J. Chem. Chem. Eng. 11 (2017) 60-64
doi: 10.17265/1934-7375/2017.02.004

About New Inorganic Polymers-Double Condensed Phosphates of Silver and Trivalent Metals

Marina Avaliani[1], Elene Shapakidze[2], Nana Barnovi[1], Marina Gvelesiani[1] and Dali Dzanashvili[1]

1. Ivane Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry, O186, Mindeli str.11, Tbilisi, Georgia

2. Ivane Javakhishvili Tbilisi State University, A. Tvalmchrelidze Caucasus Institute of Mineral Resources, O186, Mindeli str.11, Tbilisi, Georgia

Abstract: A distinctive feature of phosphates is their special and significant ability to form inorganic polymeric compounds—condensed phosphates, which are destined to play a considerable role in our "high-tech" society in the future. Numerous olygophosphates, polyphosphates, double condensed phosphates and cyclophosphates with diverse formula, such as double tetra-, octa- and dodecaphosphates were obtained and described by us last years. The offered data are the outcomes of our scientific researches: of synthesis, analysis, and estimation of results in correlation with new achievements in inorganic polymer's chemistry. Many double condensed compounds, containing monovalent metals are obtained by us during systematic investigation of polycomponent systems, containing mono- and trivalent metals at temperature range 100-600 °C. Synthesised condensed phosphates, in fact—inorganic polymers were examined in detail by chemical and thermogravimetric analysis, most compounds were examined by paper chromatography and the structures are determined by X-ray structural techniques/diffraction analysis. During our fundamental researches numerous new (about 70) unknown until now condensed phosphates have been obtained. Dependency of composition VS temperature and molar ratio, reliance of structure from duration of synthesis and radius of the ions are revealed.

Key words: Synthesis, condensed phosphates, olygophosphates, diphosphates, triphosphates, tetraphophates, Silver, Gallium, Scandium.

1. Introduction

The development of phosphate chemistry in 21st century and the tendency of increasing applications of condensed phosphates are due to the researches and progress in this domain and to the unusual optical, magnetic, electrical and/or chemical properties of mentioned condensed compounds which are flexible and adaptable to the demands and requirements now being placed on materials [1-5]. The production of the novel compounds: olygophosphates, polyphosphates, phosphates and double-condensation cyclophosphates with various formulas, such as double tetra-, octa- and dodecaphosphates, as well as compounds with mixed anions, in particular phosphato-borates, phosphato-silicates, etc., and also phosphates, in which the part of the oxygen atoms are replaced by nitrogen, fluorine or sulfur atoms, have extended areas of phosphates' applications. The phosphate's binding agents, phosphato-binders and laser materials are supplanted/replaced by biomaterials, on the base of polyphosphates and hydroxyl apatite [1, 2]. In order to look for new materials as well as to study the influence of trivalent and monovalent cations for the formation of anionic radical and the level of condensation, the authors have studied multi-component systems containing monovalent and trivalent metals. Earlier we have done systematic study of systems $M_2^IO - M_2^{III}O_3 - P_2O_5 - H_2O$ at 130-550 °C, in which M^I are alkali metals, M^{III} – Ga, In and Sc; Molar ratio $P_2O_5 : M_2^IO : M_2^{III}O_3$=15:2, 5:1; 15:5:1; 15:7, 5:1; 15:10:1. During our fundamental researches numerous (about 70) unknown condensed phosphates have been obtained

Corresponding author: Marina Avaliani, senior researcher, research field: inorganic Chemistry and electrochemistry.

[7-10].

2. Materials

The offered data are the outcomes of synthesis by crystallization from melts of polyphosphoric acids during investigation of multi-component systems containing in addition to alkali metals another monovalent metal—Silver (Ag) and such as Ga, In, Sc at 130-335 °C. The molar ratio $P_2O_5 : M_2^I O : M_2^{III} O_3$ are also slightly changed and are: 15:3.5:1.5; 15:5:1.5 ; 15:6:1.5; 15:7.5:1.5; 15:8.5:1.5; 15:12:1.5.

Obtained condensed phosphates indeed inorganic oligomers and polymers—were detailed examined by chemical, and thermogravimetric analysis, some compounds were examined by paper chromatography and the structures are determined by X-ray structural techniques and phases are identified by X-Ray phases analysis.

