(1) 15 g. of liquid, b.p. 60° at 38 mm.; (2) 14 g., b.p. 84° at 0.5 mm., $n^{25}{}_D$ 1.4973, n-$Bu_2ViSnCl$[9a]; (3) 15 g. of solid residue, n-Bu_2SnCl_2. Fraction (1) was shown by analysis to be a mixture of Vi_2AsCl and $ViAsCl_2$.

Anal. Calcd. for C_4H_6ClAs: C, 29.21; H, 3.68; Cl, 21.56. Calcd. for $C_2H_3Cl_2As$: C, 13.90; H, 1.75; Cl, 41.02. Found: C, 23.37; H, 3.01; Cl, 28.45.

(d) Vi_3Bi and PBr_3.—To 20 g. of Vi_3Bi, at −30° under nitrogen, was added dropwise 11 g. of PBr_3. A vigorous reaction ensued. The reaction mixture initially turned yellow, but before the addition was completed, strong fuming commenced with simultaneous blackening and solidification of the mixture. Only a button of metallic bismuth could be isolated.

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

Coördination Compounds of Uranium with Organic Bases in Aqueous Solution[1]

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The stoichiometry of complexes present in uranyl-urea, -thiourea and -guanidine systems in aqueous solution has been determined by absorption spectra and Job's method of continuous variation. Only a combining ratio of 1:4 is evident in the uranyl-urea system at pH 3.5. Confirmation was obtained by isolation of the compound $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_4$. In the uranyl-thiourea system, at pH 3.5, a complex having a uranyl/thiourea combining ratio of 1:4 exists. A uranyl-guanidine complex with a 1:1 mole ratio was also found.

In a previous communication[3] the complexes existing in uranyl-urea, -thiourea and -guanidine systems in absolute ethyl alcohol were reported. These systems were reinvestigated in aqueous media because it has been shown[4] that many uranyl complexes which are formed in non-aqueous solvents differ greatly from those formed in water.

Experimental

Materials.—Uranyl nitrate hexahydrate (Baker and Adamson, A.C.S.), urea (American Cyanamid Company), thiourea (Eastman Kodak Company) and guanidine (Eastman Kodak Company) were used without additional purification.

Analysis.—The method of Gertner and Inkovik[5] was used for the determination of urea. The uranium was assayed by ignition to urano-uranic oxide (U_3O_8).

Procedure.—The method of continuous variation[6] was employed using 0.300 M aqueous solutions of uranyl nitrate hexahydrate, urea, thiourea and guanidine which were adjusted to pH 3.5 by the addition of sodium hydroxide. The ion strength, in all cases was adjusted to 0.8 with sodium chloride.

Spectral-transmission curves were obtained using a model DK-2 Beckman spectrophotometer and Corex cells of 10 mm. light path.

Diaquotetraureadioxouranium(VI) Nitrate.—To 100 ml. of an 1.7 M aqueous solution of uranyl nitrate hexahydrate, 51 g. of urea was added with continuous stirring. The resulting solution was permitted to stand for 24 hours, during which time a yellow precipitate was obtained which was filtered and air dried. This extremely water-soluble compound had a melting point range of 74–76°.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_4 \cdot 2H_2O$: U, 35.51; N, 20.90; urea, 35.84. Found: U, 35.49; N, 20.83; urea, 35.78.

Tetraureadioxouranium(VI) Nitrate.—The dihydrate was completely dehydrated in an oven at 110° for two hours.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot [CO(NH_2)_2]_4$: U, 37.53; N, 22.08; urea, 37.87. Found: U, 37.50; N, 22.01; urea, 37.81.

Results and Discussion

The spectral curves of the uranyl-urea, -thiourea and -guanidine systems were so similar to that of uranyl nitrate solutions that *major* differences in the spectral bands were not detectable between 420 and 600 mμ. Because of the high absorption for the 0.3 M solutions used, the operational range was limited to 450–600 mμ. However, the increase in extinction coefficients was sufficient to determine the complexes present, utilizing two peaks at 464 and 485 mμ as reference points. Since urea, thiourea and guanidine do not absorb in the visible region, the problem was greatly simplified.

For the uranyl-urea system, application of the method of continuous variation resulted in a maximum at 0.2 (Fig. 1) indicating the presence of a single complex with a 1:4 uranyl/urea mole ratio.

This conclusion was strengthened by the isolation of the compound diaquotetraureadioxouranium(VI) nitrate whose subsequent dissolution in appropriate molarities yielded spectral data coincident with the forementioned curve.

It should be noted that similar studies of the same system in alcoholic solutions resulted in the subsequent isolation of a complex (MR_2) with a 1:2 mole ratio.

