

A.I. Martiryan, Yerevan State University, Ph.D. in Chemistry,
Assistant Professor, the Faculty of Chemistry Sciences,

L.A. Nersesyan, A.B. Nalbandyan Institute of Chemical Physics NAS
of the Republic of Armenia, Ph.D. in Chemistry, Head of Innovation Group,

L.A. Tavadyan, A.B. Nalbandyan Institute of Chemical Physics NAS of the Republic
of Armenia, Professor, Doctor of Chemical Sciences, Academician of the National
Academy of Sciences of Republic of Armenia, Director of the Institute

Peroxosolvates of Magnesium and Zinc Silicates. Obtaining, structure and stability studies

Abstract: This article is devoted to methods of obtaining peroxosolvates of magnesium and zinc silicates are developed under laboratory conditions. It is established that the content of hydrogen peroxide in the peroxosolvates of magnesium and zinc silicates accounts for 14.5 wt.% and 30 wt.%, respectively. It is established that crystalline state is characteristic for the peroxosolvate of magnesium silicate, while peroxosolvate of the zinc silicate is amorphous.

Keywords: peroxosolvate, magnesium, zinc, silicate, hydrogen peroxide.

Peroxosolvates of the salts of organic and inorganic acids, some organic compounds of basic nature, as well as peroxides of the alkaline-earth metals have special importance in the chemistry of hydrogen peroxide [1-4]. Chemical reactions yielding peroxosolvates make up the only field in the chemistry of hydrogen peroxide, where the molecules of hydrogen peroxide remain stable and transform from the inherent liquid form into the solid, despite their capability to decompose rapidly in the presence of small amounts of different catalysts.

A distinctive feature of hydrogen peroxide implies that coordination with salts takes place unlike the normally expected case with the participation of two oxygen atoms containing in its molecule, by means of which hydrogen peroxide could enter into the coordination sphere of a cation, similar to water. Solvation of salts by hydrogen peroxide occurs through another mechanism: the formation of hydrogen bonds between H_2O_2 and salt anions [1-6].

Currently water-soluble peroxosolvates of salts of inorganic acids have been much studied [1,4]. Certain of those found practical application. For example, peroxosolvate of sodium carbonate is widely using in detergents as bleaching agent under the name "persalt". Peroxosolvate of carbamide under the name "hydroperit" finds use in the medicine and home as an antiseptic and the source of hydrogen peroxide. In recent years a method for production of the peroxosolvate of potassium fluoride and a disinfectant on its basis was developed [2,3].

In the literature, unlike the water-soluble peroxosolvates of alkaline metals researches are unavailable devoted to obtaining peroxosolvates of alkali-earth metals' salts and water-insoluble peroxosolvates and examinations of their structures. It is well known [1,2] that peroxide compounds of alkali-earth metals (for example, peroxides of calcium and magnesium) exhibit better thermal stability, and are less prone to the effect of moisture and atmospheric carbon dioxide as compared to those of alkaline metals. This fact made it possible to use these compounds in the metallurgy, pyrotechnics, chemistry of polymers, medicine and food industry, as well as for the treatment of sewage water [1]. Peroxosolvates of calcium and magnesium peroxides act as rich sources of active oxygen [2], however a very few studies were devoted to obtaining and studying their properties, and application fields are not yet established.

Water-insoluble peroxosolvates show interesting properties [8,9]. If at the solution of various water-soluble peroxosolvates whole hydrogen peroxide immediately passes into the liquid state, then in the case of water-insoluble peroxosolvates this transfer takes place gradually with the measurable rates typical for different peroxosolvates [8,9]. At the same time, these rates can be determined quantitatively, which is of practical importance from the viewpoint of hydrogen peroxide time dosage in the solution. So, quantitative measuring and controlling the rate of hydrogen peroxide transfer from the solid peroxosolvate into the solution is an urgent issue.

