

Distribution of Cocrystallized Microamounts of Some M^+ ions during $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ Crystallization

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Partition coefficient (D) values of trace amounts of Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ and Ag^+ have been determined during isothermal crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 20 and 25 °C. These values are affected by size of ionic radii as well as solubilities of the corresponding double salts. It was possible to estimate D values for most of the microcomponents from solubilities of their double salts. Some of them are in good agreement with experimental ones.

Cocrystallization and coprecipitation of microcomponents is very important in analytical chemistry, as well as in many other fields of chemistry. Cocrystallization is one of the major factors which influence the effectiveness of crystallization as a purification process. One of the indicators of this effectiveness is the distribution (cocrystallization) coefficient of each microcomponent, D . Knowledge of the greatest possible number of such coefficients allows one to predict the applicability of crystallization for the removal definite microcomponents from a given substance. However, the literature data concerning the subject in question are not ample. Hence, it seems reasonable to determine the dependence of distribution coefficients on various physicochemical and crystal-chemical factors (such as ionic charges and radii, similarity of crystal structure and unit cell dimensions, ability to form solid solutions as well as solubilities of corresponding salts), which would allow one to predict value of coefficients D for various crystallization systems which have not been investigated so far.

As shown by (among others) investigations on the cocrystallization of microcomponents with selected sulfates,^{1–4} the effect of the said factors on the coefficients D is different for various crystallization systems, and very often these influences overlap. The selection of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which belongs to a group of double salts $\text{NiSO}_4 \cdot \text{M}^2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (where $\text{M}^1 \{ \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Tl}^+ \}$) of a very similar structure, allows one to eliminate the influence of this factor on the coefficients D and to define their dependence on ionic radius and solubility.

Cocrystallization of microamounts of M^+ ions with $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ has not been investigated yet.

Experimental

Reagents and solutions. These compared the following: nickel(II) and ammonium sulfate hexahydrate, p.a., additionally purified by crystallization twice; solutions of Na^+ , K^+ , Rb^+ , Cs^+ and Tl^+ sulfates and Ag^+ nitrate of respective concentrations: ammonia solution (14 M) was obtained by saturating distilled water with ammonia gas; sodium versenate p.a. (POCh, Gliwice) – 0.1 M water solution; murexide ind. (POCh, Gliwice).

Apparatus. An atomic absorption spectrometer (model 3300, Perkin Elmer) was used.

Analytical methods. Nickel(II) was determined by complexometric titration with sodium versenate in ammoniacal solution in the presence of murexide.⁵ Microcomponents were determined by means of direct atomic absorption spectrometry (K^+ , Na^+ , Ag^+ and Tl^+) or flame emission (Rb^+ and Cs^+) from solutions containing 1.00 g (or less) of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 25 ml. Absorbances of the samples and sets of standards, whose concentrations of double salt were the same as in the samples, were measured under the same conditions.

Method of determining coefficients D and λ . After crystallization the crystals were separated from the mother solution by means of filtration through a Büchner funnel with a sintered glass disk, weighed, washed with saturated purified $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution and dissolved in water. From the nickel(II) content in both solutions the degree of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ crys-

tallization, α , was found from the following formula:

$$\alpha = \frac{m_{Ms}}{m_{Mk} + m_{Mr}}$$

where: m_{Ms} is the mass of the macrocomponent [$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] in the solid phase; m_{Mk} is the mass of the macrocomponent in the crystal; m_{Mr} is the mass of the macrocomponent in the mother solution;

$$m_{Ms} = m_k \frac{C_k - C_r}{100 - C_r}$$

m_k is the mass of the crystal; C_k is the percentage of the macrocomponent in the crystal; $(100 - C_k)$ is the crystal humidity (percent); C_r is the percentage of the macrocomponent in the mother solution.

Based on the results of nickel(II) determinations the volumes of the samples necessary to determine the microcomponents were calculated. The concentration was equal to 1.00 g (or less) of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 25 ml.

