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Thermodynamical Study on the Magnesium Selenate-Nickel Selenate-Water System at 25 °C

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Summary. Activity coefficients of the salt components in both the saturated solutions and the $(Mg_xNi_{1-x})SeO_4\cdot 6H_2O$ mixed crystals of the $MgSeO_4$–$NiSeO_4$–H_2O system at 25 °C have been determined by the isopiestic method. It has been established that the formed mixed crystals deviate only slightly from ideality and can be adequately described by a regular model. The *Pitzer* ion-interaction model has been used to calculate the thermodynamic properties of the salt components in the ternary system. The calculated data are in good agreement with those obtained experimentally by the isopiestic method.

Keywords. Magnesium nickel selenate; Activity coefficients; *Gibbs* energy of mixing; Isopiestic method; *Pitzer* model.

Thermodynamische Untersuchungen am Magnesiumselenat-Nickelselenat-Wasser-System bei 25 °C

Zusammenfassung. Die Aktivitätskoeffizienten der Salzkomponenten sowohl der gesättigten Lösungen als auch der Mischkristalle (Zusammensetzung: $(Mg_xNi_{1-x})SeO_4\cdot 6H_2O$) des Systems $MgSeO_4$–$NiSeO_4$–H_2O wurden bei 25 °C mit Hilfe der isopiestischen Methode bestimmt. Es konnte gezeigt werden, daß die gebildeten Mischkristalle nur leicht vom idealen Zustand abweichen und mit einem regulären Modell gut beschrieben werden können. Zur Berechnung der thermodynamischen Eigenschaften der Salzkomponenten des ternären Systems wurde das *Pitzer*sche Ionenwechselwirkungsmodell herangezogen. Die berechneten Werte stimmen mit den mittels der isopiestischen Methode gewonnenen experimentellen Ergebnissen gut überein.

Introduction

The present paper continues our previous thermodynamical studies on selenate systems [1–5]. The water activity and the activity coefficients of the salts $M\mathrm{SeO_4}\cdot n\mathrm{H_2O}$ (M = Mg, Co, Ni, Cu, Zn) in their binary unsaturated and saturated solutions have been determined by the isopiestic method [1]. It has been established that the *Gibbs* energy of mixing of $(Mg_xCo_{1-x})SeO_4\cdot 6H_2O$ and $(Zn_xNi_{1-x})SeO_4\cdot 6H_2O$ crystals shows a positive deviation from ideality [2, 3], whereas that of $(Zn_xCo_{1-x})SeO_4\cdot 6H_2O$ crystals shows a negative deviation [4].

The aim of the present paper is to determine some thermodynamical characteristics of the salt components (water vapour pressure, activities, activity coefficients of the salts in both saturated solutions and mixed crystal hydrates, and molar *Gibbs* energy of mixing) by the isopiestic method. The same thermodynamical characteristics have been calculated using the *Pitzer* ion-interaction model.

Results and Discussion

The isopiestic studies (Fig. 1) 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‰; that is, they obey the *Zdanovskii* rule [20], expressed by equation 2.

$$\frac{1}{m^{\mathrm{ter}}}=\frac{1}{m_1^{\mathrm{bin}}}+x_2\left(\frac{1}{m_2^{\mathrm{bin}}}-\frac{1}{m_1^{\mathrm{bin}}}\right)\quad \text{at } a_{\mathrm{w}}=\text{const} \qquad 2$$

$$\left(m^{\mathrm{ter}}=m^{\mathrm{ter}}_{\mathrm{MSeO_4}}+m^{\mathrm{ter}}_{\mathrm{M'SeO_4}};\ x_2=\frac{m_{M'\,\mathrm{SeO_4}}}{m^{\mathrm{ter}}}\right)$$

m_1^{bin} and m_2^{bin} are the molalities of the salts in their binary solutions isopiestic with the corresponding ternary solutions, x_2 is the mole fraction of component 2 in the salt part of the solution.

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

$$a_{\mathrm{w}}=\frac{P_{\mathrm{H_2O}}(\mathrm{l})}{P_{\mathrm{H_2O}}(\mathrm{l_0})} \qquad 3$$

The water activities in the ternary saturated solutions were determined by extrapolation of the data for the ternary unsaturated solutions ($m=f(a_{\mathrm{w}})$) at a constant mole ratio to the points lying on the solubility isotherm (Fig. 1).

