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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Solubility and Stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in Aqueous Solutions and Change in Some Crystallographic Parameters of $(NH_4)_2SO_4$ Precipitates

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Abstract—Stability of $(NH_4)_2SO_4 \cdot H_2O_2$ aqueous solutions and some structural changes in ammonium sulfate in the course of its solvation and subsequent desolvation were studied.

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The ability of ammonium sulfate to be solvated by hydrogen peroxide was first mentioned in [1]. The composition of the peroxo solvate was found by studying the solubility of ammonium sulfate in anhydrous hydrogen peroxide and by determining the H_2O_2 content of the solid phase being crystallized [2]. In [3], the optimal conditions of synthesis, stabilization, and storage of ammonium sulfate monoperoxo solvate were reported, which provide that the sulfate retains hydrogen peroxide for more than 100 days. The fact that efficient stabilizers have been found among chemical compounds of various classes for other peroxo solvates [2] suggests that the stable state of $(NH_4)_2SO_4 \cdot H_2O_2$ can be substantially prolonged.

Ammonium sulfate peroxo solvate combines in itself an effective nitrogen fertilizer and a disinfectant in the form of coordinated hydrogen peroxide. Practical use of this compound in general disinfection science, plant growing, and, possibly, other fields requires data on its solubility and stability in aqueous solutions, because, apparently, a dry preparation is less suitable for these purposes.

This communication reports on study of the solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ aqueous solutions. In separate experiments, we examined precipitation of ammonium sulfate, whose X-ray diffraction patterns markedly differ in line intensity from those of the starting sulfate.

EXPERIMENTAL

Ammonium sulfate peroxo solvate was synthesized using sodium diphosphate as stabilizer [3]. Solutions for study (nearly saturated) were prepared by gradual addition of a dry solvate to water until there appeared indications of turbidity. After 24 h of keeping, no precipitate was observed. The thus obtained solutions, both undiluted and diluted to appropriate concentrations, were kept in closed polymeric containers at 20 ± 2°C. At regular intervals of time, the solutions were analyzed for the content of hydrogen peroxide by permanganatometric titration. The decomposition rate constants were calculated by the equation

$$\ln c_0/c = k(\tau - \tau_0).$$

The precipitates formed during storage of the solutions were removed, squeezed between two sheets of a filter paper, dried in air, analyzed for the content of H_2O_2, and subjected to X-ray diffraction analysis.

The X-ray diffraction patterns of powders were recorded on an ADP-2-01 diffractometer (CuK_α radiation, Ni filter) using the software for automation of data acquisition, processing, and analysis, developed for DRON X-ray diffractometers.

The values of the solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in water are listed in Table 1.

As can be seen from Table 1, the decomposition of hydrogen peroxide occurs uniformly at an initial H_2O_2 concentration of 8.24% in solution at an average constant rate $k = 2.7 \pm 1.5$, which corresponds to 40.2% $(NH_4)_2SO_4 \cdot H_2O_2$, with 36.2% loss of H_2O_2 relative to the starting solution. The content of hydrogen peroxide remaining in solution is 5.34%, which makes it suitable for further use. Similar results were also obtained for a solution containing 4.66% H_2O_2.

However, the following deviation was found in a solution containing 2.51% H_2O_2. After 9 days of storage, a hardly noticeable precipitation of crystals from solution commenced, with the H_2O_2 concentration increasing from 1.96% (in 9 days) to 2.48% (in 30 days). In further storage of the solution, the amount of the precipitate became lower and the H_2O_2 concentration gradually decreased. These data were the reason why the experiments were repeated.

We prepared the second set of solutions containing 9.57 and 3.89% H_2O_2. In a solution containing 9.57% H_2O_2, the concentration of H_2O_2 started to gradually increase from the first days of storage (Table 2) and a precipitate containing 1.02% H_2O_2 was formed in 8 days. In the second solution, the hydrogen peroxide concentration also increased and a precipitate containing 1.07% H_2O_2 was formed after 8 days of storage. No other outward changes (intense gas evolution, change of solution color) were observed. The content of SO_4^{2-} in the precipitate was 71.4%, and that of NH_4^+, 26.9%. For $(NH_4)_2SO_4$, values of 72.7% and 27.3%, respectively, were calculated. Apparently, ammonium sulfate was precipitated.

The content of $(NH_4)_2SO_4$ in the first starting solution was 37.2% in terms of hydrogen peroxide. Thus, the amount of the liquid phase was (100 – 37.2)% = 62.8%. Taking into account that the solution contains 5.34% H_2O_2, the content of the aqueous solution of hydrogen peroxide is 62.8% per 37.2% ammonium sulfate.

