https://www.proconference.org/index.php/usc/article/view/usc19-01-010
DOI: 10.30888/2709-2267.2023-19-01-010

UDC 546.185

ON THE OPTIMUM CONDITIONS FOR THE SYNTHESIS OF BINARY MAGNESIUM-MANGANESE(II) DIPHOSPHATE

Antraptseva N.M.
d.c.s., prof.
ORCID: 0000-0002-5661-6133
Tkachenko A.E.
student
National University of Life and Environmental Sciences of Ukraine,
Kyiv, Geroev Oboronu, 15
Podobii O.V.
c.t.s., as.prof. / к.т.н., доц.
ORCID: 0000-0002-2540-6811
Bila G.N.
c.c.s., as.prof. / к.х.н., доц.
National University of Food Technologies, Kyiv, Volodymyrska str., 68, 01601

Abstract. *The work was carried out with the aim of studying the optimum conditions for the synthesis of binary magnesium-manganese(II) diphosphate and obtaining their main characteristics. There is practically no information about them in the literature. The synthesis of binary diphosphates was carried out by co-precipitation of Mg^{2+} and Mn^{2+} cations from a mixture of aqueous solutions of their sulfates, using an aqueous solution of potassium diphosphate as a precipitant. Deposition was carried out under the following conditions: the ratio of cations in the starting reagents (K=Mg/Mn, molar) was varied from 0 to 100%. The selection of the concentration of the initial solutions, the ratio $n = P_2O_7^{4-}/\Sigma Mg^{2+},Mn^{2+}$ in their composition, and the duration of crystallization were carried out in separate series of experiments. It was determined that diphosphates obtained under the conditions of $19.0 \le K \le 99.0$ have the same type of structure, but different chemical composition. Their identification proved the formation of compounds of variable cationic composition – a solid solution of magnesium and manganese(II) hydrated diphosphates of composition $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$. The areas of its homogeneity are defined as $0 \le x \le 0.23$. The optimal conditions for its production were determined: - the ratio in the composition of the initial solutions $n=P_2O_7^{4-}/\Sigma Mg^{2+},Mn^{2+}=0.05 \le n \le 0.4$; - ratio K = Mg/Mn (mol) = $19.0 \le K \le 99.0$; - concentration of solutions – C = 0.05-0.5 mol/l; - duration of interaction – upon reaching*

equilibrium and crystallization of the solid phase; - temperature interval of interaction – 293-298 K. The features of formation, chemical nature and main physicochemical characteristics of the synthesized solid solution of hydrated diphosphates of the composition $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$ $0 \le x \le 0.23$ have been established.

Key words: *hydrated diphosphates, deposition, optimum conditions, solid solution.*

Introduction

Recently, a lot of attention has been paid to the study of synthesis conditions and various properties of inorganic compounds containing several different cations in their structure. They can form solid solutions or double salts, which differ in the variety of composition, structure, and properties, and therefore are widely used in various fields of modern science, technology, and agriculture [1,2].

Solid solutions of hydrated diphosphates of divalent metals are promising in this regard. Synthesis conditions, composition, properties and areas of application of solid solutions of hydrated diphosphates of cobalt(II) and manganese(II), zinc and manganese(II), zinc and cobalt(II) are sufficiently fully investigated and summarized in the monograph [2].

Regarding binary hydrated diphosphates of magnesium-manganese(II), there is almost no information in the literature.

The purpose of this work is to determine the optimal synthesis conditions and main characteristics of binary magnesium-manganese(II) hydrated diphosphates.

Experimental

The synthesis of binary magnesium-manganese(II) diphosphates was carried out by co-precipitation of Mg^{2+} and Mn^{2+} cations from a mixture of aqueous solutions of their sulfates, using an aqueous solution of potassium diphosphate as a precipitant.

Deposition was carried out under the following conditions: the ratio of cations in the starting reagents (K=Mg/Mn, mol) was varied from 0 to 100%. The selection of the concentration of the initial solutions, the ratio $n = P_2O_7^{4-}/\Sigma Mg^{2+}$, Mn^{2+} in their composition and the duration of crystallization were carried out in separate series of experiments, similarly to that described in [3].

The content of phosphorus (quinolinemolybdate method), magnesium and manganese(II) (complexonometric titration), water (gravimetric method) was

determined by chemical analysis in the composition of the solid phase. X-ray analysis (DRON-4M, connected to a computer complex, FeKα, internal NaCl standard) and IR spectroscopic (Nexus-470 spectrometer, frequency range 400-4000 cm^{-1}, 20°C and -190°C, pressing of a fixed mass into a matrix of potassium bromide) were used to identify phosphates.

