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## Distribution of low amounts of $M^{2+}$ ions during the crystallization of $NiSeO_4 \cdot 6H_2O$ at $25^\circ C$

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### ABSTRACT

Distribution coefficients ( $D_{2/1}$ ) of low amounts ( $10^{-2}$ - $7 \cdot 10^{-1}$  %) of  $M^{2+}$  ( $M^{2+} = \{Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Ca^{2+}\}$ ) have been determined during the crystallization of  $NiSeO_4 \cdot 6H_2O$ . The obtained equilibrium coefficients range from  $< 0,005$  (for  $Ca^{2+}$ ) to  $0,31$  (for  $Zn^{2+}$ ). The dependence of  $D_{2/1}$  coefficients on physicochemical properties of crystallizing  $M(II)$  selenate hydrates as well as  $Ni^{2+}$  and  $M^{2+}$  ions have been analyzed.

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### KEYWORDS

Cocrystallization of impurities;  
Distribution coefficients  $D$  (Henderson-Kracek, Khlopin);  
Nickel(II) selenate hexahydrate crystallization.

### INTRODUCTION

Crystallization is one of the most important methods of purification of many inorganic substances and other compounds. The main indicator of its effectiveness is the distribution coefficient  $D_{2/1}$  (Henderson, Kracek<sup>[1]</sup>, Chlopin<sup>[2]</sup>) and therefore it is often determined in various crystallization systems. Selenate crystallization systems are less investigated on that score. In the case of  $NiSeO_4 \cdot 6H_2O$  crystallization, only three distribution coefficients  $D_{2/1}$  are available: for  $Mg^{2+}$  at  $25^\circ C$  ( $D_{2/1} = 0,28$ )<sup>[3]</sup>, for  $Zn^{2+}$  at  $25^\circ C$  ( $D_{2/1} = 0,31$ )<sup>[4]</sup>,  $Co^{2+}$  at  $35^\circ C$  ( $D_{2/1} = 0,35$ )<sup>[5]</sup>. However these data refer to macroamounts of cocrystallized salts and distribution coefficients of microamounts of any ions have not been investigated so far in selenate crystallization systems. Hence it seems to be reasonable to determine them.

Moreover it was proved to be possible in some crystallization systems (such as sulfate, nitrate, chloride)

to evaluate the values of  $D_{2/1}$  by means of some chemical, physicochemical and crystal-chemical properties of cocrystallizing salts and ions<sup>[6]</sup>, but selenate crystallization systems have not been investigated on that score.

So the purpose of the present study is to determine distribution coefficients,  $D_{2/1}$ , of low amounts ( $10^{-2}$ - $7 \cdot 10^{-1}$  %) of  $M^{2+}$  ions ( $M^{2+} = \{Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Ca^{2+}\}$ ) during the crystallization of  $NiSeO_4 \cdot 6H_2O$  as well as to identify relations between these coefficients and the mentioned physicochemical and crystal-chemical factors and to compare these relations with those established earlier for the same microcomponents during their cocrystallization with nickel sulfate heptahydrate<sup>[7]</sup>.

### EXPERIMENTAL

#### Reagents

Nickel(II) selenate hexahydrate was prepared by

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neutralization of dilute selenic acid (obtained by oxidation of  $\text{SeO}_2$  with  $\text{H}_2\text{O}_2$  in the presence of gaseous oxide<sup>[8]</sup>) with nickel(II) hydroxide (obtained from nickel(II) sulfate (POCh- Gliwice) by precipitation with NaOH solution and washing).

Solutions of {Mg(II), Cu(II), Co(II), Zn(II), Mn(II), Cd(II)} selenate were obtained in the same way by reaction of selenic acid with corresponding metal oxide (in the case of Mg, Zn, Cd) and metal hydroxide (in the case of Cu, Co) and metal carbonate (in the case of Mn).

In preparation of each selenate the solutions were filtered and evaporated. The crystals obtained after cooling were dissolved and recrystallized from water at room temperature.

Solution of  $\text{Ca}(\text{NO}_3)_2$  (POCh-Gliwice)- 1,000 mg/ml was used.

Ammonia solution 25% p.a.(POCh-Gliwice), sodium versenate p.a. (POCh-Gliwice)-0,1 mol/dm<sup>3</sup> water solution, murexide indicator (POCh-Gliwice) were used.

### Apparatus

Atomic absorption spectrometer, model 3300 manufactured by Perkin Elmer was applied.