The activity coefficients of the salt components in the ternary solutions have been calculated using the *McKay–Perring* equation [8]:

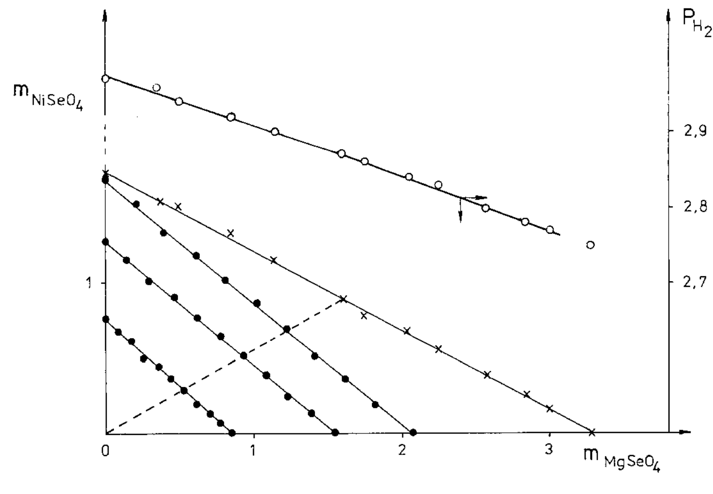

Fig. 1. Isopiestic equilibria in the $MgSeO_4$–$NiSeO_4$–H_2O system at 25 °C; × – solubility isotherm; ○ – water vapour pressure above ternary saturated solutions; ● – compositions of isopiestic unsaturated solutions corresponding to $a_{\mathrm{w}}=0.980$, 0.960, and 0.940

$$\nu M_{H_2O} \ln\left(\frac{\gamma_1 m^{ter}}{\Gamma_1 m_1^{bin}}\right) = -\int_0^{\ln a_w}\left[\frac{1}{(m^{ter})^2}\left(\frac{\partial m^{ter}}{\partial \ln x_2}\right)_{a_w} + \frac{1}{m^{ter}} - \frac{1}{m_1^{bin}}\right]\partial \ln a_w \qquad 4$$

where Γ_1 and γ_1 are the activity coefficients in the binary and ternary solutions, respectively. The data for the binary selenate solutions are taken from Ref. [1].

The integral value is a measure for the deviation of the system from the additivity law. In the case of systems which obey the *Zdanovskii* rule, the integral value vanishes [21]. Then, the activity coefficients of the salts in the ternary unsaturated and saturated solutions can be calculated using equation 5.

$$\gamma_1 = \left[\frac{m_1^{bin}\Gamma_1}{m^{ter}}\right]_{a_w} \qquad \gamma_2 = \left[\frac{m_2^{bin}\Gamma_2}{m^{ter}}\right]_{a_w} \qquad 5$$

The experimental results for the ternary saturated solutions are listed in Table 1. The experimental error for the activity coefficients is about 2%.

The activities of the salt components in the mixed crystals could be calculated on the basis of the results for the ternary saturated solutions:

$$K_N = \frac{a_i(s)}{a_i(l)} = \frac{1}{a_i(l_0)} \qquad 6$$

Here, K_N is *Nernst* distribution constant and $a_i(s)$, $a_i(l)$, and $a_i(l_0)$ are the activities of component i in the solid phase, in the ternary saturated solution, and in the binary saturated solution, respectively.

The activity of component 1 in the solid phase in the case of anhydrous salts is given by equation 7.

Table 1. Activity coefficients of the salt components in the ternary saturated solutions of the $MgSeO_4$-$NiSeO_4$-H_2O system at 25 °C

$MgSeO_4$ m_1	$NiSeO_4$ m_2	$P_{H_2O}(l)$ (kPa)	$MgSeO_4$ $\gamma\pm$	$NiSeO_4$ $\gamma\pm$	$MgSeO_4$ $\gamma\pm$	$NiSeO_4$ $\gamma\pm$
			isopiestic method		*Pitzer model*	
3.281	–	2.752	0.116	–	0.126	–
2.988	0.163	2.773	0.114	0.128	0.122	0.167
2.838	0.257	2.789	0.111	0.136	0.121	0.165
2.575	0.379	2.804	0.113	0.132	0.117	0.151
2.251	0.561	2.835	0.106	0.127	0.114	0.150
2.041	0.678	2.845	0.107	0.124	0.112	0.147
1.754	0.785	2.861	0.108	0.129	0.109	0.139
1.614	0.881	2.879	0.103	0.126	0.109	0.138
1.146	1.154	2.905	0.102	0.120	0.109	0.134
0.847	1.319	2.924	0.100	0.118	0.109	0.132
0.509	1.494	2.941	0.101	0.119	0.109	0.130
0.368	1.526	2.965	0.098	0.116	0.109	0.127
–	1.729	2.971	–	0.122	–	0.126

$$a_1(\mathrm{s})=\frac{a_1(\mathrm{l})}{a_1(\mathrm{l}_0)}=\frac{\gamma_1^2 m_1^{\mathrm{ter}}(m_1^{\mathrm{ter}}+m_2^{\mathrm{ter}})}{(m_1^{\mathrm{bin}}\Gamma_1)^2} \qquad 7$$