Relative concentrations of microcomponents [ppm in relation to $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] in the mother solution (a'_r) and in the washed crystal (a'_k) determined by direct atomic absorption or flame emission permitted calculation of the homogeneous distribution coefficient, D (Henderson–Kracek, Khlopin), and heterogeneous distribution coefficient, λ (Doerner–Hoskins), from the following relations:

$$D = a'_k/a'_r$$

$$\lambda = \frac{\log\left(1 - \frac{\alpha D}{\alpha D + 1 - \alpha}\right)}{\log(1 - \alpha)}$$

Conditions of crystallization.

Establishing the effect of degree of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ crystallization on the distribution coefficients, D , of Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ and Ag^+ when crystallizing at 25 °C. Nickel(II) and ammonium sulfate solution [26.7% of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] saturated at 75 °C was poured into 16 beakers. After addition of different amounts of water [to obtain the preset degrees of crystallization (α)], the resulting solutions were cooled to temperatures close to 25 °C (except for solutions for which the highest α -values had been obtained, where the crystallization started at higher temperature), and then placed in beakers with a water jacket, after which, having been covered with a watch glass, they were stirred with a magnetic stirrer (ca. 300 rpm) at 25 ± 1 °C over 6 h. The results obtained are presented in Table 1 and in Fig. 1.

Determination of equilibrium distribution coefficients, D , of the microcomponents (Na^+ , K^+ , Rb^+ , Cs^+ and Tl^+) at 20 ± 1 °C. In order to determine the equilibrium distribution coefficients the method of long-time stirring of crushed crystals in saturated solution was applied.⁶ It was assumed that the equilibrium could be reached

starting either from coefficients exceeding the equilibrium coefficients (D_{max}°) or from coefficients lower than the equilibrium ones (D_{min}°). When selecting values D_{max}° and D_{min}° the highest and the lowest values of D obtained during crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 25 °C (series 1) were taken into consideration. The experiments were carried out in the following way: Crushed, contaminated $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ crystals ($\phi < 0.1$ mm) were introduced into several beakers together with saturated purified nickel(II) and ammonium sulfate solution. Crushed crystals of purified $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ($\phi < 0.1$ mm) and contaminated saturated solution of nickel(II) and ammonium sulfate were introduced to some other beakers. The beakers, covered with watch glasses, were placed in a closed room in a water bath. Their contents were stirred for ca. 410 h with magnetic stirrers. Fluctuations of temperature, which facilitated recrystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and helped attain equilibrium and homogeneous partition of the microcomponents in the crystal, were read every 12 h. The mean temperature was 20 ± 1 °C. The results are presented in Table 2.

Results and discussion

Cocrystallization of M^+ ions is effected in a diverse way. Distribution coefficients of some of them (K^+ , Rb^+ , Tl^+ and Ag^+) are higher than 1, which means that they undergo concentration in crystals, and the other microcomponents (with $D < 1$) enrich in the mother solution. Dependences $D = f(\alpha)$ and $\lambda = f(\alpha)$ presented in Fig. 1 show that the distribution of Tl^+ and K^+ during the crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is approximately homogeneous ($D \approx \text{const.}$) over the whole range of α investigated. In the case of the remaining microcomponents their coefficients λ depend on α to a smaller degree than D (particularly for Rb^+ , whose coefficient λ_{Rb} decreases very slightly with increasing α) (Fig. 1).

The distribution coefficients of some ions M^+ { Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ } for two series (D_{max}° and D_{min}°) do not differ from each other considerably, which means that the equilibrium condition was reached for them, and average values for both series are equilibrium values (Table 2). Average distribution coefficients obtained for different degrees of crystallization at 25 °C are very close to equilibrium coefficients at 20 °C (in the case of Cs^+ and K^+) or higher than D_{eq} (in the case of Rb^+ , Tl^+ and Na^+).

The dependence of cocrystallization coefficients D of the microcomponents M^+ with $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ on the ionic radius is presented in Fig. 2. The said dependence has a regular run: coefficients D increase monotonically from Na^+ , achieving the highest values for Rb^+ and Tl^+ , whose ionic radii are closest to the macrocomponent (NH_4^+) radius, and then decrease with a further increase of ionic radius (for Cs^+).

