[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY OF OHIO CHEMICAL DEPARTMENT]

Spectrophotometric Studies of Uranyl-Urea, -Thiourea and -Guanidine Systems in Absolute Ethyl Alcohol[1]

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Analysis of absorption spectra and continuous variation studies have been employed to determine the stoichiometry of complexes present in uranyl-urea, -thiourea and -guanidine systems in absolute ethyl alcohol. Evidence is presented to show that only one complex is formed with each of the ligands. The urea and thiourea complexes were found to exist in a 1:2 (uranium/organic base) mole ratio. However, the guanidine complex exhibited a stoichiometry of 1:1. In addition, isolation of the compound $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_2$ from alcoholic solution supports the interpretation of the spectral measurements made with the urea system.

It had previously been reported[2] that no evidence of compound formation was observed at room temperature when attempts were made to prepare coordination compounds of uranyl nitrate with various organic ligands in alcoholic solutions. The complexing agents cited were urea, thiourea, guanidine, nitrilotriacetic acid and ethylenediaminetetraacetic acid. In the course of some studies conducted in our laboratories, evidence was obtained for uranyl compound formation with urea, thiourea and guanidine, a summary of which is presented in this paper.

Experimental

Materials.—Uranyl nitrate dihydrate was obtained by vacuum drying the hexahydrate (Baker and Adamson, A.C.S.) over sulfuric acid. The urea (American Cyanamid Company), thiourea (Eastman Kodak Company), guanidine (Eastman Kodak Company) and the absolute alcohol (U. S. Industrial Chemical Company, Reagent Grade, U. S. P.) were used without further purification.

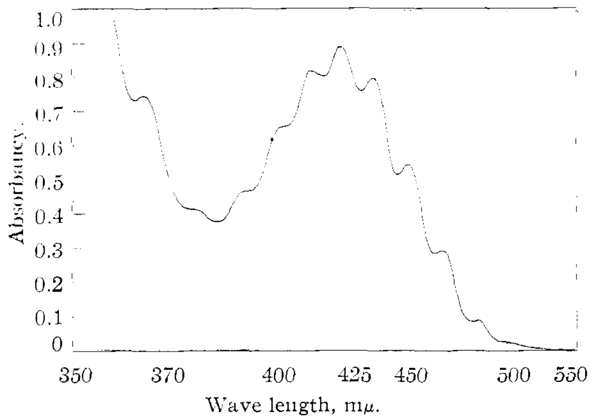

Fig. 1.—The absorption spectrum of a 0.076 *M* uranyl nitrate dihydrate solution in absolute ethyl alcohol. The absorption curves for 0.076 *M* solutions of uranyl-urea and thiourea are so similar that major differences are not detectable throughout the range of 420–600 mμ. Except for minor shifts in some spectral bands, the uranyl-guanidine curve was similar to that shown above.

Analysis.—Urea was determined according to the method of Gertner and Inkovik.[3] The uranium was assayed by ignition to uranouranic oxide (U_3O_8).

Procedure.—In applying Job's[4] technique of continuous variation, 0.076 *M* solutions of uranyl nitrate dihydrate, urea, thiourea and guanidine were prepared and arbitrarily allowed to stand 24 hours in the dark prior to making measurements. The instability of the solutions toward light necessitated this precaution.

Initial spectral transmission curves were obtained with a model DK-2 Beckman spectrophotometer while subsequent studies were made with a model DU Beckman spectrophotometer using Corex cells of 10 mm. light path.

Diureadioxouranium(VI) Nitrate.—To 60 ml. of a 4 *M* alcoholic solution of uranyl nitrate dihydrate, urea (19.7 g.) was added in small increments. A finely divided yellow precipitate was obtained which was filtered and air-dried. This compound melted at 203–205° and was extremely water-soluble.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_2$: U, 46.30; N, 16.34; urea, 23.36. Found: U, 46.07; N, 15.83; urea, 22.51.

In an analogous manner, the addition of thiourea to an alcoholic solution of uranyl nitrate dihydrate resulted in the formation of a deep red-colored solution showing a reaction had taken place. However, all efforts to isolate a uranyl-thiourea complex were unsuccessful.

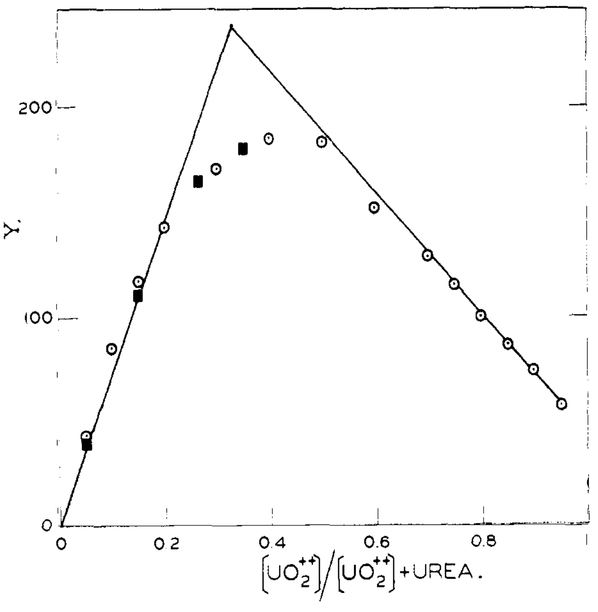

Fig. 2.—Method of continuous variation applied to a uranyl nitrate–urea system. The concentrations (UO_2^{++} + urea) were 0.076 *M* for each solution. The value *Y* represents the difference between the absorbancy of the complex mixture and that of uranium if no reaction had occurred. The solid squares represent solutions of diureadioxouranium(VI) nitrate in molarities equivalent to that of the corresponding uranium concentration used for continuous variation studies. Since these points are coincident with the curve obtained, it provides further supporting evidence for the existence of an MR_2 complex in alcoholic solutions.

