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Studies of the Complex Formation between Uranium and Thiosalicylic Acid

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Orange-yellow coloured complexes formed by the interaction of uranium and thiosalicylic acid in 40% ethanol have been investigated by spectrophotometric, potentiometric, and magnetic susceptibility measurements. Spectrophotometric studies reveal that a 1 : 1 complex is mainly formed below pH 4.5, while at higher pH's (5.5) a 1 : 2 (metal : ligand) complex is mainly formed. Magnetic susceptibility measurements point towards the diamagnetic character of the complexes. The stereochemical configuration of the complex ions has been discussed.

Not much work has been reported on the complexing properties of sulphur-containing ligands and uranyl ions. However, a few ligands, like thiourea,1) thiocyanate,2) ammonium diethanoldithiocarbonate,3) and thiomalic acid,4) which contain sulphur as one of the donor atoms have been used to study the chelating properties of uranyl ions with sulphur.

In the present communication, attempts will be made to study the complex formation between thiosalicylic acid (hereafter abbreviated as TSA) and uranyl ions. Detailed spectrophotometric and potentiometric studies show that a 1 : 1 complex is formed below pH 4.5, while a 1 : 2 (metal : ligand) complex is formed above pH 5.5. However, at an intermediate pH of 5, both the complex ions exist in equilibrium and an apparent ratio of 2 : 3 of uranyl ions to TSA is obtained.

Reagents and Apparatus. A stock solution of uranyl nitrate was prepared from an Anala-R grade (B.D.H.) reagent and was standardised gravimetrically5) using the oxine method. Standard solutions of TSA were freshly prepared from a 99.7% pure reagent procured from Evans Chemetics, Inc., New York, by direct weighing. The hydrogen ion concentration was adjusted with very dilute solutions of sodium hydroxide and hydrochloric acid. Absorbance measurements were made with a Unicam SP 600 spectrophotometer. A Leeds and Northrup pH Meter was used for the pH measurements and for the potentiometric titrations. The ethanol concentration was kept at 40% for all the solutions except in potentiometric titrations, where the medium was 50% ethanol.

Absorbance Measurements. Solutions containing uranyl ions and TSA in a molar ratio of 1 : 10 were prepared at different pH's, and their detailed spectra were taken over a wavelength range of 400—750 mμ (Figs. 1, 2, 3). From various measurements, it has been observed that the complex shows a maximum absorbance at 420 mμ in the pH range from 4.2 to 5.0. Below and above this range the maximum absorbance appears at 410 mμ. This indicates that two complexes might be formed at different pH values. Job's continuous-variation method6) at different pH's indicates that

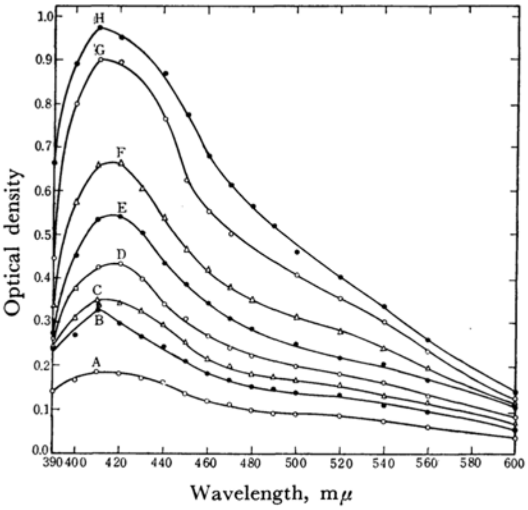

Fig. 1

Curve	pH	Curve	pH
A	=3.5	B	=3.8
C	=4.0	D	=4.3
E	=5.0	F	=5.8
G	=6.5	H	=8.3

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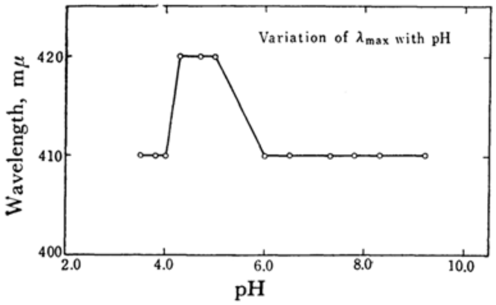
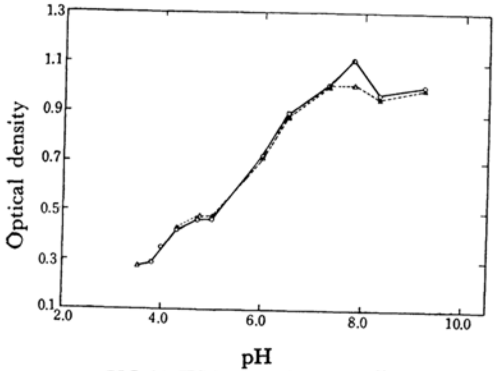