### Analytical methods

#### 1. Determination of the macrocomponent

Nickel(II) was determined by complexometric titration with sodium versenate in ammonia solution using murexide as indicator<sup>[9]</sup>.

#### 2. Determination of the microcomponents

The microcomponents {Cu(II), Mg(II), Zn(II), Co(II), Cd(II), Ca(II)} were determined by means of direct atomic absorption spectrometry from solutions containing 0,300g of  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$  in 25ml solution. Absorbances of samples and sets of standards having the same concentration of  $\text{NiSeO}_4$ , were measured under the same conditions.

#### Methods for determination of coefficient ( $D_{2/1}$ )

After crystallization, crystals were filtered from mother solutions using sintered glass funnel (funnel Schott). The green crystals of  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$  were washed with saturated purified  $\text{NiSeO}_4$  solution, weighed and dissolved in water. Mother solutions were

diluted with water in volumetric flasks. The concentrations of  $\text{NiSeO}_4$  in both solutions determined by method given above permitted to calculate the degree of crystallization ( $\alpha$ ) using equation:

$$\alpha = \frac{m_{Ms}}{m_{Mk} + m_{Mr}} \quad (1)$$

where:  $m_{Ms}$  = mass of macrocomponent in the solid phase,  $m_{Mk}$  = mass of macrocomponent in the crystal,  $m_{Mr}$  = mass of macrocomponent in the mother solution

as well as the volumes of both solution necessary to determine the microcomponents (the concentration of macrocomponent was equal to 0,300 g  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$  in 25 ml solution). The relative concentration of microcomponents in washed crystals ( $a'_k$ ) and in mother solutions ( $a'_r$ ) determined by atomic absorption spectrometer, made it possible to calculate  $D_{2/1}$  according to the equation:

$$D_{2/1} = \frac{a'_k}{a'_r} \quad (2)$$

where:  $a'_k$  ( $a'_r$ ) - the relative concentration ([ppm] in relation to  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$ ) of microcomponent in the washed crystal (mother solution) respectively.

The determination of distribution coefficients  $D_{2/1}$  was carried out in the following two series.

#### Preliminary determination of distribution coefficients - series 1

The supersaturated nickel(II) selenate solution containing different initial concentrations of microcompo-

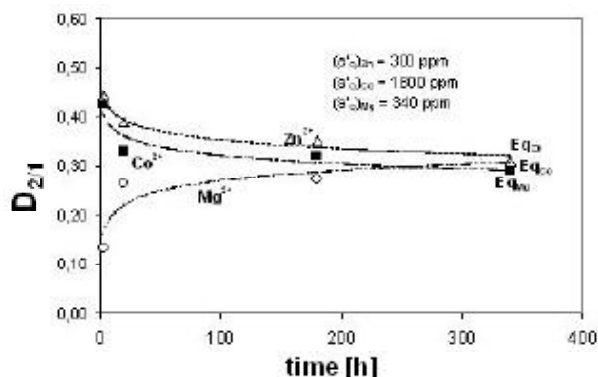


Figure 1: The dependence of crystallization coefficients  $D_{2/1}$  of  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  on time during  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$  crystallization:  $a'_0$  - initial concentration of  $M^{2+}$  relation to  $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$ , Eq - equilibrium values of  $D_{2/1}$  obtained in the second series

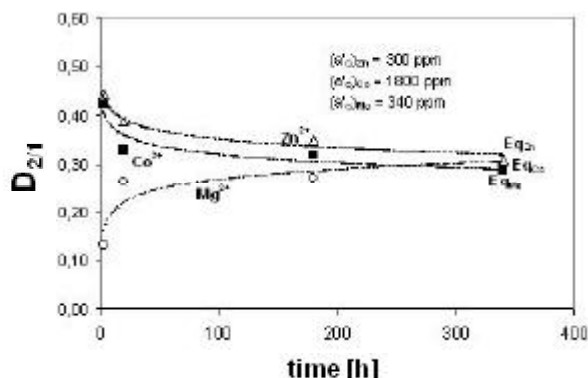
nents was cooled to temperature 25°C and poured into several bottles. The bottles were closed and solutions stirred with magnetic stirrer (~250 rpm) at 25°C over 3-120 hours. The coefficients determined in this series have been presented in figure 1 and figure 2, together with the equilibrium distribution coefficients obtained in the second series.

