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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Solubility and Stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in Organic and Aqueous-Organic Media

K. V. Titova, V. V. Buyanov, V. P. Nikol'skaya, O. B. Pudova, and O. A. Zharkova

Institute for Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia
State Research Institute of Biological Instrument-Making, Federal State Unitary Enterprise, Moscow, Russia

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Abstract—Solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in organic solvents (glycerol, ethylene glycol, TOSOL-A40 OM antifreeze), in mixtures of an organic solvent and water, and in pure water was studied. Crystallographic properties of the ammonium sulfate precipitating from aqueous-organic solvents and aqueous solutions in various time intervals and differing from ordinary $(NH_4)_2SO_4$ in solubility and one of crystallographic parameters were analyzed.

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It has been shown previously [1] that ammonium sulfate peroxosolvate is soluble in water. Solutions of this compound are rather stable; however, an ammonium sulfate precipitate is formed in the course of their storage after various intervals of time. This precipitate differs from ordinary $(NH_4)_2SO_4$ in the solubility in aqueous hydrogen peroxide and in relative intensities I_{rel} of reflections in X-ray phase analysis (XPA) of the substance. The solubility of $(NH_4)_2SO_4$ in water at 0°C is 70.4 per 100 g of water [2], and that in anhydrous hydrogen peroxide, 69.4 g per 100 g of H_2O_2 [3]. In an aqueous solution of $(NH_4)_2SO_4 \cdot H_2O_2$, nearly saturated in H_2O_2, the concentration of $(NH_4)_2SO_4$ does not exceed 24 g per 100 g of the solvent.

According to XPA data, the ammonium sulfate precipitates have the same lattice parameter d (Å), but differ from the known $(NH_4)_2SO_4$ in I_{rel}, i.e., in the positions of atoms in the unit cell [4].

In this study, the solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in glycerol, ethylene glycol, and TOSOL-A40 OM antifreeze, as well as in their mixtures with water, was examined. The composition and crystallographic properties of the precipitates formed were determined.

EXPERIMENTAL

Ammonium sulfate peroxosolvate was synthesized by the previously described method [1]. The solutions were prepared by gradual addition of the sulfate to the solvent under cautious agitation, kept for 24 h, and, if the solid phase completely disappeared, left in storage in a closed polymeric vessel at 20±2°C. The precipitates were analyzed for the content of H_2O_2, NH_4^+, and SO_4^{2-}. X-ray diffraction patterns of the precipitates were measured with an instrument described previously in [1].

Table 1 lists data on the solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in glycerol and water–glycerol mixtures. It can be seen that, in anhydrous glycerol, the nearly saturated solution is rather stable in the initial stage of storage (16 days): the loss of H_2O_2 is 5.6%. Then, the decomposition rate increases and, on being stored for 29 days, the solution loses 60.3% of hydrogen peroxide, with a small amount of a precipitate formed. By 43nd day of storage, the loss of H_2O_2 reaches a value of 74.6%, with the amount of the precipitate increasing only slightly. In a glycerol–water mixture (80% glycerol + 20% water), the loss of H_2O_2 is observed earlier, 12.1% in 9 days, and a precipitate appears. After 43 days of storage, the loss of H_2O_2 is

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

τ, days	H_2O_2 content of a solution, %	Loss of H_2O_2, % relative to the initial content	Notes
100% glycerol			
0	2.52	0	
1	2.53	0	
9	2.45	2.4	
16	2.38	5.6	
29	1.00	60.3	Solution turbidization
43	0.64	74.6	
80% glycerol + 20% water			
0	4.22	0	
1	4.09	3.1	
9	3.71	12.1	
22	1.94	54.7	
29	1.15	72.8	
43	0.40	90.5	A small amount of precipitate
60% glycerol + 40% water			
0	2.79	0	
1	2.48	11.1	
6	3.19	+14.3	A large amount of precipitate
9	3.44	+23.3	
22	2.39	14.3	
36	1.25	55.2	
43	1.15	58.0	

90.5%, with the amount of the precipitate increasing only slightly. The precipitate cannot be isolated. In a solution containing 60% glycerol and 40% water, the situation changes dramatically. Already on the 6th day, the H_2O_2 content of the solution increases, rather than decreases, which is accompanied by the formation of a large amount of the precipitate. The rise in the H_2O_2 concentration terminates by 22nd day, as also does the increase in the amount of the precipitate. According to the results of a chemical analysis, the precipitate is composed of ammonium sulfate with an admixture of glycerol. The precipitate contains 25.9% NH_4^+ and 69.4% SO_4^{2-}, which corresponds to a 0.72 M solution of $(NH_4)_2SO_4$ with 0.28 M of glycerol. Glycerol could not be completely removed at 20°C.

