salts, a discontinuous series of mixed crystals is expected to be formed in the studied system.

Results and Discussion

The solubility data of the zinc selenate–cobalt selenate–water system at 25 °C are given in Table 1 and Fig. 1. It can be seen from Fig. 1 that mixed crystals are formed in the system. The distribution coefficients of the salt components between liquid and solid phases have been calculated according the equations

$$D_{Zn/Co} = \frac{C^{S}_{ZnSeO_4} C^{L}_{CoSeO_4}}{C^{L}_{ZnSeO_4} C^{S}_{CoSeO_4}} \text{ and } D_{Co/Zn} = \frac{1}{D_{Zn/Co}} \qquad 1$$

where C^L and C^S are the concentrations of the salts in the liquid phase and in the dry solid phase, respectively.

It can be seen from Table 1 that the distribution coefficients retain a practically constant value within the entire studied concentration range ($D_{Zn/Co} = 0.54$ and $D_{Co/Zn} = 1.85$).

As it was mentioned, however, the two salts $ZnSeO_4 \cdot 6H_2O$ and $CoSeO_4 \cdot 6H_2O$ crystallize in different crystal systems (tetragonal and monoclinic, respectively). As a consequence, two branches on the solubility isotherm are expected to appear corresponding to the formation of two types of solid phases. Indeed, the X-ray diffraction patterns of the mixed crystals $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ $(0.11 \leq x < 1.0)$ are identical with the simple zinc selenate hexahydrate pattern indicating the formation of tetragonal mixed crystals. Peaks of two solid phases (monoclinic and tetragonal) are observed in the pattern of the mixed crystals containing about 5 mol% zinc selenate and 95 mol% cobalt selenate. This composition of the solid phase in the solubility diagram is known as an eutonic composition (point E, Fig. 1) and limits the two crystallization fields: a crystallization field of mixed crystals having the tetragonal structure as a matrix which is considerably wide, thus covering the entire investigated concentration range; and a crystallization field of the monoclinic

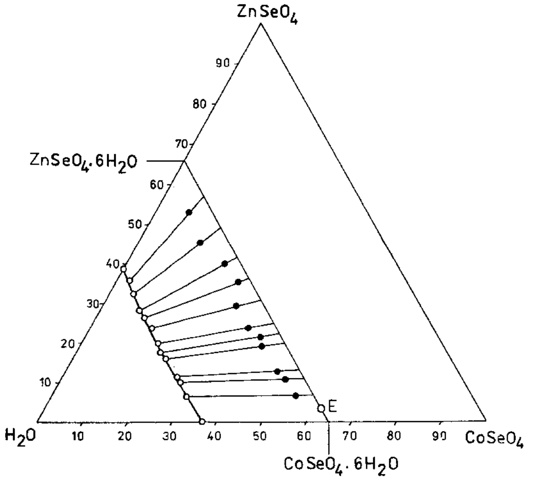

Fig. 1. Solubility diagram of the $ZnSeO_4$–$CoSeO_4$–H_2O system at 25 °C; ○: concentration of the salt components in the liquid phase; ●: concentration of the salt components in the wet solid phase

Table 1. Solubility in the $ZnSeO_4$–$CoSeO_4$–H_2O system at 25 °C

Liquid phase (mass%)		Wet solid phase (mass%)		Dry solid phase (mass%)		Distribution coefficients	
$ZnSeO_4$	$CoSeO_4$	$ZnSeO_4$	$CoSeO_4$	$ZnSeO_4$	$CoSeO_4$	$D_{Zn/Co}$	$D_{Co/Zn}$
38.88	–	–	–	–	–	–	–
35.50	3.00	53.00	7.50	57.10	8.90	0.54	1.85
32.27	6.07	45.20	14.02	49.00	16.50	0.55	1.82
28.48	8.65	39.96	21.85	41.72	23.87	0.53	1.87
26.50	11.50	35.32	27.20	36.44	29.10	0.54	1.85
24.36	14.56	29.56	29.97	30.97	34.52	0.54	1.85
20.18	16.86	23.46	35.53	25.00	40.02	0.52	1.92
17.85	18.31	21.84	39.29	22.52	42.87	0.54	1.85
16.46	20.67	19.24	40.21	19.97	45.39	0.55	1.82
11.50	25.50	12.80	47.10	13.02	52.10	0.55	1.82
10.02	27.03	10.98	51.15	11.01	54.10	0.55	1.82
6.50	29.77	6.80	54.50	7.02	58.10	0.55	1.82
–	36.13	–	–	–	–	–	–

structure which is very narrow and is limited by the eutonic composition and the pure $CoSeO_4 \cdot 6H_2O$. So the X-ray diffraction results show that the monoclinic crystal structure of $CoSeO_4 \cdot 6H_2O$ is unstable and changes into a tetragonal structure due to the included zinc ions. The lattice parameters of the mixed crystals are listed in Table 2.

