Mixed selenates in the systems $[(CH_3)_4N]_2SeO_4$ —MSeO₄—H₂O (M = Mg and Ni)

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The solubility diagrams in the $[(CH_3)_4N]_2SeO_4$ —MgSeO₄—H₂O and $[(CH_3)_4N]_2SeO_4$ —NiSeO₄—H₂O systems at 25 °C were studied. Basing on the results obtained the compounds $[(CH_3)_4N]_2Mg_3(SeO_4)_4$ 21H₂O, $[(CH_3)_4N]_2Mg_2(SeO_4)_3$ 12H₂O, and $[(CH_3)_4N]_2Ni(SeO_4)_2$ 9H₂O, which were not described in the literature till now, were prepared. On the basis of the infrared and electronic spectra, thermal analysis, X-ray powder diffractometry, and the measurement of the magnetic susceptibility the bonding relations in these substances were studied. It was found that the octahedral $[M(H_2O)_6]^{2+}$ and tetrahedral $[(CH_3)_4N]^+$ cations and the selenate anions SeO_4^{2-} are the fundamental structural units in these substances.

In the systematic study of the conditions of formation of mixed selenates (*e.g.* [1-10]) the attention was focussed in this work on the systems $[(CH_3)_4N]_2SeO_4$ — —MSeO₄—H₂O (M = Ni, Mg) containing large $[(CH_3)_4N]^+$ cation (r = 300 pm [11]).

Mixed selenates, in prevailing cases of the type $M_2^{1}M^{11}(\text{SeO}_4)_2$ $6H_2O$ ($M^{1} = K$, Rb, Cs, NH₄, Tl; $M^{11} = Mg$, Mn, Fe, Co, Ni, Cu, Zn, Cd), were widely studied especially by *Tutton* [6–8], *Topsoë* [9], and *Christiansen* [10]. From among the recent studies the works by *Chandhuri* [12], *James* [13], and *Peytavin* [14] may be mentioned. These authors prepared the mixed selenates by mixing the solutions of selenates of univalent metal and of selenates of bivalent metal in the mole ratio 1 1 and by the subsequent crystallization. In a number of papers (*e.g.* in [1–5, 15]) the solubility diagram of the M_2^1 SeO₄— M^{11} SeO₄— H_2O systems was also studied.

A considerable interest was devoted also to the study of the solid selenates. The mixed salts of the $M_2^1M^{11}(\text{SeO}_4)_2$ $6H_2O$ type belong to the group of Tutton's salts; they are isomorphic with each other and also with the respective sulfates. The crystals are formed by three basic structural units [16-18]: by tetrahedral selenate anions SeO_4^{2-} , distorted polyhedra $(M^1O_8)^+$, where the oxygen atoms belong to the anions as well as to the H_2O molecules, and hexaaqua cations $[M^{11}(H_2O)_6]^{2+}$, with approximately octahedral symmetry. The systems of hydrogen bonds are also present [16-18].

The thermal decomposition of these compounds was studied in detail by *Chandhuri et al.* [12]. By analysis of the DTA, DTG, and TG curves the activation energies for individual dehydration steps were determined. The influence of the M^+ and M^{2+} radii on the thermal stability was studied in detail in [19].

In the study of the IR and RA spectra of mixed selenates the attention was focussed mainly on the vibrations of the anion [19–22], of the $[M^{II}(H_2O)_6]^{2+}$ particle [19, 21] and on the vibrations of the H₂O molecules, including the libration modes and the hydrogen bonds [19]. It was found that in these compounds the SeO₄²⁻ anion is not coordinated to the bivalent cation (in contrast to the anhydrous mixed salts [19]) and the deviations from the symmetry T_d are caused in particular by the anion—water hydrogen bonds. Similarly as in mixed sulfates (of the M₂¹M^{II}(SO₄)₂ 6H₂O type [23]) the contrapolarization effect of the M⁺ cation on the [M^{II}(H₂O)₆]²⁺ cation in the mixed selenates was evidenced [19]. In this work an attempt was made to determine the influence of large tetramethylammonium cation (r = 300 pm) on the formation of mixed salts and on the bonding relations in them.

Experimental

Reagents and methods

The selenates $MgSeO_4$ $6H_2O$ and $NiSeO_4$ $6H_2O$ were prepared by reacting the solution of the selenic acid with magnesium carbonate and nickel carbonate hydroxide, respectively [1-5]. Both the salts were recrystallized from aqueous solution and characterized by analysis of the selenium and metal content.