The irregular variation of the content of H_2O_2 in glycerol–water solutions, as well as in other mixed solvents (from a decrease to a rise), is determined by the relationship between the rate at which the amount of H_2O_2 increases via precipitation of $(NH_4)_2SO_4$ and the decomposition rate of hydrogen peroxide in solution.

The X-ray diffraction pattern of the precipitate isolated from the solution (60% glycerol + 40% water) is identical to the diffraction patterns of precipitates isolated from aqueous solutions of ammonium sulfate peroxosolvate [1] and is markedly different from the diffraction pattern of ordinary ammonium sulfate. The interplanar spacings d (Å) remain constant, whereas values of I_{rel} are changed.

The solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in ethylene glycol and water–ethylene glycol mixtures are listed in Table 2. In anhydrous ethylene glycol, the solubility of ammonium sulfate peroxosolvate is on the same order of magnitude as that in glycerol. At a 80 : 20 ethylene glycol-to-water ratio, the concentration of hydrogen peroxide in the solution grows during the first 6 days and a precipitate is formed. By the end of a 36-day storage, when a rather large amount of the precipitate is formed, the H_2O_2 concentration ceases to grow and starts to decrease. According to chemical analysis data, the precipitate formed in a mixture of 80% ethylene glycol and 20% water is composed of ammonium sulfate.

The X-ray diffraction patterns isolated from water–ethylene glycol solutions are identical to the diffraction pattern formed from a water–glycerol solution (Table 3).

In anhydrous TOSOL (Table 4), the solubility of the solvate is somewhat higher than that in glycerol and ethylene glycol. In this multicomponent solution without addition of water, and also in mixtures with water to antifreeze ratios of 80 : 20 and 60 : 40, the concentration of hydrogen peroxide in solution starts to grow after several hours and precipitation begins. The results of chemical analyses of the precipitates fully coincide with the data for precipitates from glycerol and ethylene glycol solutions. The following

Table 2. Solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in ethylene glycol and water–ethylene glycol mixtures at 20°C

τ, days	H_2O_2 content of a solution, %	Loss of H_2O_2, % relative to the initial content	Notes	τ, days	H_2O_2 content of a solution, %	Loss of H_2O_2, % relative to the initial content	Notes
100% glycerol							
0	1.89	0		29	1.22	34.5	A small amount of precipitate
6	1.61	14.8		36	1.11	41.3	
16	1.66	12.2					
80% glycerol + 20% water							
0	2.54	0		22	2.55	+0.4	
6	2.58	+1.5		29	2.44	4.0	
16	2.82	+11.1	Precipitate	26	2.35	4.5	A large amount of precipitate
60% glycerol + 40% water							
0	3.34	0		16	2.72	+16.2	
6	2.63	+14.9	A small amount of precipitate	22	2.86	+22.2	A large amount of precipitate
9	2.67	+14.0		29	2.94	+25.6	
				36	2.69	+14.9	

Table 3. X-ray diffraction data for $(NH_4)_2SO_4$ precipitated from aqueous and aqueous-organic solutions of $(NH_4)_2SO_4 \cdot H_2O_2$ in comparison with published data for the known $(NH_4)_2SO_4$

Published data [6]		From aqueous solution		From water–glycerol solution		From water–ethylene glycol solution		From aqueous antifreeze	
d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}	d, Å	I_{rel}
5.293	55	5.200	17	5.293	29	5.246	3	5.208	17
4.379	76	4.375	30	4.332	17	4.396	12	4.375	30
3.875	12	3.875	100	3.883	100	4.892	100	3.875	100
3.132	3	3.132	7	3.137	4	3.126	4	3.132	7
3.043	20	3.048	35	3.053	5	3.053	19	3.048	25
2.988	15	2.988	22	2.988	3	2.667	2	2.988	22
2.659	100	2.636	9	2.652	4	5.525	4	2.636	9
2.607	14	2.607	7	2.603	3	2.324	3	2.607	7
2.522	8	2.515	14	2.518	5	2.173	4	2.515	14

was found for the precipitate formed from the 80 : 20 antifreeze–water mixture (%): NH_4^+ 26.9 and SO_4^{2-} 72.1. The X-ray diffraction patterns of the precipitates formed in the mixtures under study are identical to the diffraction patterns of precipitates from water and other aqueous-organic mixtures studied (Table 4). Thus, the solvate is comparatively stable in the anhydrous solvents in the initial stage. As, however, it