Distribution coefficients, D , of the microcomponents M^+ decrease monotonically with increasing solubility of

Table 1. Effect of degree of NiSO₄ · (NH₄)₂SO₄ · 6H₂O crystallization (α) on the distribution coefficients D and λ of microcomponents when crystallizing for 6 h at 25 ± 1 °C.^a

α	Na ⁺				K ⁺				Rb ⁺				Cs ⁺				Tl ⁺				Ag ⁺			
	a ₀ = 160 ppm		a ₀ = 56 ppm		a ₀ = 50 ppm		a ₀ = 75 ppm		a ₀ = 190 ppm		a ₀ = 5.5 ppm		a ₀ = 190 ppm		a ₀ = 5.5 ppm		a ₀ = 190 ppm		a ₀ = 5.5 ppm		a ₀ = 190 ppm		a ₀ = 5.5 ppm	
	a _k	a _r	D	λ	a _k	a _r	D	λ	a _k	a _r	D	λ	a _k	a _r	D	λ	a _k	a _r	D	λ	a _k	a _r	D	λ
0.171	16.7	202	0.083	0.091	69	52	1.33	1.29	106	37	2.9	2.5	64	81	0.79	0.80	635	87	7.3	4.9	12.2	3.0	4.1	2.7
0.354	16.0	252	0.064	0.079	64	58	1.10	1.08	89	30	3.0	2.2	63	90	0.70	0.74	444	55	8.1	3.9	8.8	3.2	2.8	2.1
0.355	20.0	253	0.079	0.097	64	58	1.10	1.08	83	29	2.9	2.2	65	88	0.74	0.78	431	61	7.1	3.6	12.4	3.4	3.6	2.5
0.374	16.0	260	0.061	0.076	58	60	0.97	0.98	80	31	2.6	2.0	50	92	0.54	0.60	393	65	6.0	3.3	12.4	3.4	3.6	2.5
0.408	15.0	256	0.058	0.075	52	53	0.98	0.98	75	28	2.7	2.0	47	89	0.53	0.59	351	58	6.1	3.1	5.8	1.8	3.2	2.2
0.411	15.0	285	0.053	0.069	59	55	1.07	1.05	84	28	3.0	2.1	56	90	0.62	0.68	395	55	7.2	3.4	8.8	2.0	4.4	2.7
0.416	15.0	270	0.056	0.073	59	54	1.09	1.07	86	28	3.1	2.2	52	90	0.58	0.64	404	55	7.3	3.4	9.4	2.2	4.3	2.6
0.461	15.2	264	0.058	0.078	57	52	1.10	1.07	83	28	3.0	2.1	55	95	0.58	0.65	370	52	7.1	3.2	7.8	1.4	5.6	2.8
0.590	14.5	336	0.043	0.067	62	52	1.19	1.12	71	16	4.4	2.2	54	98	0.55	0.65	297	60	5.0	2.4	6.6	2.6	2.5	1.7
0.591	15.1	358	0.042	0.066	56	54	1.04	1.03	65	21	3.1	1.9	50	110	0.45	0.56	290	58	5.0	2.4	12.2	2.8	4.4	2.2
0.614	15.1	396	0.038	0.062	56	54	1.04	1.03	68	17	4.0	2.1	52	103	0.50	0.61	289	42	6.9	2.6	4.2	2.2	1.9	1.5
0.615	16.3	420	0.039	0.063	62	58	1.07	1.04	74	20	3.7	2.0	54	106	0.51	0.62	308	55	5.6	2.4	7.0	2.8	2.5	1.7
0.772	17.8	668	0.027	0.059	60	52	1.15	1.07	62	13	4.8	1.9	55	139	0.40	0.58	240	32	7.5	2.2	7.8	2.4	3.3	1.7
0.776	16.4	682	0.024	0.053	55	50	1.10	1.05	61	14	4.4	1.9	54	143	0.38	0.56	235	34	6.9	2.1	5.2	2.2	2.4	1.5
0.781	17.4	690	0.025	0.056	58	56	1.04	1.02	61	14	4.4	1.9	56	149	0.38	0.56	230	30	7.7	2.2	5.0	2.2	2.3	1.5
0.783	16.2	690	0.023	0.052	61	57	1.07	1.03	62	14	4.4	1.9	56	149	0.38	0.57	218	29	7.5	2.2	5.8	1.8	3.2	1.7

^a a_r is the concentration of microcomponents (ppm) in relation to NiSO₄ · (NH₄)₂SO₄ · 6H₂O; a₀, initial; a_k and a_r, in washed crystal and in mother solution after crystallization, respectively.