Fig. 2



UO_2^{2+}-TSA complex pH-effect

Fig. 3

—○— at 410 mμ --△-- at 420 mμ

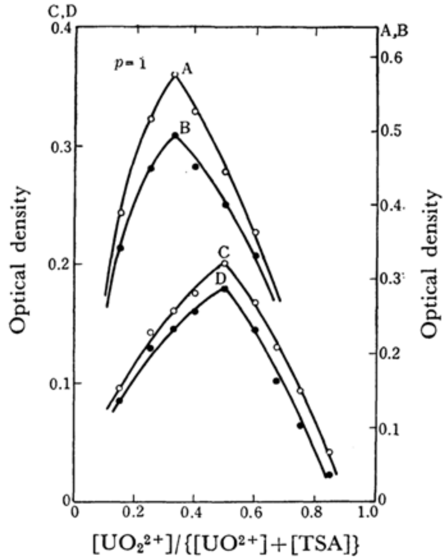


Fig. 4. Composition by Job's method.
Initial concn. of the reactants$=4\times10^{-2}$ M
Total volume of the solutions$=12.5$ ml
pH=6.5 pH=3.5
A ○ 410 mμ C ○ 410 mμ
B ● 430 mμ D ● 430 mμ

a 1 : 1 complex is formed below pH −4.5, and that above pH 5.5, metal and the ligand are present in a 1 : 2 ratio (Fig. 4). At an intermediate pH value of 5, the apparent molar ratio of the uranyl ions to TSA is 2 : 3 (Fig. 5), thereby indicating either an equilibrium between the two complex ions or the formation of a polynuclear species. (Here it may be mentioned that no absolute demarcation can be drawn between the different pH values and the formation of the complex ions. It may be that at lower pH's (<4.5) the 1 : 1 complex is more stable and hence dominates the other one. At higher pH's, the 1 : 2 complex may be more stable than that of 1 : 1 and, therefore, more prominent.) The readings were taken against a 40% ethanol-water blank, and the absorbance (though very small) due to ligand and uranyl ions was taken into consideration before drawing the final plots.

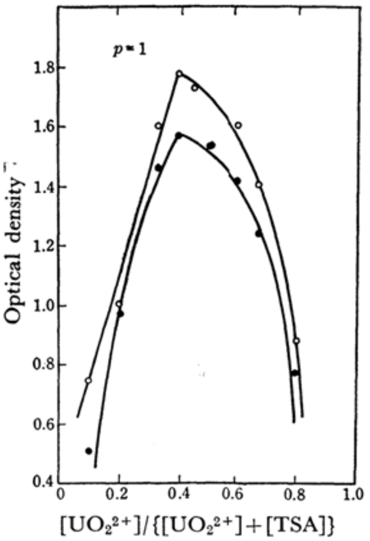


Fig. 5. Initial concentrations of the reactants and total volume of the solutions is the same as given for Fig. 1.
pH=5.0: ○ 410 mμ, ● 430 mμ

The colour of the uranyl-TSA system fades away with time at all pH's. Hence, the readings were taken within ten minutes of the preparation of the solutions. By making absorbance measurements at different time intervals, it has been concluded that the 1 : 1 complex is kinetically more stable than the 1 : 2 one.

Potentiometric Titrations. Potentiometric titrations were carried out in a nitrogen atmosphere. The ionic strength of the solutions was kept constant by adding sodium perchlorate and perchloric acid in 50% ethanol. The titrations were carried out with the standard sodium hydroxide solution in 50% ethanol.

