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THE SYSTEM THORIUM NITRATE - WATER - NITRIC ACID AT 25° AND THE HYDRATES OF THORIUM NITRATE

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ABSTRACT

The dodecahydrate, hexahydrate, pentahydrate, tetrahydrate, and dihydrate of thorium nitrate have all been reported, and recently, a hemihydrate ($Th(NO_3)_4 \cdot 5.5H_2O$). As a result of combined phase study of the ternary system $Th(NO_3)_4$ - H_2O - HNO_3, crystallization experiments, and X-ray information it has been established that the pentahydrate and tetrahydrate are the stable hydrates of thorium nitrate. Crystallization experiments have failed to yield a hexahydrate or dodecahydrate, and the alleged $Th(NO_3)_4 \cdot 5.5H_2O$ appears to be a mixture of pentahydrate with some partially hydrolyzed salt.

The nature of the hydrates of thorium nitrate has long been in a state of uncertainty. Berzelius,[1] Cleve,[2] and Koppel and Holtkamp[3] reported preparing a dodecahydrate by allowing aqueous thorium nitrate solutions to stand over sulfuric acid. When placed over very concentrated sulfuric acid, the dodecahydrate changed to the tetrahydrate.[2] Meyer and Jacoby[4] and Fuhse[5] reported the formation of a hexahydrate from warm aqueous solutions. Brauner[6] prepared the pentahydrate from solutions at

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*Grateful acknowledgement is made to Dr. Stanley Siegel for taking and interpreting the X-ray powder diagrams of the solids studied in this paper.

[1] J. J. Berzelius, Pogg. Ann. 16, 385 (1829).

[2] P. T. Cleve, Bull. soc. chim. (2) 21, 115 (1874).

[3] I. Koppel and H. Holtkamp, Z. anorg. Chem. 67, 290 (1910).

[4] R. J. Meyer and R. Jacoby, ibid. 27, 359 (1901).

[5] O. Fuhse, Z. angew, Chem. 10, 115 (1897).

[6] B. Brauner, J. Chem. Soc. 73, 951 (1898).

80°C. containing nitric acid, and Hebert and Lister[7] prepared it from similar solutions at 25°. Kolb[8] reported obtaining a dihydrate by heating thorium nitrate with fuming nitric acid at 105 to 110°. Misciatelli[9] did the first work with the composition-temperature curve and identified a hexahydrate. Marshall, Gill, and Secoy[10] made a study of the thorium nitrate - water system from room temperature to the decomposition temperature of the salt and identified a hexahydrate phase (M.P. 111°), a tetrahydrate phase (M.P. 151°), and an unidentified lower hydrate phase. Templeton[11] studied the thorium nitrate - water system from 20° to 160° and reported a tetrahydrate phase and second phase, which he called a 5.5 hydrate.

The present paper is an investigation of the hydrates of thorium nitrate and the ternary system thorium nitrate - water - nitric acid at 25°. The results of these studies show that the stable hydrates of thorium nitrate are the pentahydrate and the tetrahydrate.

EXPERIMENTAL

Method - Mixtures of water and nitric acid were saturated with Baker and Adamson Reagent Grade thorium nitrate at a temperature around 70°C., and the solutions were then equilibrated in a thermostatted bath at 25 ± 0.03°C. for a minimum period of 48 hours. In the low water region General Chemical Co. anhydrous nitric acid and anhydrous thorium nitrate[12] were used to prepare the solutions. The method of wet residues[13] was used. Thorium nitrate was determined by ignition of the sample to thoria. Water was determined by titration with the Karl Fischer reagent. Nitric acid was determined by difference.

Solids used for identification purposes and for X-ray powder diagrams were dried between sheets of filter paper.

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[7] J. A. Hebert and M. W. Lister, MX-185 (1945).

[8] A. Kolb, Z. anorg. Chem. 83, 143 (1913).

[9] P. Misciatelli, Gazz. chim. ital. 60, 833 (1930).

[10] W. L. Marshall, J. S. Gill, and C. H. Secoy, J. Am. Chem. Soc. 73, 4991 (1951).

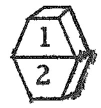
[11] C. Templeton, AECU-1721 (1950).

[12] J. R. Ferraro, unpublished work.

[13] F. A. H. Schreinemakers, Z. physik. Chem. 11, 81 (1893).