The isopiestic studies (Fig. 2) show that ternary unsaturated solutions with a different mole ratio of salts and having the same water activity display a linear dependence with an accuracy of 0.2%, expressed by equation 2:

$$\left[\frac{1}{m} = \frac{1}{M_1} + X_2\left(\frac{1}{M_2} - \frac{1}{M_1}\right)\right]_{a_w} \qquad 2$$

Table 2. Lattice parameters of $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals

Composition	a(Å)	c(Å)
$ZnSeO_4 \cdot 6H_2O$, single crystal[a]	6.947(1)	18.592(1)
$ZnSeO_4 \cdot 6H_2O$, this paper	6.938(3)	18.56(2)
$(Zn_{0.90}Co_{0.10})SeO_4 \cdot 6H_2O$	6.941(2)	18.56(3)
$(Zn_{0.77}Co_{0.23})SeO_4 \cdot 6H_2O$	6.943(3)	18.57(2)
$(Zn_{0.69}Co_{0.31})SeO_4 \cdot 6H_2O$	6.945(2)	18.57(1)
$(Zn_{0.61}Co_{0.39})SeO_4 \cdot 6H_2O$	6.945(3)	18.59(2)
$(Zn_{0.51}Co_{0.49})SeO_4 \cdot 6H_2O$	6.948(3)	18.62(4)
$(Zn_{0.37}Co_{0.63})SeO_4 \cdot 6H_2O$	6.950(1)	18.60(2)
$(Zn_{0.25}Co_{0.75})SeO_4 \cdot 6H_2O$	6.951(2)	18.64(1)
$(Zn_{0.15}Co_{0.85})SeO_4 \cdot 6H_2O$	6.950(2)	18.64(3)

[a] According to Ref. [6]

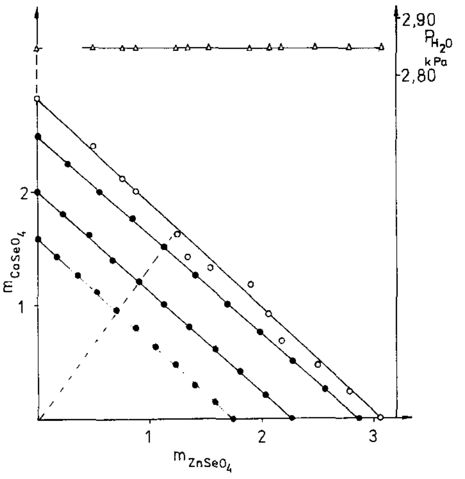

Fig. 2. Isopiestic equilibria in the $ZnSeO_4$–$CoSeO_4$–H_2O system; ○: solubility isotherm; △: water vapour pressure above ternary saturated solutions; ●: compositions of isopiestic unsaturated solutions corresponding to $a_w = 0.910$, 0.940, and 0.960

Here, $m = m_{MSeO_4} + m_{M'SeO_4}$, $X_2 = \frac{m_{M'SeO_4}}{m}$, and M_1 and M_2 are the molalities (mol kg^{-1}) of the salts in their binary solutions isopiestic with the corresponding ternary solutions X_2 is the molar part of the component 2 in the salt part of the solution. The data for the binary selenate solutions are reported elsewhere [1].

The water vapour pressure above the ternary saturated solutions was calculated using equation 3:

$$a_w = \frac{p^L_{H_2O}}{p^o_{H_2O}} \qquad 3$$

The water activities in the ternary saturated solutions were determined by extrapolation of the data for the ternary unsaturated solutions $m = f(a_{H_2O})$ along untersectant at a constant mole ratio to the points lying on the solubility isotherm (Fig. 2).