In the starting substances as well as in the prepared compounds the determination of selenium was realized using the modified Bode's gravimetric method [24] after preceding reduction of Se^{V1} to Se^{IV} [19], the [(CH₃)₄N]⁺ cation was determined as [(CH₃)₄N] [Cr(NH₃)₂(SCN)₄] precipitate [25], Mg²⁺ and Ni²⁺ as Mg₂P₂O₇ resp. Ni₂P₂O₇ [26]. The titration methods were used by the solubility study. Selenium was determined by iodometry [1, 27], nickel and magnesium by complexometry [28]. The crystalline water was determined by the thermal analysis.

The thermal stability was studied by the thermogravimetric method (TG), by the differential thermal analysis (DTA) and by the quasistationary decomposition (KTG). The first two methods were realized using the Derivatograph OD-102 (MOM, Budapest) in the temperature range of 25—300 °C with the heating rate of $2.5 \,^{\circ}$ C min⁻¹ The KTG measurements were carried out in the interval of $25-250 \,^{\circ}$ C. The samples were heated for several days in a regulated electrical furnace ($\pm 1.5 \,^{\circ}$ C) and weighed. The temperature was raised by 20 °C in a day. The powder diffractograms were obtained using a Mikrometa 2 (Chirana, Prague) device with a Siemens cell (diameter 57.3 mm) and Cu anode. The samples were placed in Lindemann's capillaries (diameter 0.3-0.5 mm). The

diffractograms were obtained using the diffractograph (Chirana, Prague) with a Cu anode. The infrared spectra were measured at room temperature, using the PE-684 (Perkin—Elmer) equipment, in the suspension of nujol or KELF using the KBr cell in the range of $\tilde{v} = 350-4000$ cm⁻¹ The diffuse reflection spectra were measured against MgO by means of a spectrophotometer VSU-2 (Zeiss, Jena) in the range of $\lambda = 200$ -1200 nm. The magnetic susceptibility was measured using a magnetic balance based on the Faraday's method. Copper sulfate pentahydrate, CuSO₄ 5H₂O, was used as a standard substance.

Preparation and characterization of tetramethylammonium selenate

Tetramethylammonium selenate $[(CH_3)_4N]_2SeO_4$, which was not described in the literature till now, was prepared by neutralization of the 10% aqueous solution of tetramethylammonium hydroxide $[(CH_3)_4N]OH$ with 15% aqueous solution of selenic acid H_2SeO_4 . The solution with pH = 6.6—7.0 was thickened in a vacuum evaporizator to an oily liquid and kept for crystallization in a desiccator over P_2O_5 during 5—6 days. After filtration the crystals were dried in a vacuum desiccator over P_2O_5 .

The melting temperature of tetramethylammonium selenate is 30-32 °C. In the ¹H NMR spectrum (D₂O as solvent, measured contents were 20, 40, and 52 %) only a singlet at $\delta = 3.14$ corresponding to the presence of the methyl groups bonded to nitrogen [29] was observed. The position of the peak was not dependent on the concentration; no additional peaks were observed nor in highly concentrated solutions. The substance was further characterized by gravimetric analysis of selenium [24] and of the [(CH₃)₄N]⁺ cations [25], by the IR spectrum and powder diffractogram. The results are given in Tables 1-5.

The solubility in the [(CH₃)₄N]₂SeO₄---MgSeO₄---H₂O system at 25°C

The solubility in the system under investigation was studied using the method of *Schreinemakers* [30]. The samples were prepared fully dissolving precisely weighed amounts of salts and water and by subsequent spontaneous evaporization in open test-tubes in an air thermostat at 25 °C (± 0.5 °C) until the first crystals appeared. The test-tubes were then closed and kept in a thermostat for next 3—6 days. The liquid and solid (the wet remainder) phases were next separated for analysis. In some cases the solid phase was also verified by X-ray analysis. The results of the solubility study in the [(CH₃)₄N]₂SeO₄—MgSeO₄—H₂O system at 25 °C are summarized in Table 1.

It is obvious that in the mentioned system two next compounds crystallize beside the starting selenates: the incongruently soluble mixed selenate with the composition $[(CH_3)_4N]_2Mg_2(SeO_4)_3$ 12H₂O and the congruently soluble compound with the composition $[(CH_3)_4N]_2Mg_3(SeO_4)_4$ 21H₂O. The solubility of the latter substance in water at 25 °C is 50.24 g in 100 g H₂O. Both the above-mentioned compounds were not described in the literature till now.