The basic objective of this research is to study the possibility of obtaining peroxosolvates of water-insoluble compounds: magnesium and zinc silicates (MgSiO_3 , ZnSiO_3); to determine the quantity of solvated hydrogen peroxide; to study structural features of peroxosolvates; to evaluate the stability, as well as the rates of molecular oxygen liberation from the suspensions of peroxosolvates.

Experimental

Several synthetic methods were tested under laboratory conditions to obtain peroxosolvates of magnesium and zinc silicates. From the viewpoint of maximum yield of the target product the most optimal method is as follows. 30% solution of hydrogen peroxide is poured into a flat-bottom flask equipped with a stirrer and the flask is cooled up to 0°C. Then an insoluble salt is added into the flask at stirring (with the amount of 14 times less than that of hydrogen peroxide in the solution), kept for 40 min and poured into a flat-bottom flask, cooled up to -5°C and kept for 2 hrs at this temperature. The precipitate is filtered and dried by air flow in a drying oven at 50°C. The yield of final products is 88-90% for magnesium silicate and 92-95% for zinc silicate.

The content of hydrogen peroxide in the products obtained was determined by the permanganometry. For this purpose the products were mixed with distilled water and the content of hydrogen peroxide in the suspension was determined by titration of the liquid phase. During this procedure gradual transition of hydrogen peroxide into the solution was observed. Such behavior was detected by the following feature. After titration of the first portion of hydrogen peroxide in the solution no decoloration was registered. However, after the certain period (5-10 min) decoloration takes place, which testifies to continuous transfer of peroxosolvates' hydrogen peroxide into the solution. Decoloration after titration of the first portion of the solution during 15-30 minutes is a conditional indicator of the second stage of hydrogen peroxide transfer into the solution. If decoloration does not occur during 30 min and more the titration is considered to be completed, thus total amount of hydrogen peroxide from the peroxosolvates of magnesium and zinc passed into the solution is determined.

Hydrogen peroxide transfer from the peroxosolvate of magnesium silicate into solution was observed to be taking place through three stages. 0.12 mol hydrogen peroxide passes into the solution during the first stage, and 0.17 mol and 0.21 mol for the second and third stages, respectively. Thus, total amount of hydrogen peroxide of 0.5 mol per one mol of magnesium silicate was determined, that is the content of hydrogen peroxide in the peroxosolvate of magnesium silicate accounts for 14.5 wt.%.

In the case of peroxosolvate of zinc silicate two stages of hydrogen peroxide transfer into the solution were registered. 0.5 mol and 1.5 mol of hydrogen peroxide

is transferred into the solution at the first and second steps, respectively. Thus, total amount of hydrogen peroxide in the peroxosolvate of zinc silicate is 30.0 wt.%.

Stability of the peroxosolvates under consideration was determined on the basis of titration results, presented in the Tables 1 and 2.

Table 1. Stability of the peroxosolvate of magnesium silicate at 22±2°C

<i>T, days</i>	<i>Hydrogen peroxide content in the solvate, wt. %</i>	<i>Degree of hydrogen peroxide decomposition, η, %</i>
0	14,50	0,00
2	14,50	0,00
3	14,45	0,20
4	14,43	0,20
7	14,35	0,50
14	14,32	0,50
22	14,30	0,80
28	14,23	0,80
35	14,11	0,70
45	14,02	0,80
50	13,93	1,70

Table 2. Stability of the peroxosolvate of zinc silicate at 22±2°C

<i>T, days</i>	<i>Hydrogen peroxide content in the solvate, wt. %</i>	<i>Degree of hydrogen peroxide decomposition, η, %</i>
0	30,00	0
2	30,00	0
3	29,87	0,20
4	29,86	0,50
7	29,85	0,50
14	29,81	0,50
22	29,78	0,50
28	29,72	0,80
35	29,60	1,00
45	29,01	1,40
50	28,83	1,60

The volume of liberated oxygen was measured by the gasometry [7] and based on the obtained data the rate of active oxygen release at decomposition of hydrogen peroxide in the suspensions (particle size in the suspension is less than 10^{-5} mm) of peroxosolvates of magnesium and zinc silicates was calculated. Average rates of

oxygen release from the suspensions of magnesium and zinc silicates' peroxosolvates were measured to be $6.9 \cdot 10^{-7} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$ and $6.8 \cdot 10^{-7} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$, respectively. That is oxygen liberation from both the suspensions takes place practically with the same rate.