In the case of mixed crystal hydrates, however, the activity of $MgSeO_4 \cdot 6H_2O$ (index 1) in the mixed crystal hydrates is calculated by the equation

$$a_1(\mathrm{s})=\frac{\gamma_1^2 m_1^{\mathrm{ter}}(m_1^{\mathrm{ter}}+m_2^{\mathrm{ter}})}{(m_1^{\mathrm{bin}}\Gamma_1)^2}\cdot\left[\frac{p_{\mathrm{H_2O}}(\mathrm{l})}{p_{\mathrm{H_2O}}(\mathrm{l}_0)}\right]^6 \qquad 8$$

The activities of the salts in the $(Mg_xNi_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals are listed in Table 2. The experimental error for the component activities is about 1%. The *Storonkin–Schulz* method adapted for crystal hydrates was used to calculate the activities of the nickel selenate hexahydrate as well [6]. Such calculations are not possible for the activities of magnesium selenate hexahydrate because of its very narrow crystallization field. An X-ray diffraction study shows that the monoclinic structure of $MgSeO_4 \cdot 6H_2O$ changes into the tetragonal structure of $NiSeO_4 \cdot 6H_2O$ when about 4 mol% of nickel selenate are included in the $MgSeO_4 \cdot 6H_2O$ crystals [22].

The molar *Gibbs* energy of mixing ($\Delta_{\mathrm{mix}}G_{\mathrm{m}}(\mathrm{s})$) is calculated according to equation 9:

$$\Delta_{\mathrm{mix}}G_{\mathrm{m}}(\mathrm{s})=RT(x_1\ln a_1(\mathrm{s})+x_2\ln a_2(\mathrm{s})) \qquad 9$$

x_1 and x_2 are the mole fractions of the salt components in the mixed crystal hexahydrates. It can be seen from Fig. 2 that the formed mixed crystals deviate only slightly from ideality.

Table 2. Activities of the salt components and $\Delta_{\mathrm{mix}}G_{\mathrm{m}}$ of $(Mg_xNi_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals

$MgSeO_4$ x_1^{S}	$MgSeO_4$ $a_1^{\mathrm{S}}(*)$	$NiSeO_4$ $a_2^{\mathrm{S}}(*)$	$NiSeO_4$ $a_2^{\mathrm{S}}(**)$	$MgSeO_4$ a_1^{S}	$NiSeO_4$ a_2^{S}	$\Delta_{\mathrm{mix}}G_{\mathrm{m}}$ ($\mathrm{kJ \cdot mol^{-1}}$) isopiestic method	$\Delta_{\mathrm{mix}}G_{\mathrm{m}}$ ($\mathrm{kJ \cdot mol^{-1}}$) *Pitzer* model
				Pitzer model			
1.000	1.000	–	–	1.00	–	0	0
0.835	0.887	0.126	0.160	0.87	0.20	−1.09	−0.95
0.740	0.817	0.230	0.236	0.81	0.30	−1.32	−1.15
0.670	0.744	0.310	0.340	0.69	0.41	−1.45	−1.34
0.543	0.588	0.430	0.470	0.58	0.5	−1.67	−1.40
0.478	0.528	0.493	0.501	0.50	0.64	−1.67	−1.40
0.379	0.449	0.591	0.602	0.41	0.65	−1.57	−1.42
0.330	0.385	0.650	0.639	0.37	0.73	−1.50	−1.34
0.217	0.261	0.749	0.756	0.25	0.87	−1.28	−1.01
0.163	0.181	0.815	0.821	0.18	0.93	−1.12	−0.83
0.084	0.107	0.900	0.883	0.11	0.98	−0.70	−0.52
0.061	0.071	0.905	0.950	0.07	0.94	−0.52	−0.53
–	–	1.000	1.000	–	–	0	0

(*) Calculated by *McKay–Perring* method; (**) calculated by *Storonkin–Schulz* method