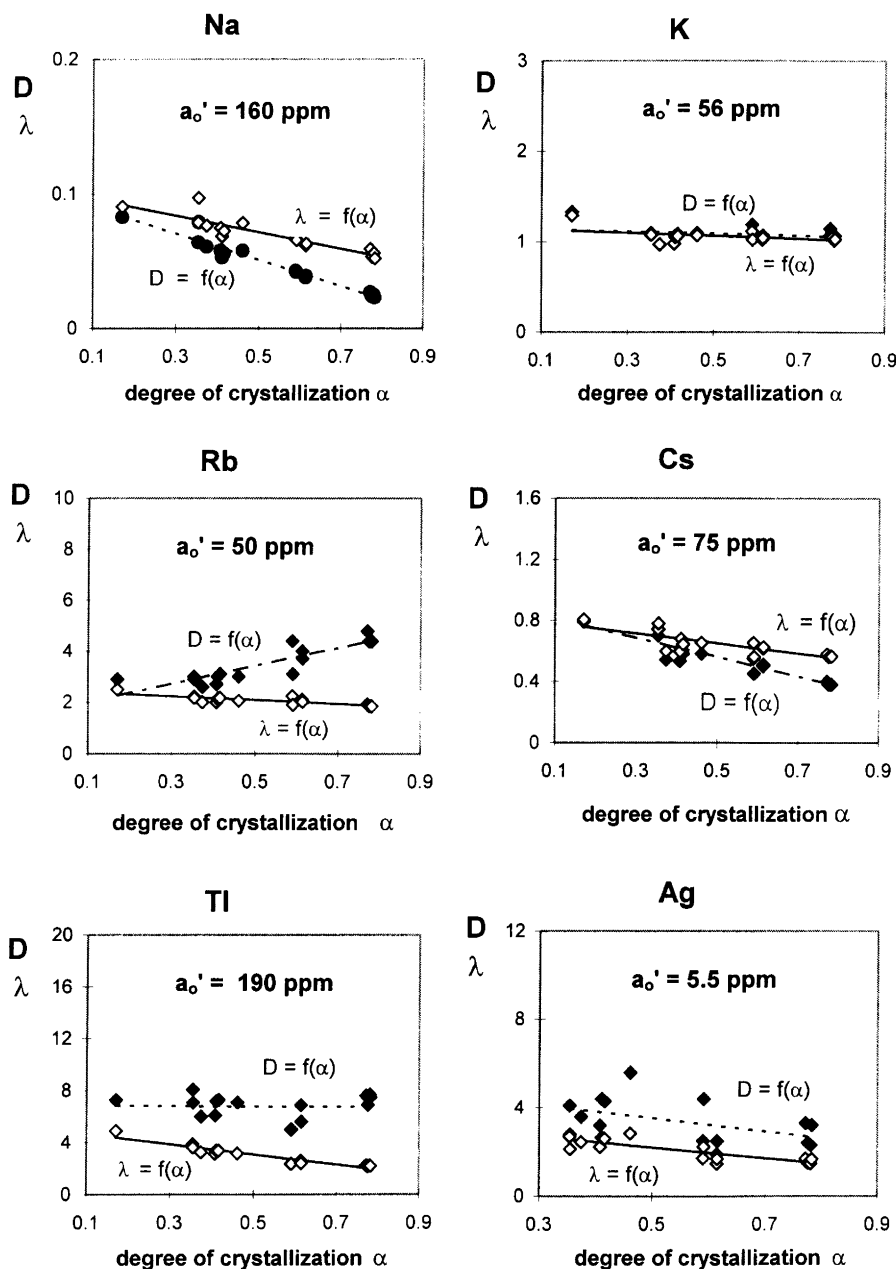


Fig. 1. Effect of degree of crystallization, α , on the distribution coefficients, D , and λ of microcomponents M^+ during the crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 25°C . a_0' is the initial concentration of M^+ (ppm) in relation to $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

the corresponding double salts (Fig. 3), and the curve $D=f(s)$ has a hyperbolic shape. The diagram of this dependency presented in a logarithmic system (Fig. 4) has a linear run, with a high coefficient of linear correlation (r_{xy}).

