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The Thorium Nitrate–Water System Above 20°

BY W. L. MARSHALL, J. S. GILL AND C. H. SECOY

Misciatelli[1] has determined the ice curve and the solubility of a hexahydrate of thorium nitrate from the cryohydric temperature up to 20°. We have extended these data to 211° to show a transition from the hexahydrate to a tetrahydrate at 111° and a transition of the tetrahydrate to a lower hydrate at approximately 151°.

The data are given in Tables I and II and in Fig. 1. These results are in good agreement with Misciatelli's solubility curve below 20° and serve to verify his determination of the hexahydrate as the stable solid phase at 20°.

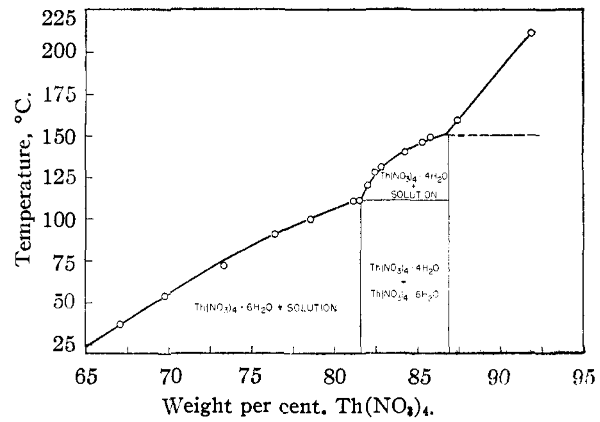

Fig. 1.—The thorium nitrate–water system above 20°.

Decomposition of the system was indicated above approximately 115° by the slight odor of nitric acid and also by the partial vapor coloration above approximately 140°. However, the rate of decomposition appeared sufficiently slow so as not to invalidate data obtained above these temperatures.

TABLE I

THE SOLUBILITY OF THORIUM NITRATE IN WATER, 37–211°

Method of determination	Temp., °C.	Liquid, per cent. $Th(NO_3)_4$	Solid, per cent. $Th(NO_3)_4$	Solid phase
Analytical	37.3	67.07	81.18 (theor., 81.62)	$Th(NO_3)_4 \cdot 6H_2O$
Analytical	54.5	69.78		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	72.0	73.39		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	90.2	76.39	80.82 (theor., 81.62)	$Th(NO_3)_4 \cdot 6H_2O$
Analytical	99.7	78.56		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	110.4	81.11		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	110.9	81.50		$Th(NO_3)_4 \cdot 6H_2O$
	111[a]			$Th(NO_3)_4 \cdot 6H_2O + Th(NO_3)_4 \cdot 4H_2O$
Analytical	120.6	82.01		$Th(NO_3)_4 \cdot 4H_2O$
Synthetic	128	82.41		$Th(NO_3)_4 \cdot 4H_2O$
	129.5		85.84 (theor., 86.95)	$Th(NO_3)_4 \cdot 4H_2O$
Analytical	130.5	82.85		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	139.5	84.27		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	146.0	85.30		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	149.0	85.81		$Th(NO_3)_4 \cdot 4H_2O$
	151[b]			$Th(NO_3)_4 \cdot 4H_2O + Th(NO_3)_4 \cdot XH_2O$
Synthetic	159	87.41		$Th(NO_3)_4 \cdot XH_2O$
Synthetic	211	91.82		$Th(NO_3)_4 \cdot XH_2O$

[a] Intersection temperature for melting point of the hexahydrate. [b] Intersection temperature for melting point of the tetrahydrate.

TABLE II

MELTING POINT DETERMINATIONS

Weight per cent. $Th(NO_3)_4$	82.41	83.72	91.82
First observed melting (T, °C.)	105–115	105–115	~160

Transition temperatures of the hexahydrate and tetrahydrate were determined from intersection points of the graphic data, from a series of cooling curves, and from initial melting points of solid mixtures in the appropriate concentration ranges. From the cooling curves the best temperature for the hexahydrate to tetrahydrate transition was fixed at 111.3 ± 0.4° after three recrystallizations. Melting point data given in Table II were rather difficult to obtain due to the small concentration differences between successive hydrates.

Experimental

Chemically pure thorium nitrate tetrahydrate obtained from the Maywood Company was used. Solubility data from 37 to 150° were obtained analytically by stirring thorium nitrate solutions in the presence of excess solid for about 40 minutes in a 200-cc. round-bottom flask set in a thermostat controllable to ±0.05°. The approach to equilibrium was made from both directions on the temperature scale to verify true equilibration. Preliminary sampling had shown that stirring for 10 to 15 minutes was a sufficient time for the establishment of equilibrium. The stirrer was stopped, the solid was allowed to settle, and duplicate samples of the clear solution were taken. These samples were weighed, evaporated to dryness and ignited directly to ThO_2 at 900°. The maximum deviation of duplicates was approximately ±0.15%.

Solubility data above 125° accurate to ±1° were obtained in 4 and 6 mm. i.d. silica tubing by a synthetic method.[2] The solubility temperature of a $Th(NO_3)_4$–H_2O

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

[2] C. H. Secoy, THIS JOURNAL, **72**, 3343 (1950).

mixture of known composition in a sealed tube was determined in a special rocker-heating apparatus by slowly raising the temperature. Supercooling phenomena prevented a check of these data by the cooling method.

Solid phase analyses were obtained by direct sampling of the solid in equilibrium with the saturated solution. The sample was then dried between filter paper, weighed, and ignited to ThO_2.