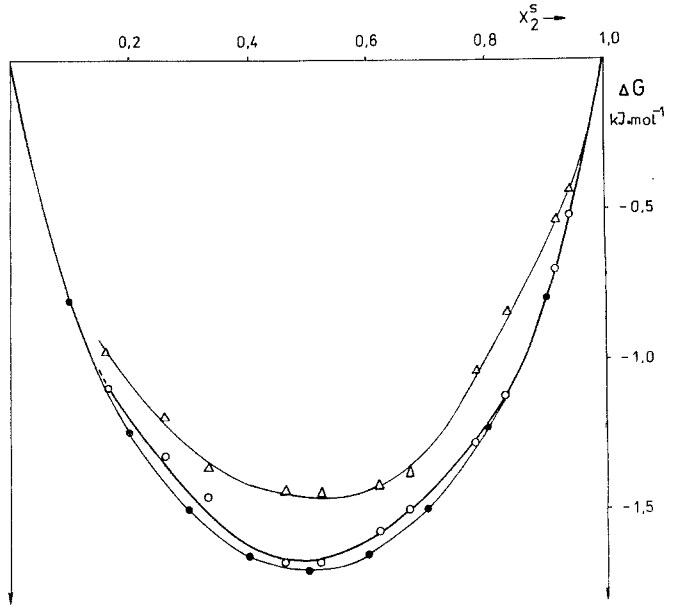

Fig. 2. Plot of the *Gibbs* energy of mixing $\Delta_{mix}G_m(s)$ [$kJ \cdot mol^{-1}$] *vs.* the mole fraction of $NiSeO_4 \cdot 6H_2O$ in $(Mg_xNi_{1-x})SeO_4 \cdot 6H_2O$ mixed crystals at 25 °C; Δ: calculated values according to equations 1 and 9; ●: $\Delta_{mix}G_m(s)$ $(f_1 = f_2 = 1)$; O: experimental results

The *Pitzer* parameters of interionc interaction for the binary sysems $MgSeO_4$–H_2O and $NiSeO_4$–H_2O ($\beta^{(0)}$, $\beta^{(1)}$, and c^{φ}) were calculated from data published elsewhere [1]. The parameters obtained are given in Table 3. They are valid up to saturated solutions.

The logarithm of the thermodynamic solubility product for the binary systems was calculated on he basis of the binary parameters obtained and of the saturated solution compositions. The following values were obtained: $\ln K_{sp}^0 = -2.608$ for $MgSeO_4 \cdot 6H_2O$ and $\ln K_{sp}^0 = -3.422$ for $NiSeO_4 \cdot 6H_2O$.

The ternary parameters θ_{MN} and ψ_{MNX} for the studied system have been calculated on the basis of the data of the binary system. The values found for θ_{MN} and ψ_{MNX} are very low; in our calculations, we assume $\theta_{MN} = \psi_{MNX} = 0$. This approach has been proposed by *Pitzer* and *Kim* [11] for a series of systems and was used by *Königsberger* [23] and *Christov et al.* [18].

On the basis of the parameters obtained for the binary and ternary solutions and using the experimental data for the compositions of the liquid and solid phases, the salt activities, the activity coefficients, and the *Gibbs* energy of mixing have been calculated. It can be seen from Tables 1 and 2 and Fig. 2 that there is a good agreement between the experimental data and those obained by the *Pitzer* model.

Table 3. *Pitzer* binary parameters for the MSeO$_4$–H_2O systems at 25 °C[a] (M = Mg, Ni)

System	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	m^{max}	$\delta^{\varphi b}$
$NiSeO_4$–H_2O	0.5517	3.2103	0.0271	1.73	0.005
$MgSeO_4$–H_2O	0.3010	4.2720	0.0163	3.28	0.005

[a] The parameters are calculated with coefficients $\alpha_1 = 1.4, \alpha_2 = 12$; [b] standard deviation of the fit

The positions of the minimum of the curves at $x_1 = 0.5$ (Fig. 2) allow us to use simple correlations for calculations of $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$, assuming the "regular" model of mixing [18]. Then,

$$\Delta_{\text{mix}}G_{\text{m}}(\text{s}) = -(6.6 \pm 0.5)\cdot x(1-x)\,\text{kJ}\cdot\text{mol}^{-1}$$

for the isopiestic method and

$$\Delta_{\text{mix}}G_{\text{m}}(\text{s}) = -(5.6 \pm 0.4)\cdot x(1-x)\,\text{kJ}\cdot\text{mol}^{-1}$$

for the *Pitzer* model.

Experimental

The metal selenates were prepared by neutralization of dilute selenic acid solutions with the corresponding metal hydroxide carbonates. The reagents used were of 'p.a.' grade (Merck).