The activity coefficients of the salt components in the ternary solutions could be calculated using the *McKay–Perring* equation [10]

$$0.036 \cdot \ln \frac{\gamma_1 m}{\Gamma_1 M_1} = \int_0^{\ln a_w} \left[\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln X_2} \right)_{a_w} + \frac{1}{m} - \frac{1}{M_1} \right] \mathrm{d} \ln a_w, \qquad 4$$

where Γ_1 and γ_1 are the activity coefficients in the binary and ternary solutions, respectively.

The integral value is a measure for the deviation of the system from the additivity law. In the case of systems which obey the additivity law (*i.e.* equation 2 is valid), the integral value is equal to zero [11]. Then the activity coefficients of the salt components in the ternary unsaturated and saturated solutions are calculated using equation 5:

$$\gamma_1 = \left(\frac{M_1 \Gamma_1}{m} \right)_{a_w}, \quad \gamma_2 = \left(\frac{M_2 \Gamma_2}{m} \right)_{a_w} \qquad 5$$

Table 3. Activity coefficients of the components in the ternary saturated solutions

$ZnSeO_4$ m_1 (mol·kg^{-1})	$CoSeO_4$ m_2 (mol·kg^{-1})	$p^L_{H_2O}$ (kPa)	$ZnSeO_4$ $\gamma_\pm$	$CoSeO_4$ $\gamma_\pm$
3.051	–	2.849	0.078	–
2.777	0.242	2.849	0.079	0.079
2.512	0.473	2.849	0.080	0.080
2.174	0.681	2.849	0.083	0.084
2.052	0.919	2.849	0.080	0.081
1.914	1.181	2.852	0.076	0.077
1.538	1.326	2.852	0.082	0.083
1.342	1.420	2.852	0.085	0.086
1.257	1.628	2.852	0.082	0.082
0.876	2.005	2.855	0.082	0.082
0.764	2.127	2.855	0.081	0.081
0.496	2.313	2.855	0.081	0.081
–	2.821	2.855	–	0.083

The experimental results for the ternary saturated solutions are listed in Table 3. The experimental error for the activity coefficients is about 2%. It can be seen from Table 3 that the ternary saturated solutions maintain the same water activity, resp. the same water vapour pressure.

The activity coefficients of the salt components in the mixed crystals could be calculated on the basis of the results for the ternary saturated solutions (K_N: *Nernst* distribution constant; a_i^S, a_i^L, a_i^{LO}: activities of the component i in the solid phase, in the ternary saturated solution and in the binary saturated solution, respectively).

$$K_N = \frac{a_i^S}{a_i^L} = \frac{1}{a_i^{LO}} \qquad 6$$

For the selenates of bivalent metals (2-2 electrolytes), one obtains

$$a_1^L = (a_1^\pm)^\nu = (m_{\pm 1}\gamma_{\pm 1})^\nu = \gamma_1^2[m_1(m_1 + m_2)] \quad \text{and} \qquad 7$$

$$a_1^{LO} = (M^\circ_{\pm 1}\Gamma^\circ_{\pm 1})^2, \qquad 8$$

where M_1° and Γ_1° are the molality and the activity coefficient of the component 1 in the binary saturated solution and ν is the number of ions. Then, in the case of anhydrous salts the activity of component 1 in the solid phase is

$$a_1^S = \frac{a_1^L}{a_1^{LO}} = \frac{\gamma_1^2 m_1(m_1 + m_2)}{(M_1^\circ \Gamma_1^\circ)^2} \qquad 9$$

In the case of mixed crystal hydrates, however, the change in the chemical potential of the components is determined as $\Delta\mu_{MSeO_4\cdot 6H_2O}$ when 1 mol $MSeO_4\cdot 6H_2O$ is transferred from its binary saturated solution (LO) to the ternary saturated solution (L):

