

SYNTHESIS AND STUDY OF PEROXOSOLVATES OF SULFATES  
OF ELEMENTS OF THE SECOND GROUP

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Continuing previous similar research, the ability of sulfates of elements of the second group – magnesium, calcium and zinc, to produce peroxosolvates, the methods for their preparation, as well as their properties have been studied. It has been shown that these sulfates are able to produce peroxosolvates with different molar ratios:  $\text{MgSO}_4 \cdot \text{H}_2\text{O}_2$ ,  $\text{CaSO}_4 \cdot 0.04\text{H}_2\text{O}_2$ ,  $\text{ZnSO}_4 \cdot 0.05\text{H}_2\text{O}_2$ . The authenticity, composition and nature of the obtained peroxosolvates have been elucidated by the methods of X-ray and IR spectroscopy. Quantitative data on the decomposition of hydrogen peroxide in dry peroxosolvates of magnesium and zinc sulfates were calculated.

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**Keywords:** peroxosolvate, hydrogen peroxide, magnesium, zinc and calcium sulfates.

**Introduction.** The great interest in hydrogen peroxide in recent years is due to the fact that as a result of easily decomposition of hydrogen peroxide in solutions and in contact with solids water end oxygen are produced, which is very important from an ecological point of view.

It is known from the literature that hydrogen peroxide can participate in chemical transformations in whole molecular form, forming coordination compounds – peroxosolvates. It was shown that hydrogen peroxide can combine with many inorganic and some organic acids salts, a number of basic organic compounds, and alkaline-earth metals peroxides without decomposition.

Note that another mechanism of the solvation of salts with  $\text{H}_2\text{O}_2$  is also possible: by the formation of hydrogen bonds between salt ions and  $\text{H}_2\text{O}_2$ . In these compounds, the coordination of  $\text{H}_2\text{O}_2$  as a ligand does not proceed in the same way as in the case of water, based on the electron pair of oxygen atom.  $\text{H}_2\text{O}_2$  does not coordinate with the salts cation, but through its positively charged hydrogen atoms forms hydrogen bonds with the anion due to its unshared pair of electrons. This bond is quite strong with an energy of 60–80 *kJ/mol* [1].

Under normal conditions, peroxosolvates are crystalline substances and can be used as sources of anhydrous hydrogen peroxide, as they are readily soluble in water, forming the initial salt and peroxide. This is the reason for the large use of

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peroxosolvats in various fields, in particular in medicine, in the production of bread, various creams and toothpastes. Peroxosolvates have bactericidal, bleaching properties, and less corrosive activity than other substances. Peroxosolvats have important ecological significance, as they can be very effectively used for water purification and neutralization.

It was revealed that the elements of the second group of the periodic table, with the exception of Be, form peroxide compounds [2], whereby the peroxides of Ca, Sr, Ba, and Hg belong to the  $\text{Me}^{2+}\text{O}_2^{2-}$  type, and the peroxides of Mg, Zn and Cd with a gross composition of  $\text{MeO}_2 \cdot x\text{H}_2\text{O}$  belong to the HO–Me–OOH type. Due to the variety of applied fields, peroxosolvates of sulfates of some elements of the second group have recently gained great interest, the studies of which tend to create new, more effective, and ecologically safe compounds.

It has been established, that alkaline-earth metal peroxides have greater thermal stability and are less affected by humidity and carbon dioxide of atmosphere than alkali metal peroxides. This allows their use in areas, where alkali metal peroxides are not permissible such as metallurgy, pyrotechnics, polymer chemistry, medicine and food industry, as well as sewage treatment [3]. Peroxide compounds of some metals are widely used for medicinal purposes, for the treatment of malignant tumors, for the treatment of poisoning, etc. [4].

In industry, peroxide compounds are used as catalysts, fillers and pigments. Peroxosolvates purify water from heavy metals, phosphates, sulfates and bacteria. Calcium and magnesium peroxide compounds are used as feed additives for farm animals and birds.

A number of studies have been carried out to synthesize peroxosolvate compounds of water-soluble salts. As a result, many of these compounds are manufactured on an industrial scale [3, 4]. Research into the production of water-insoluble peroxosolvats is still ongoing, as data on the latter are scarce.