The solubility of $(NH_4)_2SO_4$ in water is 70.1 g per 100 g water at 0°C [4] and that in anhydrous H_2O_2 at 0°C, 70.4% [2].

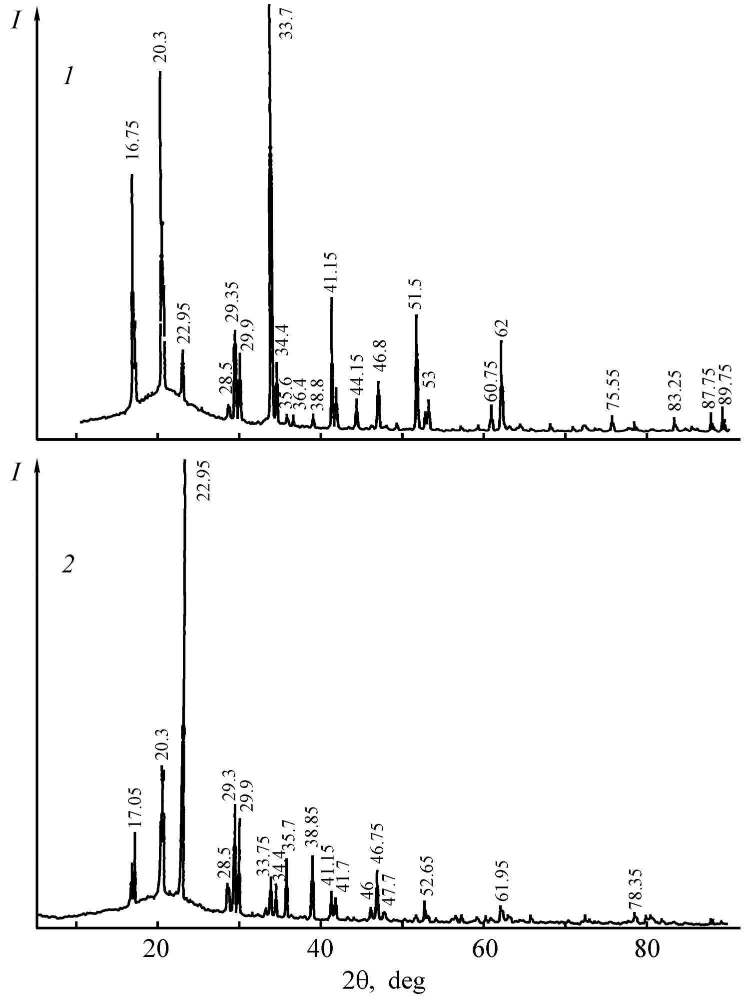
It seems unlikely that an unchanged ammonium sulfate precipitated in the initial state at such a high solubility in water and hydrogen peroxide. Because no outward changes in the system $(NH_4)_2SO_4 \cdot H_2O_2$–solvent were revealed, it is natural to suggest that ammonium sulfate precipitated in another crystalline form, which is less soluble in aqueous hydrogen peroxide.

Table 1. Solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in water at 20°C

τ, days	H_2O_2 concentration in solution, %	Loss of H_2O_2, % relative to the initial amount	$k \times 10^4$, h^{-1}	H_2O_2 decomposition
0	8.24	0	0	Uniform, $k_{av} = 2.7 \pm 1.5$
1	8.13	1.3	5.6	
3	7.94	3.7	5.1	
9	7.71	6.4	3.1	
23	7.04	14.6	2.8	
30	6.81	17.4	2.6	
40	6.30	23.6	2.5	
60	5.66	31.3	2.6	
67	5.34	35.2	2.7	
0	4.46	0	0	Uniform, $k_{av} = 2.6 \pm 0.6$
3	4.32	3.1	4.4	
9	4.26	4.5	2.1	
23	3.81	14.6	2.8	
37	3.68	17.5	2.2	
53	3.49	21.8	1.9	
67	3.05	31.6	2.3	
0	2.51	0	0	Uniform, $k_{av} = 2.6 \pm 0.6$
1	2.50	0.4	0	
3	2.36	6.0	8.5	
9	1.96	21.9	11.4	
23	2.27	9.6	1.8	
30	2.48	1.2	0.17	
37	2.13	15.1	1.8	
60	1.81	27.9	2.3	

Table 2. Solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ at 20°C (second series of experiments)