The solubility	diagram o	f the	$[(CH_3)_1N$],SeO1-	-MgSeO ₁ -	-H ₂ O system	at 25°C
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System —		w _i /%	Calid abuse"		
	TMA	MgSeO ₄	H ₂ O	- Solid plia	ise
1	55.66	0.00	44.34	ТМА	
2	52.95	0.93	46.12	$TMA + S1^{h}$	Α
3	48.71	1.24	50.05	S1	
4	43.46	2.05	54.49	S1	
5	39.31	3.37	57.32	S1	
6	39.10	4.27	56.63	S1	
7	34.69	7.50	57.81	S1	
8	31.54	8.96	59.50	$S1 + S2^{b}$	В
9	28.60	9.77	61.63	S2	
10	24.20	12.66	66.86	S2	
11	12.24	21.20	66.55	S2	
12	8.34	24.91	66.72	S2	
13	3.87	29.52	66.61	S2	
14	0.98	32.89	66.13	S2	
15	0.75	35.99	63.26	Mg + S2	С
16	0.66	36.40	62.94	Mg	
17	0.00	35.18	64.82	Mg	

a) TMA – $[(CH_3)_4N]_2SeO_4$: Mg – MgSeO₄ 6H₂O; S1 – $[(CH_3)_4N]_2Mg_2(SeO_4)_3$ 12H₂O; S2 – $[(CH_3)_4N]_2Mg_3(SeO_4)_4$ 21H₂O: A and C – eutonic points, B – peritonic point.

b) The identity of the solid phase was not verified by X-ray analysis.

The composition of the liquid phase which corresponds to the invariant points A—C is given in Table 1.

The solubility in the [(CH₃)₄N]₂SeO₄—NiSeO₄—H₂O system at 25°C

The solubility in this system was studied by means of the same procedure as in the previous system. The results are summarized in Table 2. It is evident that in the above-mentioned system only one compound, the congruently soluble mixed selenate with the composition of $[(CH_3)_4N]_2Ni(SeO_4)_2$ 9H₂O, is formed. This compound was not described in the literature as yet. Its solubility in water at 25 °C is 85.11 g in 100 g H₂O. The composition of the liquid phase which corresponds to the invariant points A and B is given in Table 2.

Preparation and characterization of mixed selenates

On the basis of the results of the solubility study the above-mentioned compounds were prepared by crystallization at 25 °C. The crystals were filtered, washed with mini-

System		w _i /%			Salid phase(
	ТМА	NiSeO ₄	H ₂ O	- Solid pha	ise	
1	55.66	0.00	44.34	ТМА		
2	54.30	0.65	44.85	TMA + S'	Α	
3	53.75	0.89	45.36	S		
4	52.88	0.99	46.13	S		
5	45.20	2.18	52.62	S ^h		
6	44.35	3.66	51.99	S		
7	38.53	6.55	54.92	S		
8	32.40	11.64	55.96	S		
9	26.12	17.34	51.18	S		
10	22.75	21.98	55.27	$Ni + S^{h}$	В	
11	16.85	23.14	60.01	Ni		
12	10.46	23.38	66.16	Ni [*]		
13	5.76	25.59	68.65	Ni		
14	4.88	25.89	69.23	Ni [*]		
15	2.97	26.49	70.54	Ni ^b		
16	0.00	28.02	71.98	Ni		

The solubility diagram of the [(CH₃)₄N]₂SeO₄-NiSeO₄-H₂O system at 25 °C

a) TMA – $[(CH_3)_4N]_2SeO_4$; Ni – NiSeO₄ $6H_2O$; S – $[(CH_3)_4N]_2Ni(SeO_4)_2$ $9H_2O$; A and B – eutonic points.

b) The identity of the solid phase was not verified by X-ray analysis.

Table 3

Gravimetric analysis of new prepared compounds

Substance	Appearance	w _i (calc.)/% w _i (found)/%					
		[(CH ₃) ₄ N] ⁺	Mg or Ni	Se	H ₂ O		
ТМА	Colourless	50.86		27.14			
	crystalline powder	50.40	—	27.13	—		
S	Green	22.64	8.96	24.11	24.75		
	regular crystals	22.59	8.97	24.04	24.86"		
SI	Colourless	17.61	5.77	28.14	25.68		
	needles	17.58	5.82	28.25	25.55"		
S 2	Colourless	12.66	6.22	26.96	32.30		
	transparent plates	12.69	6.19	27.02	31.31"		

a) Calculated up to 100 %.