Materials - Thorium nitrate, Baker and Adamson Reagent Grade and labeled $Th(NO_3)_4 \cdot 4H_2O$ whose maximum limits of impurities were 0.003% for chloride and 0.01% for sulfate, was used. The solid had no well-defined crystalline shape. The hydration was well in excess of the tetrahydrate, and the material evidently contained hydrolyzed salt. Anal. ThO_2, 47.15 ± 0.1; water, 15.90 ± 0.2. Nitric acid, General Chemical Div., 70%, sp. gr. 1.42, and anhydrous nitric acid, General Chemical Div., total acidity 100% minimum were the other materials used.

DISCUSSION

Thorium Nitrate Pentahydrate - Thorium nitrate pentahydrate crystals isolated from the phase studies, and from crystallization experiments at 25°, are clear and transparent, and have the shape 

with face angle 1:2 at about 140°. Anal. Calcd: ThO_2, 46.33; water 15.79. Found: ThO_2, 46.33 ± 0.1; water, 15.79 ± 0.1. The X-ray powder diagram of these crystals shows a pattern different than that of the tetrahydrate.

Thorium Nitrate Tetrahydrate - Thorium nitrate tetrahydrate isolated from the phase studies, and from crystallizations at 25° from anhydrous nitric acid in a desiccator over concentrated sulfuric acid, is finely crystalline. The solid can be prepared free of nitric acid by pumping at 50° (10 mm), or by several days' desiccation over potash. Anal. Calcd: ThO_2, 47.84; water, 13.04. Found: ThO_2, 47.86; water, 13.09. The X-ray powder diagram of these crystals shows a pattern different than that of the pentahydrate.

Thorium Nitrate Anhydrous Phase - The thorium nitrate anhydrous phase isolated in the low water region from the phase studies appeared to be coordinated with either two moles of nitric acid or the equivalent in weight. The X-ray powder diagram showed that the substance was[12] $Th(NO_3)_4 \cdot 2NO_2$.

Possible Higher Hydrates - There has been much confusion in the literature regarding the nature of the solid isolated from aqueous solutions. As previously mentioned, the solid has been variously identified as the hexahydrate, 5.5 hydrate, and even the pentahydrate.[7] It has long been known that when thorium salts dissolve in water, the solutions become acidic. A 0.1 N thorium nitrate solution shows a pH of 2.46. Other evidence points to the fact that there is liberation of the hydrogen ion with hydrolysis and an equilibrium of this nature occurring:

$$Th(H_2O)_n^{+4} + H_2O = Th(H_2O)_{(n-1)}^{+3}OH + H_3O^+ \quad (1)$$

The analyses of solids we have isolated from aqueous solutions fit well with the analytical data of the solid Templeton isolated and chose to call a hemihydrate ($Th(NO_3)_4 \cdot 5.5H_2O$), and with that of Fuhse's[5] hexahydrate.

	% ThO_2	% H_2O
$Th(NO_3)_4 \cdot 6H_2O$	44.91	18.36
Templeton's 5.5 hydrate	45.7 ± 0.1	17.5 ± 0.1
Fuhse's hexahydrate	45.5	17.6
Our results from aqueous solutions	45.6 ± 0.2	17.3 ± 0.2
$Th(NO_3)_4 \cdot 5H_2O$	46.33	15.79

These solids are probably one and the same. Moreover, the nitrogen content of this solid, as determined by the nitrometer method, showed a NO_3^-/Th ratio of 3.98.

X-ray evidence shows that this solid has a powder pattern like the pentahydrate. No basic phase could be identified by X-ray; so it is probably present to less than 5%. A hypothetical formula showing about 2-3% basic phase can be calculated to fit the analytical data. Work in aqueous solutions, adding some known amounts of basic material, although not conclusive, has given a rough value of 3% basic material present in the solid recrystallized from water. It appears that this solid is not a pure hydrate but rather a mixture of pentahydrate with some partially hydrolyzed salt. With the addition of only 1% nitric acid one can obtain pure pentahydrate as the solid phase free of hydrolytic material.

Attempts to prepare a pure hexahydrate have failed. Solids with close to six water molecules per thorium atom have been obtained from aqueous solutions at 4°, but these were always contaminated with partially hydrolyzed salt. These solids had no well-defined crystalline shape and appeared wet. Gentle drying of the solids between filter paper lowered the water content, and the analyses approached the compositions of the solids isolated from aqueous solutions at 25°. Crystallizations at 80° from 1% nitric acid solutions gave similar results.