On titrating the solution containing metal and ligand in the molar ratio of 1 : 1, there was a precipitate in the solution above pH 5, showing the hydrolysis of the 1 : 1 complex. On the other

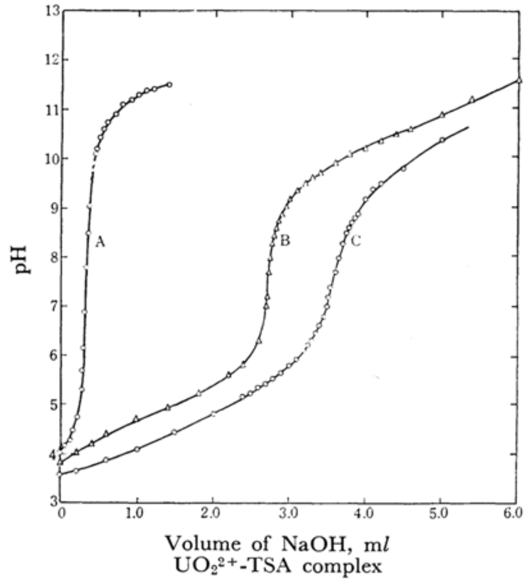


Fig. 6. Potentiometric titrations with 50% ethanolic sodium hydroxide (M/10).

A Contains 3 ml (M/100) $HClO_4$ +2.0 ml (M/25) $NaClO_4$
B Contains 3 ml (M/100) $HClO_4$ +2.0 ml (M/25) $NaClO_4$+5 ml (M/20) TSA
C Contains 3 ml (M/100) $HClO_4$ +2.0 ml (M/25) $NaClO_4$+5 ml (M/20) TSA +5 ml (M/100) UO_2^{2+}

Total volume=110 ml, medium 50% ethanolic

hand, no precipitation was observed when the solutions containing metal and ligands in the ratios of 1 : 2 and 1 : 5 (Fig. 6) were titrated. This clearly shows that the 1 : 2 complex is stable towards hydrolysis at higher pH's. The following equations have been proposed to explain the potentiometric data:

$$H_2A \rightleftharpoons HA^- + H^+$$

$$UO_2^{2+} + HA^- \rightleftharpoons [UO_2A] + H^+$$

(hydrolyses at higher pH's)

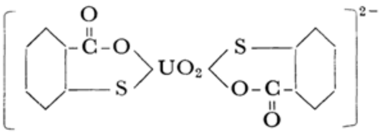
$$UO_2^{2+} + 2\,HA^- \rightleftharpoons [UO_2A_2]^{2-} + 2\,H^+$$

(stable towards hydrolysis)

Magnetic - Susceptibility Measurements. Magnetic-susceptibility measurements of the complex ions were made using Gouy's method. The final concentration of the solutions with respect to uranyl ions was M/25 in 40% ethanol. Measurements on the 1 : 1 complex ion (at pH 4.0) and the 1 : 2-complex ion (at pH 6.0) show that these ions have a slight paramagnetism, $\mu_{eff}=0.4$ B.M. for 1 : 1 and 0.6 B.M. for 1 : 2, at 29°C.

Discussion

Due to the complex nature of the splitting of energy levels in actinides and the fact that the 5f and 6d levels are very close in energy, the stereochemistry of these elements is complicated. Lister,7) from magnetic-susceptibility measurements and spectroscopic data, has concluded that moments corresponding to one or no unpaired electrons should be obtained according to whether the number of electrons is odd or even. In the present case, the 1 : 1 complex ion and the 1 : 2 complex ion have magnetic moments with values of 0.4 B.M. and 0.6 B.M. respectively, which may be due to the temperature-independent paramagnetism8,9,11) of uranium(VI). Further, Nyholm10) is of the view that uranium(VI) has a marked tendency to form a linear $(O=U=O)^{2+}$ ion, which then remains as a unit in which the uranium atom is bicovalent, or it may attach five more ligands in a plane, making a pentagonal bipyramid. For uranium in the sexavalent state, however, octahedral co-ordination is also well known. In view of the fact that the complexes are essentially diamagnetic and that a seven coordination is less likely with strong co-ordinating ligands, the complex ions may be assumed to be octahedral (spin-paired). Accordingly, the 1 : 1 complex ion may be assumed to contain two molecules of water, and the 1 : 2 complex ion may be represented by the formula:



Since more than one complex ion has been detected in the solution, no attempt was made to calculate the stability constants from spectrophotometric and potentiometric data.

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