DTA		3 m	1001 - 20 M. M.	TG				
Start of process θ° C Effect		Start of process θ/°C	$\frac{\Delta m}{\%}$	$\frac{(\Delta m)_{\rm calc}}{\%}$	Attributed process			
$[(CH_3)_4N]_2Ni(SeO_4)_2$ 9H ₂ O								
65	endo	50	2.54	2.75	– 1H ₂ O			
95	endo	90	8.64	8.79	-3H ₂ O			
115	endo	110		24.75	$(-9H_{2}O) + decomp.$			
(Total dehyd	ration runs sin	multaneously with	th decompo	sition.)				
		[(CH ₃) ₄ N]	$]_2Mg_3(SeO_4)$	₄ 21H ₂ O				
32	endo	60	4.71	4.61	-3H,O			
93	endo	85	18.18	18.48	$-12H_2O$			
122	endo	115	32.31	32.30	$-21H_2O$			
		[(CH ₃) ₄ N]] ₂ Mg ₂ (SeO ₄)	3 12H ₂ O				
55	endo	50	8.71	8.56	-4H ₂ O			
110	endo	105	14.13	14.98	$-7H_2O$			
130	endo	125		25.68	$(-12H_2O) + decomp.$			
(Total dehyd	ration runs sin	multaneously with	th decompo	sition.)				
KTG								
Start of process θ °C		End θ°C	$\frac{\Delta m}{\%}$	$\frac{(\Delta m)_{\rm calc}}{\%}$	Attributed process			
$[(CH_3)_4N]_2Ni(SeO_4)_2 9H_2O$								
45		60	11.41	11.71	-4H,O			
95		130	25.63	26.36	$-9H_2O$			
$[(CH_3)_4N]_2Mg_3(SeO_4)_4 21H_2O$								
30		115	32.19	32.30	-21H ₂ O			

Thermal decompositions of the prepared substances

 Δm — experimental mass loss. (Δm)_{calc} — calculated mass loss.

mum amount of water and dried between filtration paper sheets. The results of the gravimetric analysis and the appearance of the crystals are given in Table 3.

The results of the thermal decomposition of the investigated substances are summarized in Table 4. It is obvious that the KTG results correspond to the TG results. Only in the KTG measurements the beginning of the dehydration was shifted to the lower temperatures. By the KTG measurements of the $[(CH_3)_4N]_2Ni(SeO_4)_2$ 9H₂O compound it was possible to record the whole dehydration of the substance, whereas by the TG and DTA measurements the loss of the last H₂O molecules ran simultaneously with the total decomposition of substance. On the other hand, on the TG and DTA curves of

Bands	ТМА	S	S1	S2
SeO ₄ ²⁻		- <u>1</u>		
$v_1(\mathbf{A}_1)$	830 sh	830 vs	?	833 sh
$v_2(\mathbf{E})$?	357 w	360 w?
$v_3(\mathbf{F}_2)$	855 s	879 vs	875 s	855 vs, b
		905 sh		897 sh
$v_4(\mathbf{F}_2)$	410 s, sp	411 s	412 m	406 vs
$C_a N^{+a}$				
$v_1(\mathbf{A}_1)$	765 m	758 s, sp	731 m	731 m
$v_2(\mathbf{E})$	380 sh?	372 sh	370 sh?	?
$v_3(\mathbf{F}_2)$	965 s	949 s, sp	948 m, sp	957 s
$v_4(\mathbf{F}_2)$	465 m	445 sh	?	450 w
CH ₃				
	2940 w	2850 sh	2820 w	
	2990 sh	2940 m		2800
V _{as}	3030 m		3030 m, b	2950 ^{sn, b}
δ	1420 m	1414 m	1420 vs	1410 m
	1465 sh	1453 m		1453 sh
δ_{as}	1505 s	1485 s, sp	1490 m, sp	1487 s, sp
H ₂ O deformation vibration	_	1650 sh	1665 sh	1670 sh
-		1670 m, b	1690 m	1685 m
H ₂ O stretching vibration	_	3200	3250 sh	3190 vs, b
- 0		3300 ^{vs}	.3320 m, b	3300 sh
H ₂ O libration modes		574 m	580 w, b	640 sh
		624 m	620 w, b	667 s

IR spectra ($\tilde{\nu}$ /cm⁻¹) of tetramethylammonium selenate and of the mixed salts in the range of $\tilde{\nu} = 350-4000 \text{ cm}^{-1}$

a) According to [34].

sp — sharp.