**Determination of equilibrium distribution coefficients - series 2**

The equilibrium distribution coefficients were determined by the method of long-time stirring of crushed crystals in saturated solutions (over 2 weeks) at 25 °C. The equilibrium was achieved from "above" (where initial ratios of microcomponent concentrations in crystal and the solution were greater than expected values of equilibrium coefficient) ( $D_{min}^o$ ) and from "below" (where these ratios were lower than expected equilibrium coefficient) ( $D_{max}^o$ ). The experiments were carried out in the following ways: "contaminated"  $NiSeO_4 \cdot 6H_2O$  crystals ( $a'_{ko}$ ), crushed to pass a 0.1mm sieve were introduced into several bottles together with saturated "purified" nickel(II) selenate solution ( $a'_{ro}$ ).

Crystals of "purified"  $NiSeO_4 \cdot 6H_2O$  ( $a''_{ko}$ ) crushed to pass a 0.1mm sieve and "contaminated" saturated solution of nickel(II) selenate ( $a''_{ro}$ ) were introduced to some other bottles. The contents were stirred in closed bottles with magnetic stirrer (~250 rpm) at 25 °C over 2 weeks. The results are presented in TABLE 1.

In the case of  $Cu^{2+}$  ion, which was not investigated in the series 1, the wide range of initial distribution co-



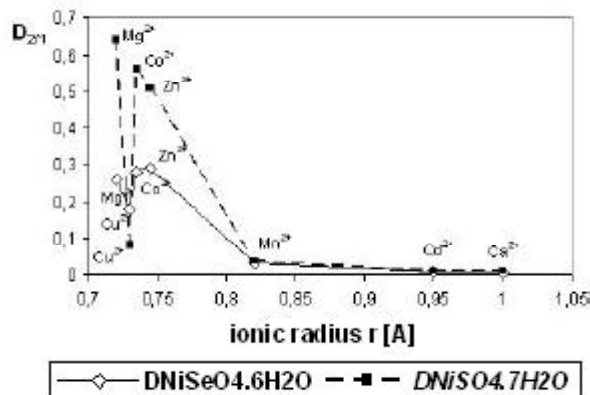
**Figure 2:** The dependence of crystallization coefficients  $D_{2/1}$  of  $Cd^{2+}$ ,  $Mn^{2+}$  and  $Ca^{2+}$  on time during  $NiSeO_4 \cdot 6H_2O$  crystallization :  $a'$  - initial concentration of  $M^{2+}$  relation to  $NiSeO_4 \cdot 6H_2O$ ,  $Eq_{2/1}$  - equilibrium values of  $D_{2/1}$  obtained in the second series

**TABLE 1:** Distribution coefficients during the crystallization  $NiSeO_4 \cdot 6H_2O$

Microcomponent $M^{2+}$	Initial distribution coefficient						Distribution coefficient after long-time stirring				Average equilibrium distribution coefficient
	$D_{min}^o = \frac{a''_{ko}}{a'_{ro}}$		$D_{max}^o = \frac{a'_{ko}}{a'_{ro}}$		For $D_{min}^o$		For $D_{max}^o$				
	$a''_{ko}$ [ppm]	$a'_{ro}$ [ppm]	$D_{min}^o$	$a'_{ko}$ [ppm]	$a'_{ro}$ [ppm]	$D_{max}^o$	$D_i$	$\bar{D} \pm t_{\alpha} \frac{s}{\sqrt{n}}$		$D_i$	
$Cu^{2+}$	24	160	0.15	105	105	1.00	0.20; 0.18; 0.20; 0.19; 0.20; 0.20	0.20±0.01	0.21; 0.19; 0.19 0.23; 0.21	0.20±0.02	0.20±0.01
$Mg^{2+}$	16	320	0.05	77	155	0.50	0.29; 0.31; 0.29; 0.31; 0.34; 0.32	0.31±0.02	0.21; 0.25; 0.26; 0.36; 0.36	0.29±0.07	0.30±0.03
$Co^{2+}$	960	6500	0.15	930	1860	0.50	0.29; 0.26; 0.32; 0.26; 0.29; 0.25	0.28±0.03	0.30; 0.27; 0.26; 0.32; 0.34	0.30±0.05	0.29±0.02
$Zn^{2+}$	87	430	0.20	95	190	0.50	0.31; 0.28; 0.25; 0.27; 0.33; 0.28	0.29±0.03	0.42; 0.31; 0.27; 0.32; 0.40	0.34±0.06	0.31±0.03
$Cd^{2+}$	11	2200	0.005	105	750	0.14	0.006; 0.002; 0.009; 0.010; 0.008; 0.006 0.031; 0.025;	0.007±0.003	0.016; 0.010; 0.007; 0.008; 0.008	0.010±0.004	0.008±0.002
$Mn^{2+}$	30	1500	0.020	175	880	0.20	0.039; 0.039; 0.040; 0.033	0.034±0.006	0.057; 0.034; 0.029; 0.032; 0.040	0.038±0.011	0.036±0.006
$Ca^{2+}$	-	-	-	-	-	-	-	-	-	-	< 0.005*