Observing the close dependency between distribution coefficients D of these microcomponents and solubilities, a determination of the values of these coefficients was attempted based on known solubility values of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (s_{NH_4}) and $\text{NiSO}_4 \cdot M^I_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ($s_{M(\text{I})}$) [s(mol/1000 g of solution)],^{7,8} using the following dependency introduced by Hill *et al.*⁹ (assuming

that the activity coefficients of the NH_4^+ ion and of a respective M^+ ion in the solid phase are equal):

$$\log D_M = 1.25(\log s_{\text{NH}_4} - \log s_{M(\text{I})})$$

The values D calculated and determined in this paper are presented in Table 3. As indicated by the results, many D values calculated and determined experimentally are in good agreement. Relatively the greatest differences between calculated and determined D values are observed for the Na^+ ion. It may be due to the fact that sodium sulfate with nickel(II) sulfate forms the double salt $\text{Na}_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 4\text{H}_2\text{O}$, which has a different struc-

Table 2. Distribution coefficients, D , of microcomponents M⁺ during long time (ca. 410 h) stirring of crushed ($\phi < 0.1$ mm) NiSO₄ · (NH₄)₂SO₄ · 6H₂O crystals in their saturated solution at average temperature 20 ± 1 °C.^a

Micro component	Initial concentration (ppm)		Concentration after stirring (ppm)		α	D_0	D_{\min}°	D_{\max}°	Initial concentration (ppm)		D_0	D_{\min}°	D_{\max}°	α	Concentration after stirring (ppm)		$\bar{D} \pm t_{\alpha}(s/n^{1/2})$ ($1-\alpha$)=0.95	D_1	$\bar{D} \pm t_{\alpha}(s/n^{1/2})$ ($1-\alpha$)=0.95	Average equilibrium distribution coefficient, D
	a'_{k0}	a'_{r0}	a'_k	a'_r					a'_{k0}	a'_{r0}					a'_k	a'_r				
Na ⁺	12	160	5.7	163	0.683	$D_{\max}^{\circ}=0.075$			3.8	190	$D_{\min}^{\circ}=0.020$			0.695	2.9	207	0.014	0.017 ± 0.007	0.023 ± 0.007	
			2.8	180	0.667									0.697	5.1	194	0.026			
			7.0	177	0.674									0.680	2.1	185	0.011			
			5.9	180	0.697									0.672	3.3	174	0.019			
			2.6	190	0.663									0.748	3.5	209	0.017			
K ⁺	18	51	31	26	0.683	$D_{\min}^{\circ}=0.35$			38	27	$D_{\max}^{\circ}=1.41$			0.695	32	30	1.07	1.15 ± 0.18	1.17 ± 0.07	
			28	24	0.667									0.697	33	32	1.03			
			28	23	0.674									0.680	38	31	1.23			
			31	27	0.697									0.672	32	30	1.07			
			28	23	0.663									0.748	37	27	1.37			
Rb ⁺	52	47	67	27	0.683	$D_{\min}^{\circ}=1.1$			87	21	$D_{\max}^{\circ}=4.1$			0.695	74	29	2.6	2.7 ± 0.3	2.6 ± 0.2	
			66	26	0.667									0.697	80	33	2.4			
			69	25	0.674									0.680	89	30	3.0			
			58	28	0.697									0.672	79	29	2.7			
			64	25	0.663									0.748	84	28	3.0			
Cs ⁺	14	120	40	77	0.683	$D_{\min}^{\circ}=0.12$			60	42	$D_{\max}^{\circ}=1.43$			0.695	38	76	0.50	0.57 ± 0.10	0.55 ± 0.05	
			40	71	0.667									0.697	44	88	0.50			
			42	70	0.674									0.680	49	75	0.65			
			32	78	0.697									0.672	40	73	0.55			
			37	67	0.663									0.748	52	78	0.67			
Tl ⁺	248	83	270	50	0.683	$D_{\min}^{\circ}=3.0$			270	42	$D_{\max}^{\circ}=6.4$			0.695	248	49	5.1	5.2 ± 0.4	5.2 ± 0.3	
			260	51	0.667									0.697	264	54	4.9			
			268	46	0.674									0.680	281	50	5.6			
			245	54	0.697									0.672	260	53	4.9			
			268	48	0.663									0.748	275	51	5.4			

^a a' is the concentration of microcomponent (ppm) in relation to NiSO₄ · (NH₄)₂SO₄ · 6H₂O: a'_k , in crystal; a'_r , in mother solution.

