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A Spectrophotometric Study of the Uranyl Chelate of 2-(1,8-Dihydroxy-3,6-disulfo-2-naphthylazo)-phenoxyacetic Acid

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2-(1,8-Dihydroxy-3,6-disulfo-2-naphthylazo)-phenoxyacetic acid reacts with the uranyl ion in an acidic medium to form a violet chelate. The composition of the chelate is 1:1 in the molar ratio. The apparent stability constants over the pH range from 3.4 to 5.2 and the formation constant of the chelate, are estimated spectrophotometrically at 25°C and an ionic strength of 0.1 by the use of KNO_3. The value of the formation constant was calculated as 1.25×10^{10} from the apparent stability constants.

A new chelating agent, 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-phenoxyacetic acid [PAC],[1] one that was first introduced by our laboratory, reacts with several metal ions to give its colored chelates. The apparent stability constants of a stable 1 : 1 chelate with the thorium ion, and the use of the chelate in the determination of micro amounts of the fluoride ion, have been reported in previous papers.[2,3]

This paper will describe the properties of the reagent and the reaction between the reagent and the uranyl ion. The acid form of the reagent has three molecules of the water of crystallization; it loses two of them at 135°C, and one at 175°C. Moreover, the anhydride gradually decomposes above 190°C. The reagent forms a 1 : 1 violet chelate with the uranyl ion between the pH values of 3.4 and 5.2; the apparent stability constants, log K', of the chelate over that pH range are measured spectrophotometrically.

In the pH range measured, the reagent exists predominantly as the diprotonated form, considering the value of its acid dissociation constants. From the relation between log K' and pH, however, it was found that the uranyl ion displaces one proton from the reagent in that pH range to form a chelate. This fact shows that the other proton existing between two oxygen atoms of chromotropic acid does not take part in the formation of the chelate.

The formation constant of the chelate is calculated from the values of the apparent stability constants to be 1.25×10^{10} at 25°C and at an ionic strength of 0.1 (KNO_3).

Experimental

Reagent. A pure reagent, 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-phenoxyacetic acid·$3H_2O$, was obtained in the form of black violet needles after purification from a concentrated hydrochloric acid. The purity was checked by flame analysis and elementary analysis.

Found: C, 39.13; H, 3.65; N, 5.07%. Calcd for $C_{18}H_{20}O_{14}N_2S_2$: C, 39.13; H, 3.73; N, 5.15%.

Uranyl Nitrate Solution. A standard stock solution of uranyl was prepared by dissolving the uranyl nitrate (E. Merck's guaranteed-grade reagent) in deionized distilled water. The standardization of the uranyl solution consisted of the precipitation of the hydrous oxide, followed by ignition to oxide.[4]

Apparatus. *Spectral and pH Measurements.* A Hitachi Model EPS-2 automatic recording spectrophotometer was used for the measurement of the absorption spectra. For quantitative measurements a Hitachi Model 139 spectrophotometer with 1-cm glass cells was used. The pH was measured by using a Towa-Denpa Model HM-8 glass electrode pH meter.

Thermal Analysis. The thermal analysis was carried out using a thermal balance and a differential thermal analyzer, both made by Rigaku Denki.

Procedure. The uranyl chelate solution at various pH values was prepared as follows. Five mililiters of a 2.7×10^{-4}M uranyl nitrate solution and the same volume of a 2.7×10^{-4}M reagent solution were placed in a 50-m*l* volumetric flask; then a 1M potassium nitrate solution was added to maintain the ionic strength at 0.1. The pH of the solution was then adjusted from 3.4 to 5.2 by the addition of nitric acid or of a sodium hydroxide solution. The solution was finally diluted to 50 m*l* with deionized distilled water. After the solutions had been allowed to stand for one hour at

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1) K. Tôei, H. Miyata, T. Shibata and S. Miyamura, This Bulletin, **38**, 334 (1965).

2) H. Miyata, *ibid.*, **40**, 1875 (1967).

3) T. Hayami and Y. Shimoishi, *ibid.*, **40**, 1139 (1967).

4) W. W. Scott, "Standard Methods of Chemical Analysis," D. van Nostrand Co., Inc., New York (1939), p. 1022.

25°C, their absorbances for water and the pH of the solutions were measured.

Results and Discussion

The Water of Crystallization of the Reagent. In order to confirm the water of crystallization of the reagent, a thermal analysis was employed. As is shown in Fig. 1, the curve from a thermal balance had inflection points in changes in the sample weight over the temperature range between 50 and 210°C. The thermal differential curves showed four changes, at 80, 135, and 175°C corresponding to an endothermic change, and above 190°C, corresponding to a exothermic change. The first endothermic change, at 80°C, corresponds to the elimination of the hydrated water of the reagent, while the second and the third changes denote the elimination of the water of crystallization. However, the reagent after the treatment at 60°C in a vacuum has no inflection points in changes in weight below 180°C. From these results, it was found that the reduced weight of the sample at 135°C and 175°C includes the weight of three moles of water of crystallization. Above 190°C, the reagent gradually decomposes.

