The Synthesis of 2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic Acid as a New Reagent and Its Thorium Complex

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Neo-thorin (2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-benzenearsonic acid)[1,2] has been applied as a reagent for the determination of thorium, zirconium and uranium. The arsono group, $-AsO_3H_2$, is most interesting as a functional group for thorium. The oxyacetic acid group, $-OCH_2COOH$, is also reactive with this element.

The present paper will describe the preparation of 2-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid, and the determination of the acid dissociation constant of the reagent by the spectrophotometric method. The complex of the reagent with thorium will also be studied spectrophotometrically.

The Synthesis of the Reagent.—The acetylation of *o*-aminophenol with acetic anhydride afforded the acetyl derivative, which was converted into *o*-acetaminophenoxyacetic acid[3] by reaction with monochloroacetic acid in an alkaline medium.

The potassium salt of *o*-aminophenoxyacetic acid[4] was prepared by the reaction of potassium hydroxide and the lactam of *o*-aminophenoxyacetic acid, which had been obtained by the hydrolysis of *o*-acetaminophenoxyacetic acid with hydrochloric acid.

2-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid was prepared by the coupling of chromotropic acid with diazotized potassium *o*-aminophenoxyacetate. Greenish needles of the disodium salt of the product were obtained by recrystallization from water.

The Spectral Properties of the Reagent and Its Acid Dissociation Constant.—The absorption

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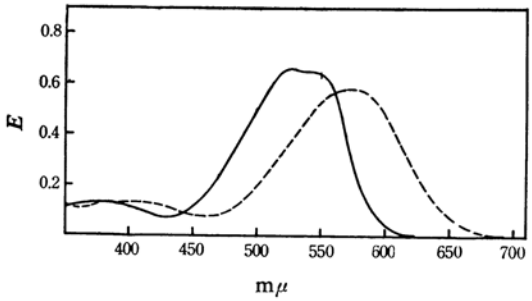

Fig. 1. Absorption spectra of the reagent and its thorium complex (broken line).
—— 2.0×10^{-5} mol./l., pH 2.9
---- Thorium concn. to the reagent concn. =4 : 1, pH 2.9

spectra of the reagent solution (2.0×10^{-5} mol./l., pH 2.9), as well as its thorium complex, are shown in Fig. 1.

The first and second dissociation constants of the reagent, pK_{a_1} and pK_{a_2}, have been estimated spectrophotometrically to be 2.9_9 and 9.7_6 (25°C, $\mu=0.1$) respectively.

The Spectral Properties of the Thorium Complex.—On the addition of thorium to the reagent solution, the absorption maxima (525 mμ) shifted toward longer wavelengths. The curve shows an absorption maximum at 575 mμ.

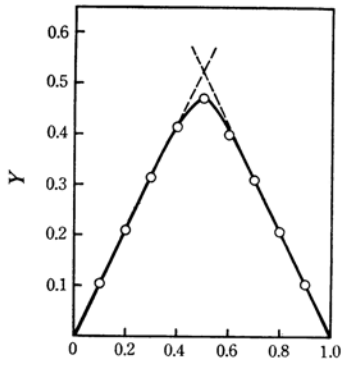

Fig. 2. Continuous variation method. Thorium concn.+the reagent concn. $=5.0\times10^{-5}$ mol./l. pH 2.7, 600 mμ

The mole ratio of thorium to the reagent was confirmed by the continuous variation method (Fig. 2) and by the mole ratio method at the pH values of 2.7 and 3.2 respectively; the results obtained indicate the formation of a 1 : 1 complex.

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