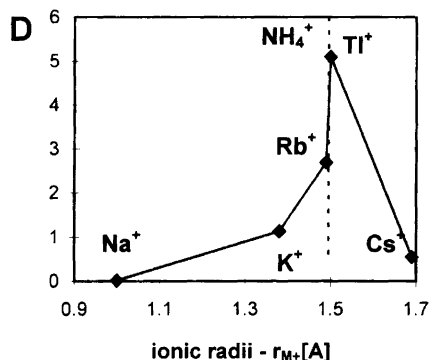


Fig. 2. Effect of ionic radii of microcomponents r_{M^+} (according to Shannon and Prewitt)¹⁰ on their distribution coefficients, D , during crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 20°C .

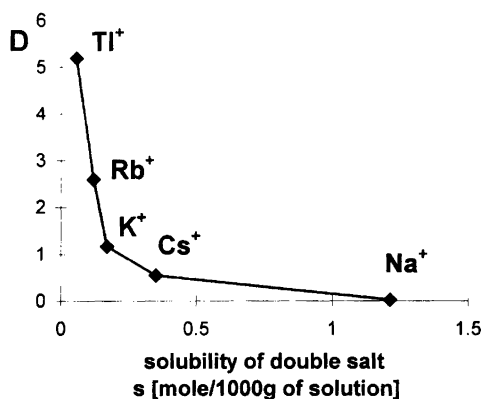


Fig. 3. Effect of solubility of double salt on distribution coefficient, D , of the corresponding microcomponent M^+ during the crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 20°C .

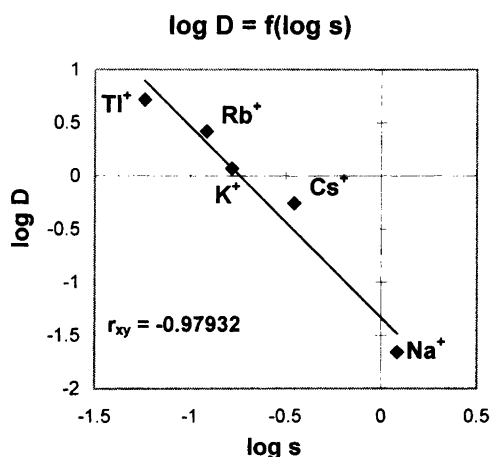


Fig. 4. Dependence: $\log D = f(\log s)$ for crystallization of $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 20°C .

Table 3. Comparison of determined and calculated coefficients, D , of M^+ microcomponents cocrystallization with $\text{NiSO}_2 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 20°C .

Microcomponent	D	
	Calculated	Determined
Na	0.115	0.022 ± 0.006
K	1.3	1.17 ± 0.07
Rb	2.1	2.6 ± 0.2
Cs	0.54	0.55 ± 0.05
Tl	5.2	5.2 ± 0.3

ture from the remaining double salts of the $M^+_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ type, and the assumption of equality of activity coefficients of Na^+ and NH_4^+ ions in the solid phase is not justified.

Conclusions

The distribution coefficients D of the microcomponents M^+ during the crystallization of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ are influenced by the ionic radii of the microcomponents. The maximum values of D occurs for the values r_{micr} most close to r_{MACR} .

Distribution coefficients D of the microcomponents M^+ during the crystallization of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ evidently depend on the solubility of the respective salts. The said coefficients decrease with increasing solubility [s (mol/1000 g of solution)] of the corresponding salt of the microcomponent. The diagrams in the system $\log D = f(\log s)$ has linear character, with the coefficient of linear correlation r_{xy} close to -1 .

An estimation of the value of distribution coefficients D for these microcomponents is possible based on the solubilities of double salts of the macrocomponent and microcomponents. The D values calculated in this way are in many cases in good agreement with the experimental values.

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