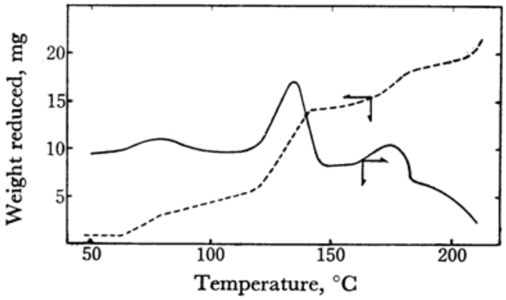

Fig. 1. Thermal analysis of the reagent.
--- Thermal balance curve
—— Differential thermal curve

The Acid Dissociation Constants. The reagent dissociates in water as follows:

$$H_3R^{2-} \rightleftharpoons H_2R^{3-} + H^+$$
$$H_2R^{3-} \rightleftharpoons HR^{4-} + H^+$$

and

K_{a1} and K_{a2} represent, respectively, the dissociation of the carboxyl group and that of one of the naphtholic hydroxyl groups in the reagent. The values of pK_{a1} and pK_{a2} were found to be 2.99 and 9.76[2] respectively at 25°C and μ= 0.1.

Absorption Spectra. The absorption spectra of the solutions containing uranyl and the reagent in a molar ratio of 1 : 1 are shown in Fig. 2 over the pH range from 3.4 to 5.2. The curves show that the absorbance at 600 mμ becomes higher with an increase in the pH value.

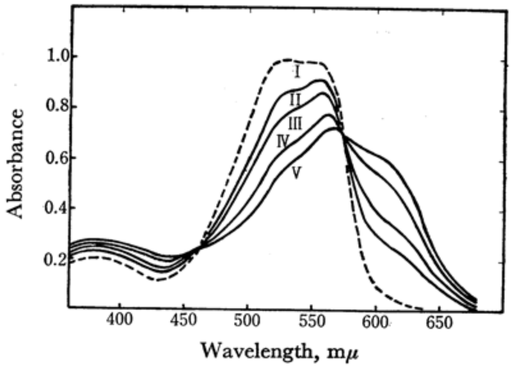

Fig. 2. Absorption spectra of the reagent (broken line) and its uranyl complex (solid line).
I 2.7×10^{-5} reagent solution at pH 5.69
II—V The solution containing uranyl and the reagent (1 : 1) at pH's 3.87, 4.01, 4.52 and 5.02 respectively.

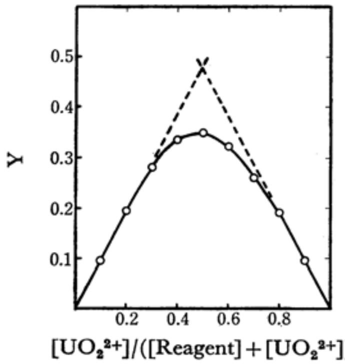

Fig. 3. Continuous variation method.
at 605 mμ, pH 5.2.
Total uranyl and the reagent concn. = 2.7×10^{-5} mol/*l*

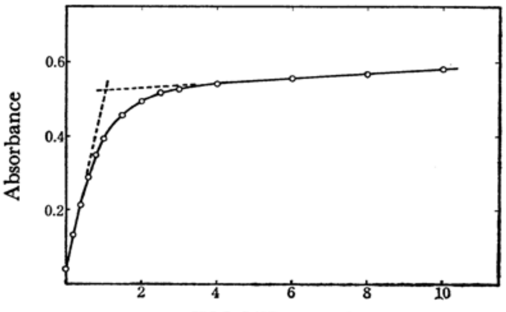

Fig. 4. Mole-ratio method.
at 605 mμ, pH 5.2.
The reagent concn. = 2.7×10^{-5} mol/*l*
Uranyl concn. varied

The Stability of the Color. The color of the complex reached its maximum within a few minutes after mixing; the absorbance then remained almost constant for at least two hours.

The Composition of the Chelate. Figure 3 shows the results obtained by the continuous variation method, the maximum absorbance of the chelate being obtained at a molar ratio of 1 : 1. The molar-ratio method in Fig. 4 was also employed at pH 5.1 for various uranyl concentrations. The results again clearly indicated the formation of a 1 : 1 chelate.