3. Results and Discussions

The most stable phase at relatively low temperatures from 130°-155°, and even to the 165 °C are double acid diphosphates: $AgSc(H_2P_2O_7)_2$; $Ag_2ScH_3(H_2P_2O_7)_2$ and acitriphosphate $AgScHP_3O_{10}$. For the first time the capacity of the synthesis of these compounds was mentioned by us in works [11, 12]. It is necessary to underline that the reproducibility of synthesised acidic diphosphate $Ag_2ScH_3(H_2P_2O_7)_2$ is not entirely satisfactory, as well as interfered with the impurity (due to crystallization of additional and/or metastable phases). The authors performed an analysis and comparison of analytical preparative data with literary publications available to date [1-5, 13-17]. We did not find some mentions on these acid di- or triphosphates of scandium-silver, although analytical chemistry is systematically described in the superb monograph [14].

Double acidic-diphosphates are received by heating of mixtures at molar ratio $M_2^I O : M_2^{III} O_3 = 7{,}5 : 1{,}5;\ 10 : 1{,}5$ (in the case of systems with Sc and Ag), and 7.5:1&10:1 (in the case of process of synthesis in systems with Ga and Sc). The heating conditions in molten mixtures of poly-phosphoric acid melts are: the temperature range from the 130° to 165-170 °C during approximately three-five days. This phase is less or more metastable. If the heating will be pursued for more than 10-12 days and longer, it gradually becomes more stable double acidic diphosphate with formula $AgSc(H_2P_2O_7)_2$ at molar ratio $M_2^I O : M_2^{III} O_3 = 10 : 1.5$ and double hydro-triphosphate $AgScHP_3O_{10}$ at ratio $M_2^I O : M_2^{III} O_3 = 15 : 5$. The full finalization the phase transition demands 25-30 days. Obtained condensed compounds are insoluble in water, but they are able to dissolve in the acids. Similarly to the previously published works and the recent experiences referred in our articles [8-12], double hydro-triphosphate $AgScHP_3O_{10}$ is a few soluble (more or less) in poly-phosphoric acids. For removing obtained crystals from melts the synthesised mixture was cooled down and after in small doses was ported inside the glass vessel (vol.≈1 L), quickly mixed with 500-700 mL distilled water.

Phase formation in system $M_2^I O - M_2^{III} O_3 - P_2O_5 - H_2O$ and the microstructure of synthesized double condensed acidic triphosphate $AgScHP_3O_{10}$ are investigated by X-Ray diffraction analyses (data summarized in three-line Table). The powder diffraction data for cited compounds, intensity data collections are obtained on diffractometer DRON-3M, anodic Cu-Kα radiation, the range 2θ=10°-60°, detector's speed 2°/min., lattice spacing d_α/n in Angströms (Å), and I/I_0—is relative intensity (used model/standard data—by American Society for Testing and Materials—ASTM). Detailed comparison with our previously obtained XRD data for similar compounds of Gallium, Indium and Scandium are also carried out/performed. On the assumption of the fact that combinations of cations (Ag-Sc) for di- and triphosphates have not been

studied and hence are not given in the file index (typical XRD data), roentgenograms were compared to our standard data models, to similar compounds of Ag-P and our standard data prototypes for similar double condensed phosphates of Gallium, Indium, Scandium with alkali metals. We perform, that any initial components: $K_2CO_3, Sc_2O_3, AgNO_3$ are already completely and irreversibly inter-reacted during synthesis process.

Based on the founded and published literary data [1-6, 13-17] also on our synthesis conditions, on experiences in this field since 1980 years [7-12], and to our standard data models, the structural composition of the compounds is set up. Phase's identification was given an accordance with standard data of

Table 1 XRD data for acid diphosphate $AgSc(H_2P_2O_7)_2$, acid triphosphate $AgScHP_3O_{10}$, tetraphosphates $AgGaP_4O_{12}$ and $AgScP_4O_{12}$