To study structural features of the peroxosolvates considered diffraction patterns of these compounds were obtained (Fig. 1) using a DRON-3 diffractometer.

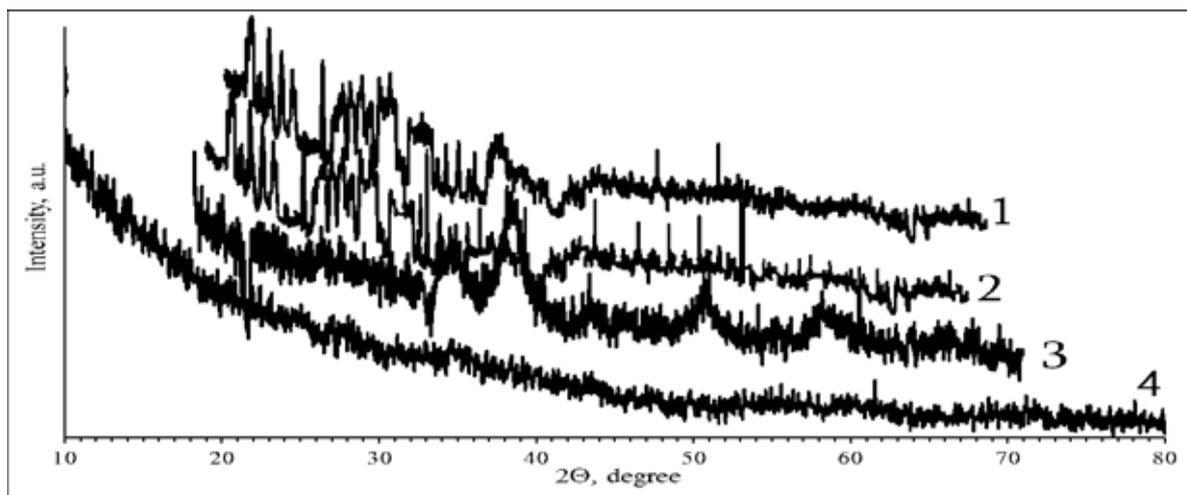


Fig. 1. Diffraction patterns of the magnesium silicate - 1; peroxosolvate of magnesium silicate - 2, zinc silicate - 3 and the peroxosolvate of zinc silicate - 4

IR spectra of magnesium silicate and its peroxosolvate were obtained using the Nicolet/FTIR NEXUS spectrometer (Fig. 2).