$$\begin{aligned}\Delta\mu_{M\mathrm{SeO_4\cdot 6H_2O}} &= \mu^{\mathrm{L}}_{M\mathrm{SeO_4\cdot 6H_2O}} - \mu^{\mathrm{LO}}_{M\mathrm{SeO_4\cdot 6H_2O}} = (\mu^{\mathrm{L}}_{M\mathrm{SeO_4}} - \mu^{\mathrm{LO}}_{M\mathrm{SeO_4}}) + 6(\mu^{\mathrm{L}}_{\mathrm{H_2O}} - \mu^{\mathrm{LO}}_{\mathrm{H_2O}})\\ &= RT\ln\frac{a^{\mathrm{L}}_{M\mathrm{SeO_4}}}{a^{\mathrm{LO}}_{M\mathrm{SeO_4}}} + 6RT\ln\frac{P^{\mathrm{L}}_{\mathrm{H_2O}}}{P^{\mathrm{LO}}_{\mathrm{H_2O}}} = RT\ln\frac{a^{\mathrm{L}}_{M\mathrm{SeO_4}}}{a^{\mathrm{LO}}_{M\mathrm{SeO_4}}}\left[\frac{P^{\mathrm{L}}_{\mathrm{H_2O}}}{P^{\mathrm{LO}}_{\mathrm{H_2O}}}\right]^6\\ &= RT\ln a^{\mathrm{S}}_{M\mathrm{SeO_4\cdot 6H_2O}} \end{aligned} \qquad 10$$

($P^{\mathrm{L}}_{\mathrm{H_2O}}$ and $P^{\mathrm{LO}}_{\mathrm{H_2O}}$: water vapour pressure for the ternary saturated and binary saturated solutions, respectively). Then the activity of $ZnSeO_4 \cdot 6H_2O$ (indice 1) in the mixed crystal hexahydrate is calculated according to equation 11:

$$a^{\mathrm{S}}_{\mathrm{ZnSeO_4\cdot 6H_2O}} = \frac{m_1(m_1+m_2)\gamma_1^2}{(M_1^{\mathrm{o}}\Gamma_1^{\mathrm{o}})^2}\left[\frac{P^{\mathrm{L}}_{\mathrm{H_2O}}}{P^{\mathrm{LO}}_{\mathrm{H_2O}}}\right]^6 \qquad 11$$

The free energy of mixed crystal formation is calculated according to

$$\Delta G^{\mathrm{F}} = RT(x_1^{\mathrm{S}}\ln a_1^{\mathrm{S}} + x_2^{\mathrm{S}}\ln a_2^{\mathrm{S}}), \qquad 12$$

where x_1^{S} and x_2^{S} are the molar parts of the salt components in the mixed crystals.

Table 4. Activities and ΔG^{F} of mixed crystals $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$

$ZnSeO_4$ x_1^{s}	$ZnSeO_4$ a_1^{s}	$CoSeO_4$ a^{s}	$ZnSeO_4$ f_1	$CoSeO_4$ f_2	ΔG^{F} (kJ·mol^{-1})
1.000	1.000	–	1.00	–	0
0.861	0.919	0.083	1.07	0.60	−1.04
0.742	0.837	0.164	1.13	0.64	−1.48
0.629	0.762	0.247	1.21	0.66	−1.71
0.548	0.691	0.320	1.20	0.71	−1.78
0.465	0.607	0.388	1.31	0.72	−1.83
0.377	0.526	0.470	1.40	0.76	−1.77
0.337	0.477	0.522	1.42	0.79	−1.69
0.299	0.428	0.573	1.43	0.82	−1.60
0.195	0.296	0.697	1.52	0.87	−1.31
0.165	0.257	0.738	1.56	0.88	−1.18
0.112	0.180	0.840	1.61	0.95	−0.859
–	–	1.000	–	1.00	0

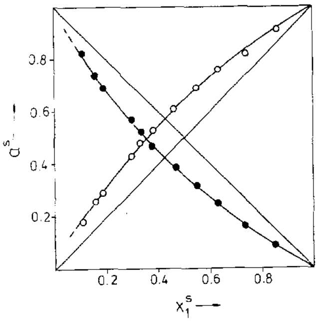

Fig. 3. Activities of the components in the $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals; ○: activities of $ZnSeO_4 \cdot 6H_2O$; ●: activities of $CoSeO_4 \cdot 6H_2O$; X_1: molar part of $ZnSeO_4 \cdot 6H_2O$ in the solid phase