X-ray powder diagrams of these solids gave a pattern like the pentahydrate.

Efforts to reproduce the work of Berzelius[1] and Cleve[2] in preparing a dodecahydrate failed. Solids with close to ten water molecules per thorium atom were obtained from 1% nitric acid solutions at 4°, but these were extremely unstable at room temperature.

Possible Lower Hydrates - Although Marshall, Gill, and Secoy[10] reported a transition from tetrahydrate to a lower hydrate at 151°, Templeton,[11] studying the system to 160°, failed to identify a lower hydrate. Thus the presence of a hydrate lower than the tetrahydrate is still in question.

Kolb[8] reported isolating a dihydrate from fuming nitric acid solutions at 105-110°. The solids we isolated under those conditions were always highly decomposed and contained water in the region of four water molecules per thorium atom.

The results of our ternary phase studies indicate that the tetrahydrate may be the lowest stable hydrate at 25°C. No indications of a dihydrate were found, which might mean only that its stability region in this system is so short as to make its resolution difficult.

The Ternary System - Thorium Nitrate - Nitric Acid - Water (Figure I, Table I).. The solubility curve of thorium nitrate pentahydrate extends toward decreasing solubility from a point at 36.08% water and 62.71% thorium nitrate to a point at about 25% water and 26% thorium nitrate. At this point there is an increase in solubility up to a maximum at 17.70% water and 28.67% thorium nitrate, which appears to be the invariant point of the tetrahydrate-pentahydrate pair. From here the solubility curve of the tetrahydrate decreases to a point at 5.10% water and 21.13% thorium nitrate, which is the invariant point of the tetrahydrate-anhydrous solid pair. The solubility curve then continues toward increasing solubility in the direction of the anhydrous solid.

From the phase diagram it can be seen that the pentahydrate will be the phase crystallizing out from solutions containing 1.2% to 54% nitric acid. This corresponds with the data obtained from the crystallization experiments at 25°, which showed that only with solutions containing less than 1% nitric acid would one fail to get the pentahydrate. With solutions containing less than 1% nitric acid the solid changes, and a solid point at 16.92% water and 83.60% thorium nitrate is obtained. This solid contains partially hydrolyzed salt. The liquid at this point is 35.96% water and 63.61% thorium nitrate. The aqueous saturation point appears to be at 35.88% H_2O. The solid in equilibrium is 17.56% H_2O and 83.40% thorium nitrate, which is the solid isolated in crystallization experiments at room temperature from aqueous solutions.