Results and discussion

The results of a complex study of the solid phase obtained under the conditions: the ratio in the composition of the initial solutions $n = P_2O_7^{4-}/\Sigma Mg^{2+}$, $Mn^{2+} = 0.3$, the concentration of the solutions 0.1 mol/l, are given in the table. 1.

Table 1 – Characteristics of diphosphates formed in the system $MgSO_4 – MnSO_4 – K_4P_2O_7 – H_2O$

K = Mg/Mn, mole	The composition of the solid phase, wt%				Chemical composition	Phase composition (according to the results of X-ray diffraction and IR spectroscopy)
	Mg	Mn	P	H_2O		
-	13,12	-	16,88	39,42	$Mg_{2,00}P_2O_7 \cdot 8H_2O$	$Mg_2P_2O_7 \cdot 8H_2O$
99,0	12,15	1,96	16,87	39,37	$Mg_{1,85}Mn_{0,15}P_2O_7 \cdot 8H_2O$	Solid solution general formula $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$, $0 \le x \le 0.23$, structure $Mg_2P_2O_7 \cdot 8H_2O$
49,00	11,75	2,55	16,82	39,16	$Mg_{1,83}Mn_{0,17}P_2O_7 \cdot 8H_2O$	
32,33	11,65	2,80	16,78	39,14	$Mg_{1,80}Mn_{0,20}P_2O_7 \cdot 8H_2O$	
24,00	11,64	3,09	16,74	38,48	$Mg_{1,78}Mn_{0,22}P_2O_7 \cdot 8H_2O$	
19,00	11,56	3,24	16,71	38,49	$Mg_{1,77}Mn_{0,23}P_2O_7 \cdot 8H_2O$	
9,00	10,47	11,75	16,57	29,01	$Mg_{1,77}Mn_{0,23}P_2O_7 \cdot 8H_2O$ + $Mn_2P_2O_7 \cdot 5H_2O$	A mixture of phases of structures $Mg_2P_2O_7 \cdot 8H_2O$ i $Mn_2P_2O_7 \cdot 5H_2O$
4,00	9,95	13,01	16,54	28,98		

Authoring

According to the results of quantitative paper chromatography, the anionic composition of the solid phase at all values of K from the region $4.0 \le K \le 99.0$ is represented by diphosphate anion (96.4 - 97.2% relative to P_2O_5).

The content of magnesium, phosphorus, and water in the composition of the diphosphate obtained in the absence of manganese(II) in the initial solutions corresponds to the calculation for individual magnesium diphosphate octahydrate $Mg_2P_2O_7 \cdot 8H_2O$. Its X-ray and IR spectroscopic characteristics correspond to those known for $Mg_2P_2O_7 \cdot 8H_2O$ [4].

The chemical composition of diphosphates obtained at different values of K from the region 4.0≤K≤99.0 varies depending on the composition of the initial solutions (Table 1). Thus, the magnesium content naturally decreases with its decrease in the composition of the initial solutions at 4.0≤K≤99.0. The content of manganese(II) in the composition of diphosphates obtained under the conditions of 19.0≤K≤99.0 increases, adequately compensating for the decrease in magnesium content, and increases sharply (on 8.51% mass) with a further decrease in the value of K from 19.0 to 9. 0.

The same applies to changes in the water content: diphosphates obtained at 19.0≤K≤99.0 are characterized by a similar water content in their composition (39.37–38.49 % mass). When K decreases from 19.0 to 9.0, the content of crystallization water in the composition of diphosphates decreases sharply (by 9.48% mass)/

The $l=H_2O/P$ ratio in the composition of diphosphates obtained under the conditions of 19.0≤K≤99.0 is 4, which corresponds to the calculated value for octahydrates, and noticeably decreases (from 3.01 to 2.81) for diphosphates obtained at 4.0≤K≤9.0.

The interpretation of the changes in the chemical composition established for diphosphates obtained at different ratios of magnesium and manganese(II) in the composition of the initial reagents (4.0≤K≤99.0) indicates that they should be considered as two different groups of hydrated diphosphates. The first of them is diphosphate, obtained under conditions of 19.0≤K≤99.0. They are octahydrates. The second one is a mixture of octa- and pentahydrate diphosphates.