$\bar{D}$  - Mean value of  $D_{M/NiSeO_4 \cdot 6H_2O}$ ;  $t_{\alpha}$  - Value of Student  $t$ -test for  $(n-1)$  degrees of freedom and for the confidence level of  $(1-\alpha) = 0.95$ ;  $n$  - Number of determinations;  $s$  - Standard deviation;  $D_{min}^o$ ,  $D_{max}^o$  - Initial minimum and maximum values of  $D_{M/NiSeO_4 \cdot 6H_2O}$  respectively. \* - Determined in the series 1

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**Figure 3:** Comparison of the dependences of distribution coefficients  $D_{2/1}$  of low amounts of  $M^{2+}$  ions ( $M^{2+} = \{Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Ca^{2+}\}$ ) on their ionic radius in the  $NiSeO_4 \cdot 6H_2O$  and  $NiSO_4 \cdot 7H_2O$  crystallization systems

efficients was appointed. On the other hand the equilibrium distribution coefficient of  $Ca^{2+}$  ion was not determined because of its very low level ( $D_{2/1} < 0,005$ ).

## RESULTS AND DISCUSSION

The distribution coefficients of each ion  $M^{2+}$  ( $Mg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}$ ) for two series ( $D_{2/1}^{max}, D_{2/1}^{min}$ ) do not differ from each other significantly, which means that the equilibrium condition was reached for them. The average values for both series are equilibrium values (TABLE 1). The obtained  $D_{2/1}$  coefficients range from  $< 0,005$  for  $Ca^{2+}$  to 0,31 for  $Zn^{2+}$ . They are the limits, to which tend  $D_{2/1}$  values in the series 1, while increasing the time of crystallization.

The cocrystallization coefficients of all studied ions  $M^{2+}$  (except  $Ca^{2+}$ ) do not depend on solubility of  $NiSeO_4$  ( $m_{01}$ ) and other selenates ( $m_{02}$ )<sup>[10-12]</sup>. The correlation coefficient of  $\log \frac{m_{01}}{m_{02}}(x)$  and  $\log D_{2/1}(y)$  is very close to zero ( $\rho_{xy} = -0,0074$ ). The analogues correlation coefficient of selenate hexahydrates ( $MgSeO_4 \cdot 6H_2O, CoSeO_4 \cdot 6H_2O, ZnSeO_4 \cdot 6H_2O$ ) is not significant as well ( $\rho_{xy} = -0,4671$ ), but in spite of that their coefficients  $D_{2/1}$  may be estimated by the simple formula:

$$D_{2/1} = \left( \frac{m_{01}}{m_{02}} \right)^2 \quad (3)$$

(where  $m_{01}(m_{02})$ -solubility [mol/1kg  $H_2O$ ] of  $MSeO_4 \cdot \{M$

$= Mg, Co, Zn \}$ ) at average relative error not exceeding 15,5%.

The dependence of cocrystallization coefficients ( $D_{2/1}$ ) of microcomponents  $M^{2+}$  with  $NiSeO_4 \cdot 6H_2O$  and  $NiSO_4 \cdot 7H_2O$  on their ionic radius ( $r_{M^{2+}}$ ) is presented in the figure 3. The coefficient diminishes as ionic radius increases and for  $Ca^{2+}$  - the most distant ion it is close to zero ( $D < 0,005$ ). However in the case of  $Cu^{2+}$  ion some irregularity in the monotonic run of dependence:  $D_{2/1} = f(r_{M^{2+}})$  is observed. It is caused by considerable difference in the structures of triclinic  $CuSeO_4 \cdot 5H_2O$  and tetragonal  $NiSeO_4 \cdot 6H_2O$ . This difference hinders the inclusion of  $Cu^{2+}$  ion in the crystal lattice of nickel selenate hexahydrate.

The same irregularity in the run of the dependence:  $\log D_{2/1} = f(r_{M^{2+}})$  may be observed for nickel(II) sulfate heptahydrate as well. In this case distribution coefficients of the ions of lower radius ( $Mg^{2+}, Co^{2+}, Zn^{2+}$ ) are considerably higher than those for  $NiSeO_4 \cdot 6H_2O$ , but they become very close to each other and tend to 0 as ionic radius increases. Generally the character of both dependences is similar.