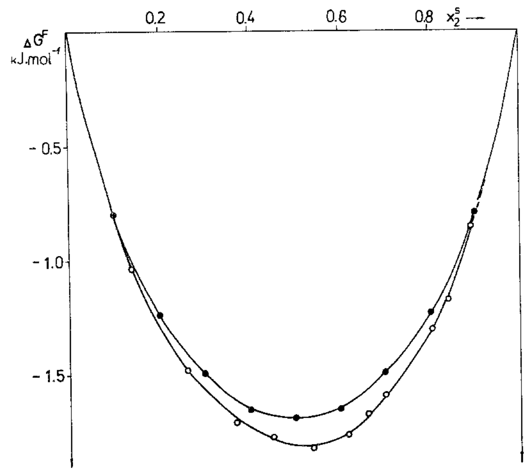

Fig. 4. Change in the free energy of mixed crystal formation; ●: ΔG^i; ○: ΔG^F of $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals; X_2: molar part of $CoSeO_4 \cdot 6H_2O$ in the solid phase

The activities, resp. the activity coefficients of the salt components in the $(Zn_xCo_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals are listed in Table 4. It can be seen that the activity coefficients of the zinc selenate are greater than unity. The experimental error for the component activities is about 1%. The change in the activities with the change in the composition of the mixed crystals is shown in Fig. 3. From Fig. 4 it can be seen that the free energy of mixed crystal formation shows a negative deviation from ideality.

Experimental

The metal selenates were prepared by neutralization of dilute selenic acid solutions with the corresponding metal oxide (in the case of zinc selenate) and metal hydroxide carbonate (in the case of cobalt selenate) at 60–70 °C. The metal selenate solutions were filtered and concentrated. The crystals were obtained after cooling the solutions at room temperature, then recrystallized from water and dried in air. The reagents used were of p.a. quality (Merck). Chemical and X-ray powder analysis showed that zinc and cobalt selenate hexahydrates were obtained.

The solubility in the $ZnSeO_4$–$CoSeO_4$–H_2O system was studied using the method of isothermal decrease of supersaturation. Aqueous solutions containing different quantities of the salts were prepared at 50–60 °C, then the solutions were cooled in a thermostat to 25.0 °C and stirred. Preliminary experiments indicated that the equilibrium between the liquid and solid phases was reached in about 15 h. Then the saturated solutions were filtered and the liquid phases and the solid phases which contain some amount of the mother solutions (so-called "wet solid phase") were analyzed. The concentrations of the metal selenates in the liquid phases and in the wet solid phases were determined as follows: the sum of zinc and cobalt selenate concentrations was determined complexometrically at $pH = 5.5$–6 using xylenol orange as indicator. In another part of the solutions the zinc and cobalt ions were masked with KCN, then the zinc complex was destroyed with 15% HCHO solution and the liberated zinc ions were determined complexometrically at $pH = 9.5$–10 using eriochrome black T as indicator. The cobalt selenate concentration was estimated by difference. In order to calculate the concentrations of the ideal dry solid phases (the corresponding points lie on the line linking the figurative points of $ZnSeO_4 \cdot 6H_2O$ and $CoSeO_4 \cdot 6H_2O$ in the solubility diagram), the variation of *Schreinemaker's* method for algebraic indirect identification of the solid phase was used [7].

The thermodynamical studies were carried out by the isopiestic method described elsewhere [8]. Isopiestic equilibria ($a_{H_2O} = \text{const}$) of ternary unsaturated solutions were studied in order to calculate the water vapour pressure above the ternary saturated solutions. The isopiestic equilibria were studied at water activity values of 0.910, 0.940, and 0.960. For every value of the water activities several solutions were prepared: 9 unsaturated solutions of zinc and cobalt selenates having the same total molality and a different molar ratio of the salts; a saturated solution of a salt having an activity close to the chosen activity; and two standard solutions of sodium chloride also having activities close to the chosen activity. During the equilibration the concentrations of the standard solutions change. A criterion of equilibrium is the same concentration, resp. the same activity of the standard solutions (about 20 days are needed). The concentrations of the solutions were determined gravimetrically. The activity of water in the solutions was determined using the dependence $a_{NaCl} = f(M_{NaCl})$ which is well known [9]. The experiments were performed at 25.0 ± 0.1 °C.

The *McKay-Perring* method was used to calculate the salt component activities and the free energy of mixed crystal formation [8, 10].

The X-ray powder analysis was carried out with a DRON-3 powder diffractometer using Fe-filtered CoK_α radiation. The 2θ diffraction range was 10–60° at a scanning speed of $1°\,min^{-1}$. The lattice constants were calculated from diffractometric data by least-squares refinements on the basis of 20 reflections.

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