Solubility data concerning the compositions of liquid and solid phases have been obtained using a method described elsewhere [2,4]. X-ray powder analysis was used to identify the type of the solid phases.

The thermodynamic study was carried out by the isopiestic method [4,6]. Isopiestic equilibria ($a_{\text{w}} = \text{const}$) of ternary unsaturated solutions were studied to calculate the water vapour pressure above ternary saturated solutions. The isopiestic equilibria were studied at water activity values of 0.940, 0.960, and 0.980. 20 days were needed to reach the equilibria. Sodium chloride solutions were used as standards. The water activity in the solutions was determined using the well known dependence $a_{\text{NaCl}} = \text{f}(m_{\text{NaCl}})$ [7]. The concentrations of the solutions were determined gravimetrically. The experiments were performed at $25.0 \pm 0.1\,^{\circ}\text{C}$. The *McKay–Perring* method adapted for hydrates was used to calculate the salt component activities and molar *Gibbs* energy of mixing ($\Delta_{\text{mix}}G_{\text{m}}$) [6,8].

Pitzer has suggested a method for the calculation of activity coefficients in unsaturated and saturated solutions of electrolytes with an accuracy of 2–6% [9–11]. In many papers the *Pitzer* model has been applied to the simulation of multicomponent water–salt systems in which phases with constant composition crystallize [12–15]. *Harvie et al.* [16] and *Filippov et al.* [17] have used *Pitzer* equations for systems in which mixed crystals are formed and have suggested the following equation for the calculation of activities of the components in the mixed crystals:

$$\ln a_i(\text{s}) = \ln a_i(\text{l}) - \ln a_i(\text{l}_0) \qquad 1$$

where l and l_0 refer to the saturated ternary and binary solutions, respectively. In previous papers, the applicability of this equation to determine $\Delta_{\text{mix}}G_{\text{m}}$ for anhydrous salts and hydrates has been proved [18,19].

References

[1] Ojkova T., Staneva D. (1989) Z. Phys. Chem. (Leipzig) **270**: 628

[2] Ojkova T., Stoilova D., Staneva D. (1992) Z. Phys. Chem. **177**: 247

[3] Ojkova T., Stoilova D., Staneva D. (1993) Bulg. Chem. Commun. **26**: 259

[4] Ojkova T., Stoilova D., Staneva D. (1994) Monatsh. Chem. **125**: 1067

[5] Ojkova T., Balarew Chr., Staneva D. (1990) Z. Anorg. Allg. Chem. **584**: 217

[6] Ojkova T., Makarov L., Balarew Chr., Milochova M. (1974) Z. Phys. Chem. (Leipzig) **255**: 443

[7] Mikylin G. (1968) Voprossi Phizitcheskoi Khimii Rastvorov Elektrolitov. Izd. Khimia, Leningrad, p. 391

[8] McKay H., Perring J. (1953) Trans Faraday Soc. **49**: 163

[9] Pitzer K. (1973) J. Phys. Chem. **77**: 268

[10] Pitzer K. S. (1975) J. Solution Chem. **4**: 249
[11] Pitzer K. S., Kim J. (1974) J. Am. Chem. Soc. **96**: 5701
[12] Harvie C., Weare J. (1980) Geochim. Cosmochim. Acta **44**: 981
[13] Filippov V., Dmitriev G., Yakovleva S. (1980) Dokl. Acad. Nauk USSR **252**: 156
[14] Balarew Chr., Christov Chr., Valyashko Vl., Petrenko S. (1993) J. Solution Chem. **22**: 173
[15] Christov Chr., Balarew Chr., Valyashkov Vl., Petrenko S. (1994) J. Solution Chem. **23**: 595
[16] Harvie C., Möller N., Weare J. (1984) Geochim. Cosmochim. Acta **48**: 723
[17] Filippov V., Rymjanzev A. (1990) Dokl. Acad. Nauk USSR **315**: 659
[18] Christov Chr., Petrenko S., Balarew Chr., Valyashko Vl. (1994) J. Solution Chem. **23**: 795
[19] Christov Chr., Petrenko S., Balarew Chr., Valyashko Vl. (1994) Monatsh. Chem. **125**: 1371
[20] Zdanovskii A. (1936) Trudy Solannoi Laboratory Acad. Nauk USSR **6**: 70
[21] Makarov L., Stupin D. (1961) Russ. J. Phys. Chem. **35**: 605
[22] Stoilova D., Ojkova T., Staneva D. (1995) Crys. Res. Techn. **30**: 3
[23] Königsberger E. (1990) Monatsh. Chem. **121**: 999

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