However the overall dependence of  $\ln D_{2/1}$  on  $r_{M^{2+}}$  for all investigated ions (except  $Ca^{2+}$ ) is linear with significant and relatively high correlation coefficient ( $\rho_{xy} = -0,9758$ ).

The effect of various factors ( $x$ ): number of molecules of crystallization water ( $\Delta n$ ), hardness of cations ( $\Delta h$ ), electronegativity ( $\Delta \epsilon$ ), crystal field stabilization energy ( $\Delta s$ ) on distribution coefficients ( $y = \ln D_{2/1}$ ) has been presented in TABLE 2. Significant values of correlation coefficients ( $\rho_{xy}$ ) are marked bold. The presented data show that values of  $D_{2/1}$  do not depend on electronegativity, hardness as well as crystal field stabilization energy of ions, but they depend on ionic radius,  $\mu^3$  (crystal-chemical parameter proportional to unit cell volume) and number of molecules of crystallization water.

Thanks to relatively high correlation coefficient of  $\ln D_{2/1}$  on  $r_{M^{2+}}$  ( $\rho_{xy} = -0,9758$ ) it is possible to calculate  $D_{2/1}$  coefficients of all investigated ions (except  $Ca^{2+}$ , for whom  $D_{2/1} < 0,005$ ) at average relative error about 27% by the simple formula:

$$D_{2/1} = e^{-16,47 \cdot r + 10,76} \quad (4)$$

It is also possible to calculate  $D_{2/1}$  for ions forming



**TABLE 2: Correlation of  $\ln D_{2/1}$  (y) and various physicochemical factors (x)**

y	x	k	$\rho_{xy}$
$\ln D_{2/1}$	r	6	-0,9758
$\ln D_{2/1}$	$\mu^3$	6	0,9120
$\ln D_{2/1}$	$\Delta n$	6	-0,9157
$\ln D_{2/1}$	$\Delta \epsilon$	6	-0,1643
$\ln D_{2/1}$	$\Delta h$	6	-0,5121
$\ln D_{2/1}$	$\Delta s$	6	-0,4188
$\ln D_{2/1}$	$\Delta s$	3	0,8708

( $\rho_{xy}$ ) correlation coefficient, r-ionic radius [ $\text{\AA}$ ]<sup>[13]</sup>,  $\Delta n = n_M - n_m$ ;  $n_n(n_m)$  - Number molecules of crystallization water of macrocomponent (microcomponents),  $\Delta \epsilon = \epsilon_M - \epsilon_m$ ;  $\epsilon_M(\epsilon_m)$  - Electronegativity of macrocomponent (microcomponents)<sup>[14]</sup>,  $\Delta h = h_M - h_m$ ;  $h_M(h_m)$  hardness of macrocomponent (microcomponents)<sup>[15]</sup>,  $\Delta s = s_M - s_m$ ;  $s_M(s_m)$  - Crystal field stabilization energy of

macrocomponent (microcomponents),  $\mu = 10^8 \cdot \sqrt[3]{\frac{M}{dN}}$  (M-mole mass [mol/g], d-density [g/cm<sup>3</sup>], N-Avogadro number)<sup>[16]</sup> k-number of cocrystallized ions (6-investigated ions without Ca<sup>2+</sup>, 3 - Mg<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>)

selenate hexahydrates (Co<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>) at relative error not exceeding 1,2% by the formula:

$$D_{2/1} = e^{0,0629 \cdot \Delta s - 1,263} \quad (5)$$

## CONCLUSIONS

The cocrystallization coefficients  $D_{2/1}$  of low amounts of M<sup>2+</sup> ions during the crystallization NiSeO<sub>4</sub>·6H<sub>2</sub>O are lower than 1. It means that they may be removed by crystallization of NiSeO<sub>4</sub>·6H<sub>2</sub>O, although this process is not very effective particularly in the case of Mg<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> ions.

Coefficients  $D_{2/1}$  of all investigated M<sup>2+</sup> ions depend on their ionic radius, number of molecules of crystallization water and  $\mu$  parameter. They may be estimated by the simple empirical formulae.

Cocrystallization coefficients  $D_{2/1}$  of investigated ions with NiSeO<sub>4</sub>·6H<sub>2</sub>O are generally lower than those determined in the case of NiSO<sub>4</sub>·7H<sub>2</sub>O crystallization, but their dependence on ionic radius has similar run.

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