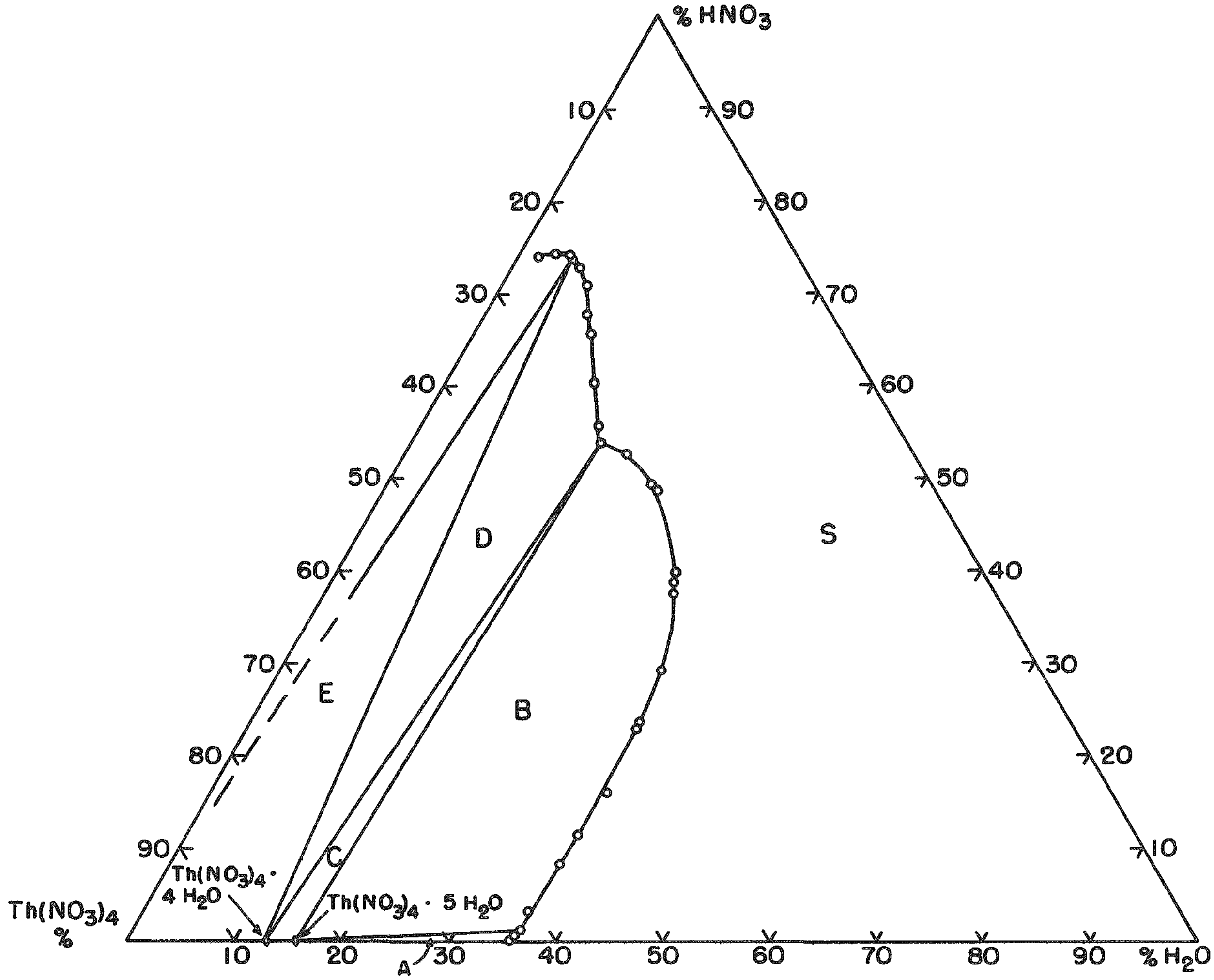


FIG. I. THE SYSTEM $Th(NO_3)_4 - H_2O - HNO_3$ AT 25 °C.

A: REGION OF HYDROLYSIS.
B: PENTAHYDRATE AND VARIABLE LIQUID.
C: PENTAHYDRATE, TETRAHYDRATE AND LIQUID.
D: TETRAHYDRATE AND VARIABLE LIQUID.
E: TETRAHYDRATE, LOWER PHASE AND LIQUID.
S: HOMOGENEOUS SOLUTION.

Table I

THORIUM NITRATE - NITRIC ACID - WATER AT 25°

Liquid Phase		Solid Phase		
H_2O (%)	$Th(NO_3)_4$ (%)	H_2O (%)	$Th(NO_3)_4$ (%)	
35.88	64.12	-	-	$Th(NO_3)_4 \cdot 5H_2O$ + Hydrolyzed Salt
35.96	63.61	16.92	83.60	
36.08	62.71	16.29	83.80	$Th(NO_3)_4 \cdot 5H_2O$
35.90	60.78	16.91	82.81	
36.07	55.34	16.44	83.90	
36.19	52.03	18.34	80.34	
36.92	47.10	16.31	83.38	
36.17	41.86	16.50	82.28	
36.24	41.24	16.12	83.24	
35.48	35.16	15.90	83.19	
32.41	30.11	16.57	82.79	
31.97	29.57	15.47	84.44	
31.66	28.76	20.60	66.64	
25.44	25.87	15.75	84.46	
24.84	26.04	15.49	84.51	
20.60	26.93	16.42	83.46	
18.93	27.95	16.01	83.74	
18.31	28.85	15.93	81.91	
18.01	28.27	15.89	82.91	
17.70	28.67	16.50	83.49	$Th(NO_3)_4 \cdot 5H_2O$ + $Th(NO_3)_4 \cdot 4H_2O$
16.56	27.93	12.82	75.68	$Th(NO_3)_4 \cdot 4H_2O$
13.87	25.95	13.67	72.14	
10.96	23.46	12.92	74.23	
9.43	22.91	12.25	71.00	
8.01	21.11	12.31	71.39	
6.02	21.17	12.47	77.97	
3.57	22.45	0.81	68.37	$Th(NO_3)_4 \cdot 2HNO_3$
3.38	22.51	3.03	69.09	or
1.77	24.48	0.21	67.52	$Th(NO_3)_4 \cdot N_2O_5$
5.30	21.19	2.96	70.33	
4.85	21.07	1.80	68.42	