One can explain the absence of the MR_2 complex in aqueous media on the basis of its instability and dissociation to MR_4 as

$$MR_2 \longrightarrow {}^1/_2MR_4 + {}^1/_2M \qquad (2)$$

where

$$M = UO_2^{++} \quad MR_2 = UO_2[CO(NH_2)_2]_2{}^{++}$$
$$MR_4 = UO_2[CO(NH_2)_2]_4{}^{++}$$

The instability of MR_2 in water was experimentally verified by two different methods. In one case, the addition of sufficient urea to MR_2 solutions, to

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

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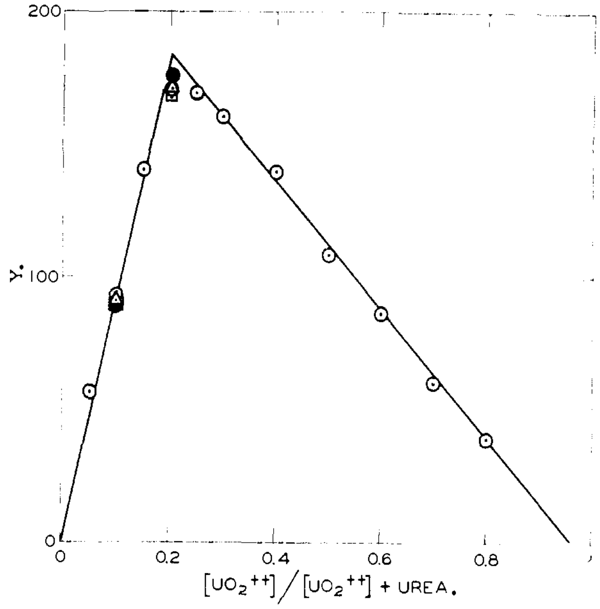

Fig. 1.—Y-curve for the uranyl-urea system: O, continuous variation values; ●, tetraureadioxouranium(VI) nitrate in molarities equivalent to that of the corresponding uranium concentration used for continuous variation studies; ⊡, diureadioxouranium(VI) nitrate (0.03 and 0.06 M with respect to uranium) + urea (0.27 and 0.24 M) see text; △, tetraureadioxouranium(VI) nitrate (0.015 and 0.03 M with respect to uranium) + uranyl nitrate (0.015 and 0.03 M) + urea (0.27 and 0.24 M), see text.

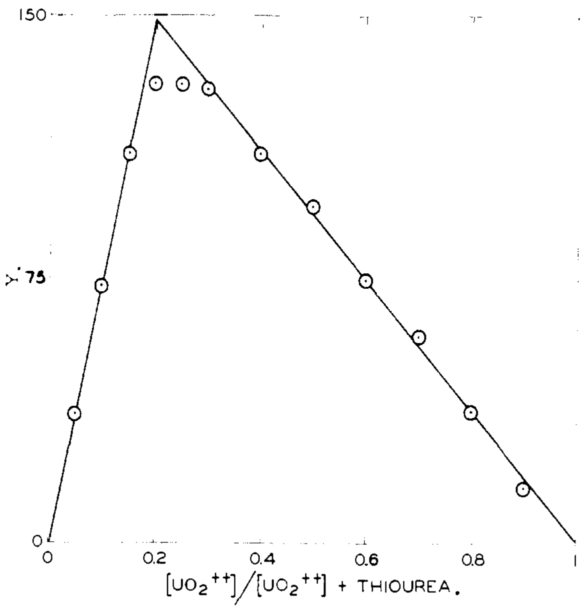

Fig. 2.—Y-curve for the uranyl-thiourea system.

yield the continuous variation conditions previously used, gave the expected Y values for the MR_4 complex. In the second case, synthetic solutions equimolar with respect to MR_4 and uranyl nitrate gave, upon addition of the appropriate amount of urea, Y-values which substantiated equation 1. In both cases, spectral data were obtained immediately after preparation of solutions indicating that dissociation of the MR_2 complex in water occurs rapidly. In view of the results obtained, one might postulate that MR_4 undergoes dissociation in ethyl alcohol as

$$MR_4 \longrightarrow MR_2 + 2R \qquad (2)$$

A solution of MR_4 in ethyl alcohol gave the Y-value of MR_2 as predicted from equation 2.

Data obtained for the uranyl–thiourea system also showed a maximum at 0.2 (Fig. 2) indicating the presence of a single species MR'_4. Since a complex, MR'_2, was shown to be present in alcoholic solution,[3] inability to isolate either the MR'_2 or MR'_4 compounds prevented studies similar to those described above. Therefore, one can only assume that in a manner analogous to uranyl-urea systems, the dithioureadioxouranium(VI) ion is unstable in water and the tetrathioureadioxouranium (VI) ion dissociates in alcohol.

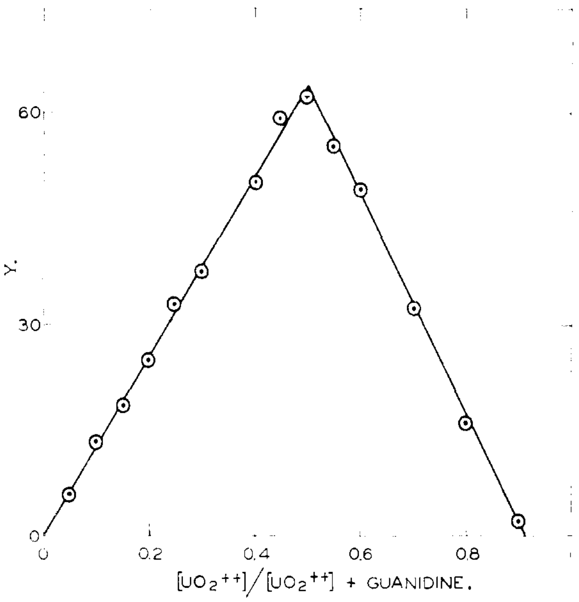

Fig. 3.—Y-curve for the uranyl–guanidine system.

There is evidence to support the presence of a complex with a 1:1 mole ratio in the uranyl-guanidine system (Fig. 3). This complex was also shown to exist in alcoholic solutions.

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