Table 4. Solubility and stability of $(NH_4)_2SO_4 \cdot H_2O_2$ in antifreeze and its aqueous solutions

τ, days	H_2O_2 content of a solution, %	Loss of H_2O_2, % relative to the initial content	Notes
		100% glycerol	
0	3.43	0	
6	3.58	+4.6	
9	3.81	+12.2	
16	3.71	+8.2	
22	3.52	+2.6	A large amount of precipitate
29	3.51	+2.6	
36	3.24	+5.5	
		80% glycerol + 20% water	
0	4.68	0	
6	6.69	42.9	
9	7.16	+53.0	
16	7.99	+70.7	A large amount of precipitate
22	8.89	+89.9	
29	8.55	+82.7	
	7.94	+69.6	
		60% glycerol + 40% water	
0	4.64	0	
6	5.03	+8.4	
9	5.07	+9.2	
16	5.25	+13.1	Precipitate
22	4.91	+5.8	A large amount of precipitate
29	4.81	+3.7	
36	4.85	+4.5	

decomposes and a minor amount of water appears in the resulting aqueous-organic medium, the decomposition of the solvate becomes markedly faster. In mixed solvents with a high content of water, the decomposition of ammonium sulfate peroxosolvate is substantially faster and is accompanied by precipitation. The precipitate is composed of ammonium sulfate, but it is less soluble in the aqueous-organic medium and has changed values of I_{rel}.

Apparently, ammonium sulfate solvated by hydrogen peroxide and having, as a result of the solvation, a changed arrangement of atoms in the unit cell, with $(NH_4)_2SO_4 \cdot H_2O_2$ formed, dissociates in water to $2NH_4^+$ and $[SO_4 \cdot H_2O_2]^{2-}$ [1]. The latter is desolvated to SO_4^{2-} and H_2O_2. The desolvated sulfate ion precipitates with an ammonium cation to give a crystallographically changed form $(NH_4)_2SO_4$-β, which has a lower solubility than ordinary ammonium sulfate.

It was found in [5] that, upon solvation by hydrogen peroxide and subsequent slow desolvation, the structural parameters of potassium fluoride, d (Å) and I_{rel}, are fully changed. It was shown in the present study and in [1] that the solvation and subsequent desolvation of ammonium sulfide by hydrogen peroxide also leads to a change in its crystallographic characteristics. However, only the relative intensities of reflections in X-ray diffraction patterns are changed in these cases.

According to [4], the relative intensities of lines in an X-ray diffraction pattern are a d-independent characteristic of any solid substance and characterize positions of atoms in its unit cell. Consequently, both the parameters, d (Å) and I_{rel}, or one of these, can be independently used for identification of unknown substances. Apparently, the solvation of ammonium sulfate by hydrogen peroxide results in the change in one of its structural parameters (I_{rel}, atomic arrangement in the unit cell), which points, according to [4], to a change in the structure. The results obtained in the present study and in [1, 5] confirm the assumption that hydrogen peroxide can change to some extent the structure of a compound solvated and these changes are preserved upon desolvation.

CONCLUSIONS

(1) Ammonium sulfate peroxosolvate $(NH_4)_2SO_4 \cdot H_2O_2$ is poorly soluble in organic and aqueous-organic media: glycerol–water, ethylene glycol–water, and TOSOL-A40 antifreeze–water.

(2) In storage of both aqueous-organic and aqueous solutions, ammonium sulfate precipitates are formed, which differ from ordinary ammonium sulfate in two characteristics: (i) lower solubility in water and hydrogen peroxide and (ii) relative intensities of

reflections in an X-ray phase analysis of a substance. These changes indicate that, in the course of solvation, hydrogen peroxide can modify the structure of a salt being solvated and these changes are preserved upon desolvation.

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