It was shown that  $\text{H}_2\text{O}_2$  is completely transferred into liquid phase state during the dissolution of water-soluble peroxosolvats. In the case of water-insoluble peroxosolvats, the transition of  $\text{H}_2\text{O}_2$  from the solid phase to the liquid phase takes place gradually, and in the case of different peroxosolvats with different rates, which are quantitatively determined. The rate of the yield of  $\text{H}_2\text{O}_2$  from coordinated compounds is quantified by controlling the amount of  $\text{H}_2\text{O}_2$  in the solution [5].

In our work we studied the ability of magnesium, zinc and calcium sulfates to form peroxosolvates, the methods of their synthesis, as well as the properties of the obtained peroxosolvates. It should be noted that the samples we have selected are relatively cheap, environmentally friendly and safe from a medical point of view.

The synthesis of solid peroxosolvats was carried out by the interaction of concentrated aqueous solutions of salts with anhydrous  $\text{H}_2\text{O}_2$  as a reliable method. Such reactions take place in the absence of other diluents, which affect the coordination bond formed between the ions and  $\text{H}_2\text{O}_2$ . In addition, the reaction of salts with anhydrous hydrogen peroxide allows to determine the properties of peroxosolvates with a higher content of  $\text{H}_2\text{O}_2$  at a given temperature.

We also studied the liquid-phase reactions of calcium, zinc, magnesium sulfate, and hydrogen peroxide to find out their ability to form peroxosolvates, to

determine the amount of solvated hydrogen peroxide, and the rate of its release from peroxosolvate.

**Experimental Part.** Peroxosolvates of magnesium, zinc and calcium sulfates ( $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CaSO}_4$ ) were obtained by slowly adding salt to 50%  $\text{H}_2\text{O}_2$  at  $0^\circ\text{C}$  under constant stirring. After placing the solution in a refrigerator for 30 min, it was filtered, then the filtrate was dried in a stream of hot air.

The presence of  $\text{H}_2\text{O}_2$  in the end product obtained was confirmed by permanganate analysis. For this purpose, certain amount of formed peroxosolvate was dissolved in distilled water and titrated with a 0.1 N  $\text{KMnO}_4$  solution. The molar composition of  $\text{H}_2\text{O}_2$  in peroxosolvate was determined by the reacted amount of  $\text{KMnO}_4$ . The titration results are shown in the Fig. 1.

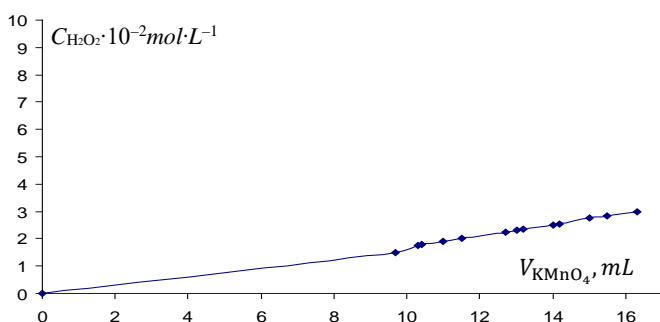


Fig. 1. Dependence of the concentration of  $\text{H}_2\text{O}_2$  titrated from  $\text{MgSO}_4 \cdot \text{H}_2\text{O}_2$  versus  $V_{\text{KMnO}_4}$ . The total amount of hydrogen peroxide is 1 mol per 1 mol of  $\text{MgSO}_4$ . The percentage of hydrogen peroxide is 21% for the final 100 g product.

**Result and Discussion.** The purpose of the titration is to provide  $\text{H}_2\text{O}_2$  output from different phases of peroxosolvates, and the determination of  $\text{H}_2\text{O}_2$  output without titration was made only from the first phase. Taking into account that many dry peroxosolvates readily excrete  $\text{H}_2\text{O}_2$  from their molecule in water [6], it can be assumed that a similar process occurs in our case, as in the first step  $\text{H}_2\text{O}_2$  is released as a result of the decomposition of peroxosolvate. Studies have shown that there are different phases of  $\text{H}_2\text{O}_2$  release from peroxosolvate, which in turn indicates the presence of different states of  $\text{H}_2\text{O}_2$  in the end products.

The fact that a new compound and not a mixture was obtained was demonstrated by X-ray diffraction analysis of the resulting compound by comparing the spectra with the standard X-ray spectra of  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$  and  $\text{CaSO}_4$ . Fig. 2 shows the resulting spectra.