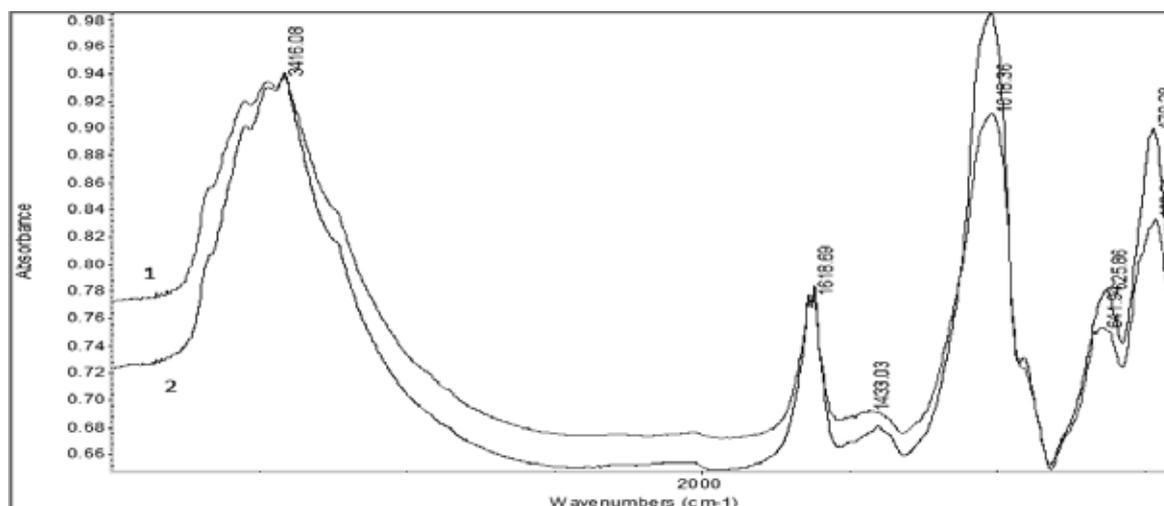


Fig. 2. FTIR spectra of magnesium silicate (1) and its peroxosolvate (2)

It is obvious from X-ray patterns that the compound obtained by interaction of magnesium silicate with hydrogen peroxide and then dried, is characterized by crystalline state. In the case of the peroxosolvate of zinc silicate the obtained product is amorphous. Similar results were presented recently at examination of a compound obtained by interaction between the zinc carbonate and hydrogen peroxide [8].

The diffractograms (Fig. 1) indicate also that main characteristics of the obtained compounds fit to those of both the initial metal silicates, as well as zinc and magnesium peroxides [9].

Analysis of IR spectra (Fig. 2) indicates that changes in the frequency of valence vibrations of the Si-O ($400\text{-}650\text{ cm}^{-1}$) and Si-OH ($3300\text{-}3400\text{ cm}^{-1}$) groups in the compound obtained at interaction between magnesium silicate and hydrogen peroxide contains hydrogen peroxide in the bound state, thus testifying about the peroxosolvate formation.

Combination of IR and X-ray analyses data indicates that reactions of magnesium and zinc silicates with hydrogen peroxide yield two substances: peroxide of the corresponding metal and peroxosolvate of the metal silicate.

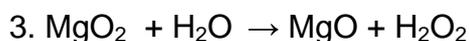
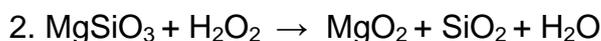
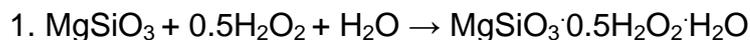
Discussion and Conclusion

The obtained experimental results have shown that interaction between hydrogen peroxide and magnesium and zinc silicates yields water-insoluble complex compounds: peroxosolvates. Stability of dry magnesium and zinc peroxosolvates and the rate of oxygen liberation from suspensions differ insignificantly. Peroxosolvates differ by the content of hydrogen peroxide: amorphous zinc peroxosolvate contains hydrogen peroxide in amount of 30,0 wt.% and the magnesium peroxosolvate – 14.5 wt.%. At the same time, as the data of X-ray and FTIR analyses have shown, peroxides of metals and water enter into the composition of these peroxosolvates.

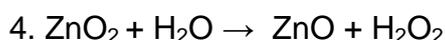
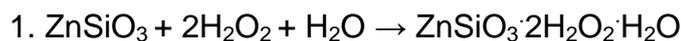
Formation of molecular complexes with participation of hydrogen peroxide may be conceived as follows. Oxygen atoms in the molecules of magnesium and zinc silicates, hydrogen peroxide and water can form weak donor-acceptor bonds via unshared paired valence p-electrons, while magnesium and zinc atoms act as acceptors of these paired electrons. Peroxosolvates represent the most probable models of complexes in which such complex compounds are formed due to above-mentioned donor-acceptor bonds between the molecules of zinc or magnesium silicates and those of hydrogen peroxide and water.

Presumable mechanisms of the formation of peroxosolvates taking into account their composition may be presented as follows:

a) in the case of magnesium silicate



б) in the case of zinc silicate



A question was raised as to how many molecules inter into the composition of these peroxosolvates. It was found that this depends on reaction conditions, in particular, on temperature, the concentration ratio of silicates and hydrogen peroxide in the solution.

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