The identification of diphosphates, obtained at 19.0≤K≤99.0, showed that,

despite their different chemical composition, they are represented by one crystalline phase, structurally of the same type as magnesium diphosphate octahydrate. X-ray and IR spectroscopic characteristics of diphosphates correspond to those known for $Mg_2P_2O_7 \cdot 8H_2O$ (Table 2). The presence of magnesium and manganese(II) in their composition indicates the manifestation of isomorphic substitutions in the $Mg_2P_2O_7 \cdot 8H_2O$ crystal structure and the formation of compounds of variable cationic composition on its basis – a solid solution of magnesium and manganese(II) hydrated diphosphates.

Table 2 – Wave numbers (cm^{-1}) of absorption band maxima in the IR spectra of $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$ ($0<x\leq0.23$) and their assignment

Wave numbers (cm^{-1}) of absorption band maxima in the IR spectra		Assignment of band maxima
$Mg_{1,96}Mn_{0,04}P_2O_7 \cdot 8H_2O$	$Mg_{1,77}Mn_{0,23}P_2O_7 \cdot 8H_2O$	
3571	3570	ν (H_2O)
3320 ш.	3315 ш.	
3267 сл.	3243 сл.	
3125 пл	3106 пл.	ν_2 (δ) (H_2O)
1672	1673	δ (POP)
1638	1637	ν_{as} (PO_3)
1229	1178	ν_s (PO_3)
1152	1151	ν_{as} (POP)
1118	1098	ν_s (POP)
1043	1041	δ (PO)
1001	989	M-O
915	914	
627	688	
573	573	
499	497	
417	418	

Authoring

The general formula of the synthesized solid solution determined by the results of chemical analysis has the form $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$. Areas of its homogeneity are defined as $0 \leq x \leq 0.23$. The composition of the saturated solid solution corresponds to diphosphate $Mg_{1,77}Mn_{0,23}P_2O_7 \cdot 8H_2O$.

A decrease K in the composition of the initial solutions within $4.0 \leq K \leq 9.00$ leads to the formation of a mechanical mixture of two phases - crystalline, similar to $Mg_2P_2O_7 \cdot 8H_2O$, and X-ray amorphous, which is similar to $Mn_2P_2O_7 \cdot 5H_2O$. Moreover, as the K values decrease, the amount of the phase with the $Mg_2P_2O_7 \cdot 8H_2O$ structure gradually decreases, and the $Mn_2P_2O_7 \cdot 5H_2O$ phase increases accordingly.

A similar conclusion was made based on the results of IR spectroscopic studies of diphosphates obtained at different values of K as part of the starting reagents.

Summary and conclusions

A solid solution of magnesium and manganese(II) hydrated diphosphates of the composition $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$ with the structure of the diphosphate-matrix $Mg_2P_2O_7 \cdot 8H_2O$ was synthesized. The region of its homogeneity is defined as $0 \leq x \leq 0.23$.

The optimal conditions for its production by the interaction of aqueous solutions of magnesium and manganese(II) sulfates with potassium diphosphate were determined: - the ratio in the composition of the initial solutions $n = P_2O_7^{4-} / \Sigma Mg^{2+}, Mn^{2+} = 0.05 \leq n \leq 0.4$; - ratio K = Mg/Mn (mol) = $19.0 \leq K \leq 99.0$; - concentration of solutions – C = 0.05-0.5 mol/l; - duration of interaction – upon reaching equilibrium and crystallization of the solid phase; - temperature interval of interaction – 293-298 K.

The features of formation, chemical nature and main physicochemical characteristics of the synthesized solid solution of hydrated diphosphates of the composition $Mg_{2-x}Mn_xP_2O_7 \cdot 8H_2O$ $0 \leq x \leq 0.23$ have been established.

References:

1. Acton A. Q. Phosphates – advances in research and application / A.Q. Acton. –Atlanta, Georgia : Scholarly Editions, 2013. – 374 p.

2. Antraptseva, N.M., Solod, N.V. (2017). The solid solution of trace elements phosphates. – Kyiv : Komprint, 2017. – 240 p.

3. Antraptseva N.M., Tkachova N.V., Nedilko S.G. About composition and the chemical nature of products of interaction in system $MnSO_4$-$ZnSO_4$- $K_4P_2O_7$-H_2O // Ukr. chem. mag. – 2007. – V. 73, № 8. – P. 88 – 94.

4. Nakamoto, K.. Infrared and Raman spectra of inorganic and coordination compounds. Part B. Applications in coordination, organometallic, and bioinorganic chemistry. – Jonh Wiley & Sons, Inc., 2009. – 263 p.

sent: 30.07.2023