 $[(CH_3)_4N]_2Mg_3(SeO_4)_4$ 21H₂O the individual dehydration steps may be seen (in contrast to the KTG measurements). In Table 5 the results of the IR spectroscopic study of all three mixed salts and of the tetramethylammonium selenate are given.

Discussion

In the $[(CH_3)_4N]_2SeO_4$ —MSeO₄—H₂O (M = Mg, Ni) systems the till now unknown compounds $[(CH_3)_4N]_2Ni(SeO_4)_2$ 9H₂O, $[(CH_3)_4N]_2Mg_2(SeO_4)_3$ 12H₂O, and $[(CH_3)_4N]_2Mg_3(SeO_4)_4$ 21H₂O are formed. These compounds differ in composition from the Tutton's type salts which are found in systems of selenates

with the alkali metal cations and the ammonium cation [1-15]. The existence of the $[(CH_3)_4N]_2Ni(SeO_4)_2$ 5H₂O salt may not be considered evidenced in spite of the presence of a long delay (*ca.* 50 °C) on the KTG curve, because the compound prepared by heating was always roentgenographically amorphous. It is clear that the change in the composition of the formed compounds is caused by the presence of a much bigger tetramethylammonium cation (r == 300 pm [11]), which affects the formation conditions of the mixed selenates both in the saturated aqueous solution and in the crystalline state.

The tetramethylammonium cation disturbs in the aqueous solution first of all the structural ordering of the H₂O molecules conditioned by the system of hydrogen bonds [31—33] and consequently releases the water molecules for the hydration of the formed compounds. The presence of the tetramethylammonium cations in the disturbed water structure leads simultaneously on the basis of the ion—dipole interaction to the limitation of the motion of the released H₂O molecules and to their retaining in the proximity of these cations [31—33]. Under these conditions the H₂O molecules pass into the crystallohydrate during the crystallization of the mixed salt easier. In contrast to the mixed selenates with alkali metals [16—18], at the crystallization of mixed selenates with such large cation the structure with a bigger volume of the elementary cell is created, in which a different number ratio of [(CH₃)₄N]⁺ and M^{2+} (in the case of Mg) cations may be present as well as a higher number of H₂O molecules will be placed due to the higher dimensions of the internal cavities (the case of Ni).

The bonding relations in the mixed selenates were studied as well. From the infrared molecular spectra (Table 5) it follows that neither the shift nor the splitting of the $v_3(\text{SeO}_4^{2-})$ band takes place. The selenate anion is then not coordinated, from which it follows that in the coordination sphere of the magnesium and nickel cation only the water molecules are present. The hexa-aquanickel cation was evidenced also on the basis of the reflection spectrum in the UV—VIS region (the band corresponding to the vibration $v_2({}^3A_{2g} \rightarrow {}^3T_{1g})$ at $\tilde{\nu} = 13\,800 \text{ cm}^{-1}$, $v_3({}^3A_{2g} \rightarrow {}^3T_{1g}(\mathbf{P}))$ at $\tilde{\nu} = 25\,300 \text{ cm}^{-1}$, $v'({}^3A_{2g} \rightarrow {}^1E_g)$ at $\tilde{\nu} = 15\,200 \text{ cm}^{-1}$) and to this particle corresponds also the value $\mu_{\text{eff}} = 3.04 \ \mu_{\text{B}}$ at $25 \,^{\circ}\text{C}$. The hexaaquamagnesium cation may be expected in both mixed selenates on the basis of the analogy with the structures of the highly hydrated magnesium salts with oxygen anions.

The weak band of the totally symmetrical vibration $v_1(\text{SeO}_4^{2-})$ which is forbidden in the IR spectrum, testifies to the small deviation from the ideal symmetry \mathbf{T}_d in accordance with the results of *Ross* and coworkers [20]. The deviation is probably caused by the hydrogen bond between the selenate anions and the water molecules. From the IR spectra it further follows that also the tetramethylammonium cation has a symmetry close to the ideal \mathbf{T}_d one. In general, it may be stated that in the structure of the investigated mixed selenates tetrahedral SeO_4^{2-} anions, tetrahedral $[(CH_3)_4N]^+$ and octahedral $[Ni(H_2O)_6]^{2+}$ as well as evidently $[Mg(H_2O)_6]^{2+}$ cations are present.

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