τ, days	H_2O_2 concentration in solution, %	Loss of H_2O_2, % relative to the initial amount	$k \times 10^4$, h^{-1}	H_2O_2 content of the precipitate, %
0	9.57	0	0	1.02
1	10.10	5.53	2.2	
3	10.36	8.2	11.0	
8	11.13	16.3	7.9	
11	11.14	16.4	5.7	
18	11.66	21.8	4.6	
24	16.49	72.3	9.4	
31	15.07	57.5	6.1	
0	3.89	0	0	1.07
1	4.13	6.2	24.9	
3	4.58	17.7	22.7	
8	5.48	40.9	17.8	
11	5.77	48.3	14.9	
18	5.99	54.0	10.1	
24	18.15	46.6	26.7	



X-ray diffraction patterns of $(NH_4)SO_4$. (*I*) Intensity and (2θ) Bragg angle. (*1*) Starting sample, (*2*) Precipitate.

The results of an X-ray phase analysis demonstrate that, being identical to the starting ammonium sulfate in interplanar spacings *d*, the precipitated $(NH_4)_2SO_4$ sharply differs in relative reflection intensities I_{rel} (see figure). Therefore, the precipitate cannot be identified as the known ammonium sulfate. At the same time, it was already mentioned that the sets of interplanar spacings for these compounds are the same, which demonstrates that their lattices are identical. The unexpectedly strong differences in the relative intensities of the X-ray reflections of the starting ammonium sulfate and the precipitate initiated measurements of X-ray diffraction patterns of all the precipitates. It was shown (Table 3) that the differences we observed cannot be accounted for by measurement errors. It should be accepted as established facts that (i) the precipitate retains the unit of the starting ammonium sulfate and (ii) the lattice cell undergoes a structural change and this rearrangement is preserved upon decomposition of hydrogen peroxide. The results obtained suggest that, under the action of solvation and subsequent desolvation of hydrogen peroxide, the arrangement of atoms in the unit cell of $(NH_4)_2SO_4$ changes and differs from that in the unit cell of the known ammonium sulfate.

Table 3. Relative intensities (I_{rel}) of reflections in the X-ray diffraction patterns for starting and precipitated $(NH_4)_2SO_4$

d, Å		I_{rel}		I_{in}/I_{pr}
starting $(NH_4)_2SO_4$	precipitate	starting $(NH_4)_2SO_4$	precipitate*	
5.293	5.200	55	13 ± 3	4.2
4.75	4.375	76	35 ± 7	2.2
3.875	3.875	12	100 ± 0	0.12
2.659	2.656	100	14 ± 5	7.2

* Average over X-ray diffraction patterns of four precipitates.

Table 4. X-ray diffraction patterns of KF obtained by various methods [7]

$KF \cdot H_2O_2$ decomposition at 20°C (during more than a year)		$KF \cdot 2H_2O_2$ dehydration at 40–60°C		Heating of α-KF to 140°C		Reference [8]	
d, Å	I_{rel}	*d*, Å	I_{rel}	*d*, Å	I_{rel}	*d*, Å	I_{rel}
3.597	44	3.084	18	3.089	19	3.087	21
3.203	6	2.671	100	2.675	100	2.674	100
3.013	9	1.890	51	1.892	60	1.891	51
2.945	5	1.612	8	1.613	11	1.612	6
2.706	13	1.543	13	1.545	18	1.544	10
2.596	3	1.337	6	1.338	8	1.337	3
2.401	100	2.227	3	2.228	4	2.227	2
1.161	3	1.196	12	1.197	19	1.196	7
New α-form		β-form		β-form		β-form	

It should be noted that, when coordinated to certain salts, e.g., to KF, hydrogen peroxide itself undergoes the following transformation: the H–O bond forms an acute angle with the O–O bonds, which confirms the formation of an intramolecular hydrogen bond [5]. It can be suggested that, in the given case too, the change in positions of atoms in the bound H_2O_2 molecule results in displacement of other atoms within the unit cell and this rearrangement is retained after the decomposition of hydrogen peroxide, i.e., ammonium sulfate is converted to another form. It is impossible to give without additional structural studies any other explanation for the decrease in the solubility of ammonium sulfate in aqueous hydrogen peroxide, apart from the gradual conversion $(NH_4)_2SO_4(\alpha) \rightarrow (NH_4)_2SO_4(\beta)$.