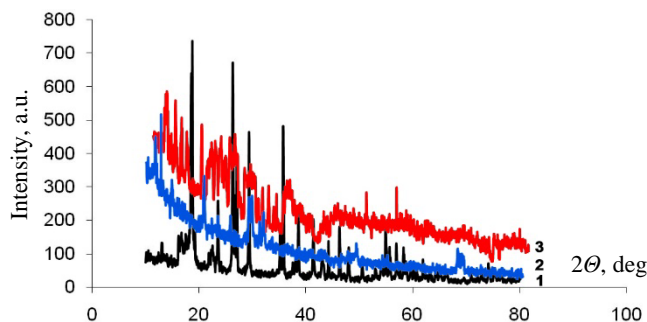


Fig.2. Diffractograms of compounds formed in the interaction of  $\text{ZnSO}_4$  (1),  $\text{CaSO}_4$  (2),  $\text{MgSO}_4$  (3) and  $\text{H}_2\text{O}_2$ .

The samples were also examined by IR-spectroscopy using a Nicolet/FTIR NEXUS spectrometer. Figs. 3 and 4 show the infrared spectra of compounds derived from  $\text{MgSO}_4$  and  $\text{ZnSO}_4$  in the dry state, which confirm the presence of  $\text{H}_2\text{O}_2$ .

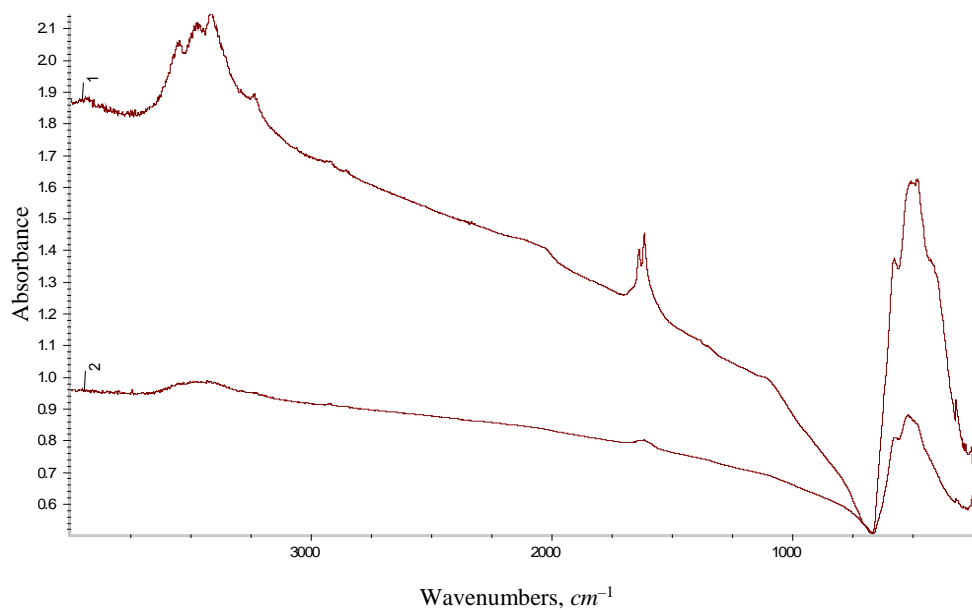


Fig. 3. FTIR spectra of magnesium sulfate (1) and its peroxosolvate (2).

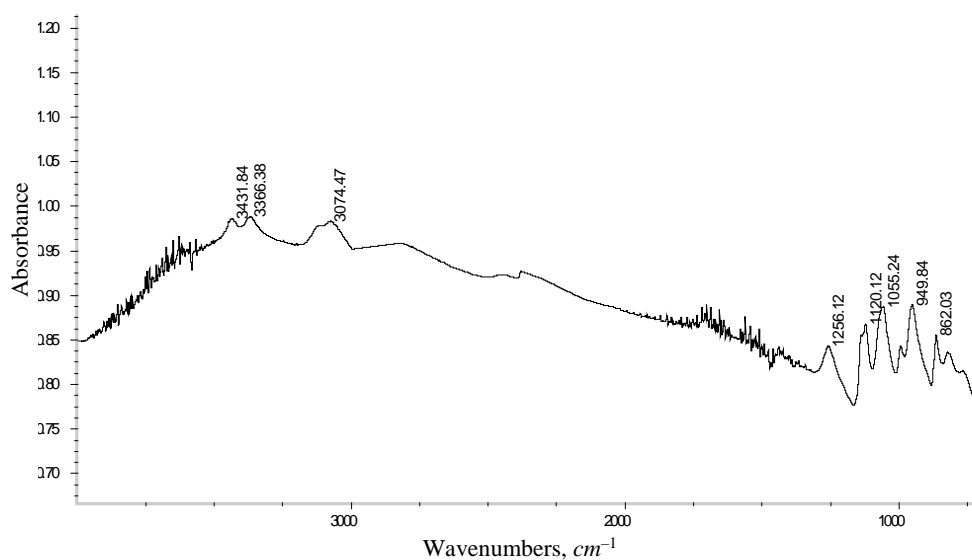


Fig. 4. FTIR spectrum of zinc sulfate peroxosolvate.