$AgScHP_3O_{10}$		ASTM-11-642, $Ag_5P_30_{10}$		$AgSc(H_2P_2O_7)_2 \cdot (1-2)H_2O$		$NaSc(H_2P_2O_7)_2 \cdot 2H_2O$ [10]		$AgScP_4O_{12}$		$AgGaP_4O_{12}$		$NaGaP_4O_{12}$ [7, 12]	
d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0	d_α/n	I/I_0
		4.81		-		-	-						
-	-	-	20	4.04	25	-	-						
4.04	24	-	-	-	-	4,17	41	4.69	5	4.67		4.71	8
-	-	-	-	-	-	4,00	37	-	-	4.43		4.43	25
-	-	-	-	-	-	-	-	3.94	5	4.20		4.27	30
-	-	3.69	-	-	-	3,67	10	3.83	100	3.94	7	3.94	49
-	-	3.60	5	-	-	3,59	4	3.63	10	3.83	15	3.80	15
-	-	-	5	3.43	33	3,49	25	3.56	10	-	19	3.65	8
-	-	3.37	-	-	-	3,35	29	-	-	-	27	3.53	5
3.36	72	3.29	10	3.32	24	-	-	3.37	31	3.38	80	-	-
-	-	3.21	10		-	3,24	96	-	-	-	-	3.35	16
3.20	29	3.15	15	3.08	33	3,18	8	-	-	-	-	3.29	5
-	-	3.04	25	3.02	30	-	-	-	-	3.08	-	3.14	5
3.03	9	2.96	15	2.98	100	2,98	100	3.03	80	3.03	38	3.08	10
-	-	-	50	-	-	2,96	19	-	-		-	3.03	100
	-	2.86	-	2.82	55	2,82	52	-	-	-	-	-	-
2.84	100	2.76	95	-	-	-	-	2.83	19	2.82	23	-	-
-	-	2.72	50	2.74	28	2,74	7	2.77	20	2.75	100	2.85	20
-	-	-	50	-	-	2,70	14	-	-		18	2.76	10
-	-	2.60	-	2.64	23	2,62	5	2.68	25	2.69	40	-	-
2.64	77	-	100	-	-	2,58	4	-	-		15	-	-
2.59	69	2.52	-	2.54	32	2,55	7	2.56	15	2.56	13	2.63	10
2.52	14	2.46	30	-	-	2,47	4	2.49	16	-	-	2.56	3
2.43	7	2.38	15	-	-	2,39	7	2.41	26	2.40	19	2.48	7
2.37	8	2.33	10	-	-	2,33	6	-	-	-	-	2.40	3
-	-	-	5	2.31	32	2,30	4	2.33	6		15	-	-
-	-	-	-	2.25	18	-	-	-	-		-	2.32	29
-	-	-	-	2.22	18	2,17	12	2.25	16	2.25	11	-	-
2.21	20	2.15	-	-	-	-	-	2.20	12	-	2.0	2.20	16
2.13	31	2.10	5	-	-	2,10	18	-	-	2.15	6	-	-
-	-	-	5	2.03	9	2,07	6	-	-	-	5	2.14	5
-	-	2.00	-	-	-	2,04	7	2.07	2	2.06	-	2.13	3
2.03	20	1.96	10	-	-	2,02	18	-	-	2.03	8	-	-
-	-	1.94	15	-	-	1,95	11	2.00	5	-	-	2.05	3
1.93	11	1.89	5	-	-	-	-	1.92	7		8	-	-
1.89	10	1.88	15	-	-	-	-	-	-	1.89		-	-
-	-	-	10	1.83	21	-	-	1.87	6	-		-	-
1.76	6	-	-	1.75	11	-	-	1.86	6			1.87	3
1.67	18	-	-	1.68	22	-	-	1.69	6	1.68		1.85	6
1.64	18	-	-	1.66	28	-	-					-	-
1.62	18	1.59	-	1.64	33	-	-						
			10	1.57	19		-						

International Center for Diffraction Data base of American Society for Testing and Materials—ASTM. The composition of the synthesised compounds are: double acidic diphosphate $AgSc(H_2P_2O_7)_2 \cdot H_2O$ (It's crystalhydrate), double acidic triphosphate $AgScHP_3O_{10}$, cyclotetraphosphate of Gallium-Silver $AgGaP_4O_{12}$ (with a certain small fraction of the impurity, minor percentage of triphosphate) and cyclotetraphosphate of Scandium-Silver $AgScP_4O_{12}$. Cyclotetraphosphates of Scandium-Silver and Gallium-Silver are isomorphs among themselves and are isostructurals with the sodium-gallium double condensed tetraphosphate. This fact is not very surprising since the ionic radius of sodium and silver are almost similar in magnitude: 0.98 Å(Na) and 1.13 Å(Ag).

4. Conclusions

During investigation of poly-component systems containing mono- and trivalent metals and with a large excess of phosphoric acid dependency of composition VS temperature & molar ratio, reliance of structure from duration of synthesis and radius of the ions are revealed.

It has been discovered that at relatively low temperatures it is more probable to produce double acidic phosphates, with increasing synthesis temperature double tetraphosphates of Gallium-Silver and Scandium-Silver are formed. Mentioned tetraphosphates are isomorphic among themselves and are iso-structural with the Sodium-Gallium double condensed tetraphosphates.

Via comparison of the obtained condensed compounds with appropriate phosphates, synthesized by us earlier (in the systems containing Ga, In and Sc, [7-12, 18] it is possible to conclude that while the radius of trivalent metal decreases, the polyphosphate chain identity period upsurges. This phenomenon is due to complication of its form-factors.