The thermometers used in the analytical determinations were standardized against a Bureau of Standards platinum resistance thermometer. The temperature readings of data obtained by the synthetic method were measured with an iron–constantan thermocouple.

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On the Nature of the Reaction between Gelatin and Some Copper(II) Complexes

BY LOUIS MEITES

During the course of some earlier work on the polarographic effects of gelatin and other maximum suppressors, it was noted that pronounced changes in the colors of some of the solutions occurred at or near the polarographic critical concentration of the surface-active material.[1] The present note describes the results of a spectrophotometric investigation of some typical systems containing gelatin and a colored metal complex.

Experimental

Spectrophotometric measurements were made with a Beckman Model B spectrophotometer, using band widths of 4 millimicrons or less. Absorbancy measurements were generally reproducible to ±0.003 unit or $\pm 1\%$, whichever was greater.

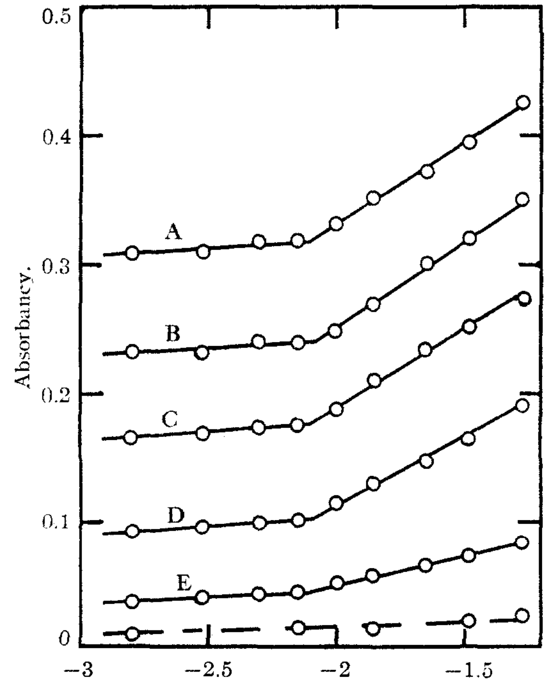

Fig. 1.—Spectrophotometric titration of 0.80 mM copper(II) in 1.0 F potassium hydroxide–0.50 F potassium citrate with gelatin at (A) 320, (B) 325, (C) 330, (D) 340 and (E) 360 mμ. The dashed line represents the absorbancies at 330 mμ of copper-free 1.0 F potassium hydroxide–0.50 F potassium citrate solutions containing various concentrations of gelatin.

The gelatin was identical with that used in the earlier study,[1] and its solutions were prepared in the same manner. They were always used within 8 hours of preparation. Other materials were ordinary reagent grade. As the polarographic characteristics of aged solutions of the copper complexes differ in some respects from those of fresh solutions, indicating a slow deterioration (precipitates of cupric oxide are frequently observed after long standing), no solution was used after standing for more than 30 hours.

Data and Discussion

Figure 1 shows the effect of gelatin on the absorbancy of a solution of copper(II) in F potassium hydroxide–0.5 F potassium citrate at wave lengths between 325 and 360 mμ. Similar curves are obtained at other wave lengths where the extinction of the solution is sufficiently high to permit accurate measurements. Although the addition of $10^{-4}\%$ gelatin increases the absorbancy at any given wave length very slightly over that in the original solution, no further detectable change occurs as the gelatin concentration is increased to about $5 \times 10^{-3}\%$. However, at the "optical critical concentration" (whose definition and measurement are clear from Fig. 1), the absorbancy begins to increase, and continues to rise in every case up to the highest gelatin concentration used (sometimes as high as 0.7%).

This behavior is very like the previously described effects of gelatin on the interfacial tension between mercury and an electrolyte solution and on various polarographic phenomena. Moreover, the optical and polarographic critical concentrations are in excellent agreement in every case where data on both are available. For example, in F potassium hydroxide–F potassium citrate the values of pC [= −log (critical concentration)] are 2.22 (2 mM copper) and 2.31 (0.5 mM copper) from optical measurements, and 2.28 from polarographic

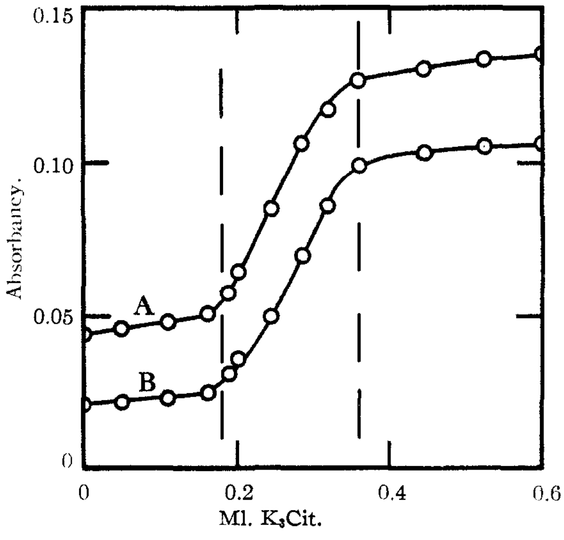

Fig. 2.—Spectrophotometric titration of 3.00 ml. of 1.20 mM copper(II) in 1.0 F potassium hydroxide with 20.0 mM potassium citrate–1.0 F potassium hydroxide containing 1.20 mM copper(II). The dashed vertical lines correspond to the consumption of one and two citrate ions per copper atom. Measurements were made at (A) 320 and (B) 340 mμ.

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[1] L. Meites and T. Meites, THIS JOURNAL, **73**, 177 (1951).