Quantitative evaluation of the stability of the obtained peroxosolvates was performed, according to the degree of decomposition of hydrogen peroxide [7]. The concentration of hydrogen peroxide in the solution was determined by permanganate

titration method [8, 9], based on which the rate of active oxygen generation due to the decomposition of hydrogen peroxide was determined. The experiments were performed at room temperature ( $22 \pm 2^\circ\text{C}$ ).

The Table below shows the results of a study of the decomposition of hydrogen peroxide in dry peroxosolvates of magnesium, calcium and zinc sulfates.

*Stability of  $\text{MgSO}_4$ ,  $\text{CaSO}_4$  and  $\text{ZnSO}_4$  peroxosolvates at  $22 \pm 2^\circ\text{C}$  over time*

$\tau$ , days	$\text{H}_2\text{O}_2$ content, %		
	in solvate of $\text{MgSO}_4$	in solvate of $\text{CaSO}_4$	in solvate of $\text{ZnSO}_4$
0	30.0	4.0	5.0
10	28.4	3.74	4.5
20	28.0	3.28	4.1
30	27.7	3.1	3.9
40	27.2	2.3	3.7
50	26.6	1.9	3.5
60	26.1	1.6	3.3

**Conclusion.** Thus, studies have shown that in the systems described above, magnesium, calcium and zinc sulfates form the corresponding crystalline peroxosolvates, the composition and nature of which have been elucidated by X-ray spectroscopic analysis.

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ԵՐԿՐՈՐԴ ԽՄԲԻ ՏԱՐՐԵՐԻ ՍՈՒԼՖԱՏՆԵՐԻ  
ՊԵՐՕՔՍՈՍՈՒՎԱՏՆԵՐԻ ՍԻՆԹԵԶԸ ԵՎ ՈՒՍՈՒՄՆԱՍԻՐՈՒՄԸ

Շարունակելով նախորդ նմանատիպ հետազոտական աշխատանքները ուսումնասիրվել են երկրորդ խմբի տարրերի՝ մագնեզիումի, կալցիումի և ցինկի սուլֆատների պերօքսոսուլֆատներ առաջացնելու ունակությունները, նրանց ստացման եղանակները և հատկությունները: Ցույց է տրվել, որ այդ սուլֆատները ունակ են առաջացնել համապատասխան պերօքսոսուլֆատներ տարբեր մոլային հարաբերություններով՝  $MgSO_4 \cdot H_2O_2$ ,  $CaSO_4 \cdot 0,04H_2O_2$  և  $ZnSO_4 \cdot 0,05H_2O_2$ : Ստացված պերօքսոսուլֆատների խկությունը, բաղադրությունը և բնույթը պարզաբանվել են նշված միացությունների՝ ռենտգենաչափական և ԻԿ սպեկտրաչափական անալիզի եղանակներով: Հաշվարկվել են մագնեզիումի և ցինկի սուլֆատների չոր պերօքսոսուլֆատներում ջրածնի պերօքսիդի քայքայման քանակական տվյալները:

A. И. МАРТИРЯН, Л. Г. ТАДЕВОСЯН

СИНТЕЗ И ИССЛЕДОВАНИЕ ПЕРОКСОСОЛЬВАТОВ СУЛЬФАТОВ  
ЭЛЕМЕНТОВ ВТОРОЙ ГРУППЫ

В продолжение предыдущих аналогичных исследований изучены способность сульфатов элементов второй группы – магния, кальция и цинка, образовывать пероксольваты, а также способы их получения и свойства. Показано, что эти сульфаты способны образовывать следующие пероксольваты с разными молярными соотношениями:  $MgSO_4 \cdot H_2O_2$ ,  $CaSO_4 \cdot 0,04H_2O_2$ ,  $ZnSO_4 \cdot 0,05H_2O_2$ . Методами рентгено- и ИК-спектроскопии установлены подлинность, состав и природа полученных пероксольватов. Рассчитаны количественные данные по разложению пероксида водорода в сухих пероксольватах сульфатов магния и цинка.