The $(NH_4)_2SO_4(\alpha) \rightarrow (NH_4)_2SO_4(\beta)$ conversion and precipitation of the less soluble β-form of ammonium sulfate can be represented by the following sequence of reactions:

$$(NH_4)_2SO_4(\alpha) + H_2O_2 \rightarrow (NH_4)_2SO_4 \cdot H_2O_2, \quad (1)$$

$$(NH_4)_2SO_4 \cdot H_2O_2 + H_2O \rightarrow 2NH_4^+ + [SO_4 \cdot H_2O_2]^{2-}, \quad (2)$$

$$[SO_4 \cdot H_2O_2]^{2-} \rightarrow SO_4^{2-} + H_2O_2, \quad (3)$$

$$SO_4^{2-} + 2NH_4^+ = (NH_4)_2SO_4(\beta) \text{ (precipitate)}. \quad (4)$$

The degree of conversion of the soluble $(NH_4)_2SO_4 \cdot H_2O_2$ into a less soluble $(NH_4)SO_4(\beta)$ is determined by the equilibrium of reaction (3), i.e., by the degree of dissociation of $[SO_4 \cdot H_2O_2]^{2-}$ anion with release of the SO_4^{2-} ion. It has been shown previously [6] that potassium fluoride peroxo solvate dissociates in aqueous solution with partial preservation of the solvated $[F...H_2O_2]^-$ ion, i.e., there exists the equilibrium

$$2KF \cdot H_2O_2 = 2K^+ + F^- + [F...H_2O_2]^- + H_2O_2. \quad (5)$$

Therefore, with account of the fact that solvated $[A...H_2O_2]^-$ ions are preserved in peroxo solvate aqueous solutions, we have that a difficultly soluble $(NH_4)SO_4(\beta)$ is precipitated when the equilibrium of reaction (3) is shifted to the right, and the soluble form, $(NH_4)_2SO_4 \cdot H_2O_2$, is preserved in the solution when the equilibrium of reaction (3) is shifted to the left. Reasons for such shifts of the equilibrium of reaction (3) remain unclear.

The suggested polymorphic conversion of ammonium sulfate, which occurs as a consequence of the coordination and subsequent release of hydrogen peroxide, is not the only example of the above conversion.

It has been shown previously [7] that another compound, potassium fluoride, undergoes a more pronounced polymorphic transformation under the action of hydrogen peroxide. It was found that, if the desolvation of $KF \cdot H_2O_2$ occurs slowly (during about a year at 20°C), the X-ray diffraction pattern is a set of bands associated with $KF \cdot 2H_2O$ formed by the reaction $2KF \cdot H_2O_2 = KF + KF \cdot 2H_2O + O_2$ and a set of bands that does not coincide with published data for KF [8] and with our data for anhydrous potassium fluoride obtained by dehydration of $KF \cdot 2H_2O_2$ or by heating of α-KF to 100–140°C (Table 4).

Table 5. Relative intensities I_{rel} of $(NH_4)_2SO_4$ precipitates at various temperatures

d, Å		I_{rel} for a chosen d					
$(NH_4)_2SO_4$	precipitate	$(NH_4)_2SO_4$ at 20°C	precipitate				Average I_{rel}
			20°C	46°C	100°C	180°C	
5.193	5.200	55	13	10	16	4	11 ± 3
4.375	4.375	76	35	22	40	17	28 ± 9
3.875	3.875	12	100	100	100	100	100 ± 0
2.659	2.656	100	14	11	11	8	11 ± 1

In this case, however, other values are observed not only for the relative intensities, but for the interplanar spacings as well. The low-temperature form, α-KF, obtained in $KF \cdot H_2O_2$ decomposition upon prolonged storage (at 20°C), is transformed to its common β-form at 100–140°C (Table 4). In the case of ammonium sulfate, the crystallographic change in I_{rel} in the precipitated sulfate is also preserved in the sulfate at higher temperatures (Table 5).

The results of this study can be understood on the assumption that hydrogen peroxide can change the structure of a solvated compound.

CONCLUSIONS

(1) Aqueous solutions of $(NH_4)_2SO_4 \cdot H_2O_2$ are rather stable in a wide range of concentrations, up to 40.2%. Such solutions containing simultaneously a fertilizing soil and disinfecting components, can be used first of all in plant growing. Owing to the full ecological safety, they are also suitable for use in general disinfection.

(2) In some cases, $(NH_4)_2SO_4$ precipitates from solution. According to tentative results of an X-ray phase analysis, this is due to the $(NH_4)_2SO_4(\alpha) \rightarrow (NH_4)_2SO_4(\beta)$ phase transition that occurs under the influence of the solvation and subsequent desolvation of the sulfate. In this case, $(NH_4)_2SO_4(\beta)$ less soluble in hydrogen peroxide is precipitated.

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