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(1) This paper is based on work performed for the Atomic Energy Commission by the National Lead Company of Ohio at Cincinnati, Ohio.

(2) G. W. Watt and A. R. Machel, THIS JOURNAL, **72**, 2801 (1950).

(3) A. Gertner and H. Z. Inkovik, *Anal. Chem.*, **142**, 36 (1954).

(4) P. Job, *Compt. rend.*, **184**, 204 (1927).

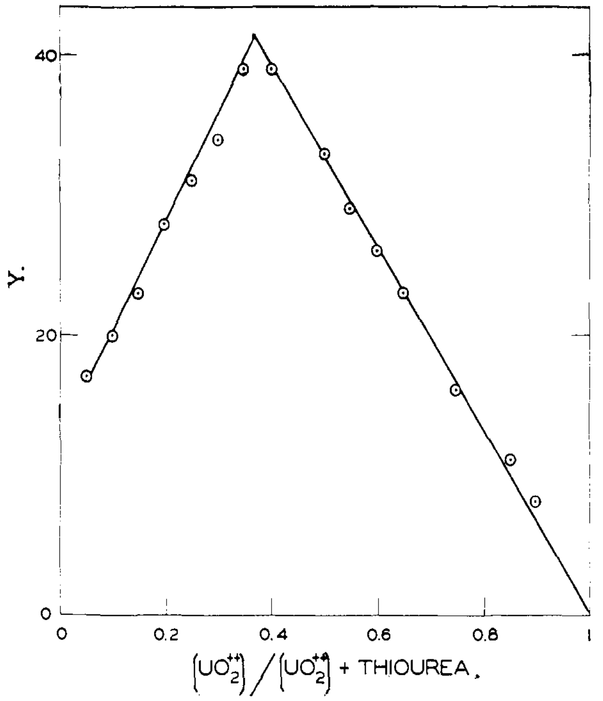

Fig. 3.—Uranyl complex with thiourea.

Solutions of guanidine and uranyl nitrate retained the characteristic yellow color of uranyl compounds and the isolation of a complex was not realized.

Results and Discussion

For the low concentration employed (0.076 *M*) at maximum absorbancy, all the solutions displayed the typical yellow coloration of uranyl compounds. The absorption curves were so similar that *major* differences in the spectral bands were not detectable throughout the range of 420–600 mμ (Fig. 1). It is not surprising, therefore, that Watt and Machel,[2] employing 0.057 *M* solutions, reported no evidence for compound formation in these systems. However, at high concentrations, unlike the urea and guanidine systems, the uranyl-thiourea solution is deep red in color indicating major changes in the spectral curves. Unfortunately, these curves could not be obtained readily with available facilities due to high absorbancy in this concentration region.

For the urea and thiourea system, the differences in spectral bands as compared to uranyl nitrate are so slight as to be virtually undetectable. The presence of new chemical species was indicated by abnormal increases in the absorbancy which were unattributable to the uranyl ion concentration present.

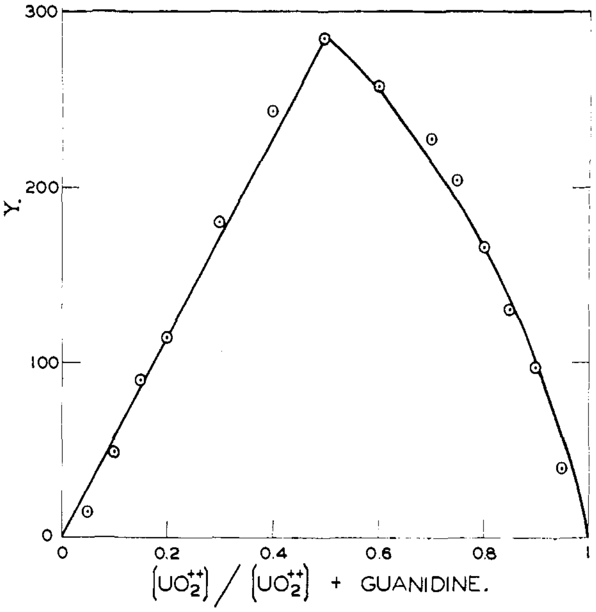

Fig. 4.—Uranyl complex with guanidine.

For the guanidine system, the 356 mμ band vanished and the 366, 368 and 488 mμ bands of uranyl nitrate shifted slightly to 364, 464 and 480 mμ. The 480 mμ band also was characterized by a relatively large increase in extinction coefficient. In the region of 370–465 mμ, there was virtually no change in the spectral bands.

Continuous variation data for uranyl-urea mixtures were examined at 423, 435 and 467 mμ. As seen in Fig. 2, the experimental data show the presence of a uranyl-urea complex with a 1:2 mole ratio as indicated by a maximum at 0.33. The broad maxima are characteristic of compounds that display appreciable dissociation. Isolation of the compound $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_2$ and subsequent absorption studies in solution (Fig. 2) provides supporting evidence for the interpretation of the spectral measurements.

Uranyl-thiourea mixtures examined at 412, 423 and 435 mμ (Fig. 3) indicate the presence of a complex with a uranyl/thiourea mole ratio of 1:2. As in the case of urea, it is very unlikely that other complexes exist in solution. The absence of major differences in the spectral bands, as compared to uranyl nitrate, indicates that if other complexes are present, it would be difficult to detect them in the concentration range utilized (0.076 *M*).

For the uranyl-guanidine system (Fig. 4), there is evidence to support the presence of only one complex, namely, a coördination compound with a 1:1 mole ratio. Spectral measurements were made at 402, 423 and 450 mμ.

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