The cycles slowly appear, the number of structural types growths caused by correlation of average distances between $(M^{III} - O)$ and $(M^{I} - O)$. It should be emphasized: the less of the correlation/ratio, the greater is the possibility of big cycle formation, for example—obtaining of cycloocta- or cyclododecaphosphates. Optimal fulfilment for the realization of the big cyclic anions is parity of big cations of monovalent metal versus trivalent metals with small ion radius.

Finally, the authors would like to express our gratitude to our colleague Mister Giorgi Mamatsashvili for assistance in the work.

References

[1] Tananaev, I. V., Grunze, X., and Chudinova, N. N. 1984. "Prior Directions and Results in the Domain of Condensed Phosphates' Chemistry." *J. Neorgan. Materialy* 20 (6): 887-900.

[2] Tananaev, I. V. 1980. "New Dataon the Phosphates of Polywalent Metals." Pure & Appl. Chem., Pergamon Press Ltd. 52: 1099-115.

[3] Durif, A. 2005. "The Development of Cyclophosphate Crystal Chemistry." *Solid State Sci.* 7: 760-6.

[4] Durif, A. 2013. *Crystal Chemistry of Condensed Phosphates*. 2nd edition. Plenum Press,

[5] Averbouch-Pouchot, M. Th., and Durif, A. 1996. "Topics in Phosphate Chemistry." *World Scientific*, 174-209.

[6] Marsh, T. P. 2011. "Studies into the Ion Exchange and Intercalation Properties of $AlH_2P_3O10 \cdot 2H_2O$." PhD Thesis, University of Birmingham.

[7] Avaliani, M. A. 1982. PhD Thesis, N. Kurnak of Institute of General and Inorganic Chemistry, Moscow.

[8] Avaliani, M. A., Tananaev, I. V., and Gvelesiani, M. K. 2011. "Synthesis and Investigation of Double Condensed Phosphates of Scandium and Alkali Metals."Abstracts for Synthesis Chemists, FIZ CHEMIE Berlin. J. Phosphorus, Sulfur Silicon Relat. Elem. ISSN 1042-6507, ©2003-2011

[9] Avaliani, M., and Gvelesiani, M. 2006. "Areas of Crystallization of Condensed Scandium and Caesium Phosphates and Regularities of Their Formation." *Proceeding of the Georgian Academy of Sciences* 32 (1-2): 52-8.

[10] Avaliani, M. 1990. "Double Condensed Phosphates of Sodium-Scandium." *J. Inorgan. Materials* 26 (12): 2647-8.

[11] Avaliani, M. Gvelesiani, M., Barnovi, N., Purtseladze, B., and Dzanashvili, D. 2016. "New Investigations of Polycomponent Systems." *Proceeding of the Georgian*

Acad. of Sciences, Chem. Ser. 42 (4): 308-11.

[12] Avaliani, M. 2016. "Main Types of Condensed Phosphates Obtained in Open Systems from Solution-Melts of Phosphoric Acids." Abstracts, Published by TECHN. UNIVERS. Tbilisi, Georgia 4th Int. Conf. NANO-2016.

[13] Murashova, E. V., and Chudinova, N. N. 2001. "Double Condensed Phosphates of Caesium-Indium." *J. Neorgan. Materialy* 37 (12): 1521-4.

[14] Komissarova, L. N. 2011. *Inorganic and Analytical Chemistry of Sc*. Editorial URSS, 512.

[15] Vassel, N. P., Vassel, S. S., Pavlova, I. V., and Kaklyugin, A. V. 2011. "Thermal Study of Systems Involving the Metaphosphates of Trivalent Metals and Silver." *Proceedings of Institutions of Higher Education, Physics.*

[16] Strutinska, N., Zatovsky, I., Ogorodnik, I., and Slobodiannik, N. 2013. "Rietveld Refinement of $AgCa_{10}(PO_4)_7$ from X-ray Powder Data." *ActaCrystallogr Sect E Struct Rep Online* 69 (Pt 5): i23.

[17] Suthanthiraraj, S. A., and Sarumathi, R. 2013. "A New Silver Ion Conducting SbI_3-$Ag_4P_2O_7$ Nanocomposite Solid Electrolyte." *Appl Nanosci* 3: 501. doi:10.1007/s13204-012-0155-z.

[18] Grunze, I., Palkina, K. K., Chudinova, N., and Avaliani, M. 2009. "Energy Citations Database." *Inorg. Mater. (Engl. Transl.)* 23 (4): 539-44; OSTI ID: 5847982.