The Apparent Stability Constants. The apparent stability constant, K', and the acid dissociation constants, K_{a1} and K_{a2}, are expressed as follows:

$$K' = [\mathrm{MHR}]/[\mathrm{M}][\mathrm{H_3R} + \mathrm{H_2R} + \mathrm{HR}] \qquad (1)$$

$$K_{a1} = [\mathrm{H}][\mathrm{H_2R}]/[\mathrm{H_3R}] \qquad (2)$$

$$K_{a2} = [\mathrm{H}]/[\mathrm{HR}]/[\mathrm{H_2R}] \qquad (3)$$

where the ionic charge was neglected for the sake of convenience. The total concentrations of the reagent and uranyl are given as:

$$C_\mathrm{R} = [\mathrm{H_3R}] + [\mathrm{H_2R}] + [\mathrm{HR}] + [\mathrm{MHR}] \qquad (4)$$

$$C_\mathrm{M} = [\mathrm{M}] + [\mathrm{MHR}] \qquad (5)$$

where [M] represents the uranyl ion concentration. Under the experimental conditions studied, at pH values below 6 [HR] can be disregarded, judging from the pK_{a2} value (9.76[1]).

On the other hand, the absorbance of the chelate solution, E, is given by Eq. (6). The uranyl ion gives no absorption at around 605 mμ and ε_M[M] can be neglected.

$$E = \varepsilon_{\mathrm{H_3R}}[\mathrm{H_3R}] + \varepsilon_{\mathrm{H_2R}}[\mathrm{H_2R}] + \varepsilon_{\mathrm{MHR}}[\mathrm{MHR}] \qquad (6)$$

where $\varepsilon_{\mathrm{H_3R}}$, $\varepsilon_{\mathrm{H_2R}}$, and $\varepsilon_{\mathrm{MHR}}$ are the molar absorption coefficients of the reagent and the uranyl chelate respectively. The value of $\varepsilon_{\mathrm{MHR}}$ was calculated from the absorbance of a solution in which an excess amount of uranyl was added to the reagent; the complete formation of the chelate from the reagent could be assumed.

The apparent stability constant was estimated from the following equation by substituting Eqs. (2)−(6) into Eq. (1):

$$K' = [C_\mathrm{R} - A]/[C_\mathrm{M} - (C_\mathrm{R} - A)]A \qquad (7)$$

where:

$$A = (1 + K_{a_1}/[\mathrm{H}])(E - \varepsilon_{\mathrm{MHR}}\, C_\mathrm{R})/[\varepsilon_{\mathrm{H_3R}} + \varepsilon_{\mathrm{H_2R}}(K_{a_1}/[\mathrm{H}]) - \varepsilon_{\mathrm{MHR}}(1 + K_{a_1}/[\mathrm{H}])]$$

The constants, log K', estimated from Eq. (7) are listed in Table 1.

The Relation between the Apparent Stability and the Acid Dissociation Constants. Owing to the existence of a strong hydrogen bridge between two oxygen atoms of the chromotropic acid of the reagent, the remaining naphtholic hydroxyl group, corresponding to K_{a3}, does not dissociate under ordinary experimental conditions. Therefore, the reagent may be considered to be a tetrabasic acid; the reaction steps and the probable structure of chelate are:

$$\mathrm{UO_2}^{2+} + \mathrm{H_2R}^{3-} \rightleftarrows \mathrm{UO_2HR}^{2-} + \mathrm{H}^+,$$

under the present experimental conditions (in the pH range between pK_{a1} and pK_{a2}).

In these experimental conditions (pH values from 3.4 to 5.2), the reagent exists predominantly in the diprotonated form and uranyl ion may displace one proton to form a 1 : 1 chelate.

TABLE 1. APPARENT STABILITY CONSTANT AND STABILITY CONSTANT OF THE URANYL CHELATE (25°C, μ=0.1)

$C_\mathrm{R} = C_{\mathrm{UO_2}} = 2.70 \times 10^{-5}\,\mathrm{M}$

Values of constants employed in the calculation.

$K_{a_1} = 1.002 \times 10^{-3}$ $\varepsilon_{\mathrm{H_3R}} = 9.778 \times 10^2$
$K_{a_2} = 1.738 \times 10^{-10}$ $\varepsilon_{\mathrm{H_2R}} = 1.463 \times 10^3$
$\varepsilon_{\mathrm{MHR}} = 2.230 \times 10^4$

pH	E	log K'	log K
3.41	0.090	3.64	10.13
3.48	0.105	3.76	10.16
3.66	0.126	3.94	10.13
3.92	0.175	4.19	10.05
4.11	0.214	4.39	10.07
4.44	0.289	4.73	10.07
4.54	0.310	4.82	10.07
4.85	0.361	5.06	10.09
5.03	0.380	5.16	10.09
5.19	0.394	5.23	10.11

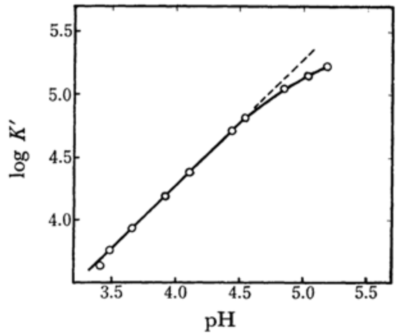

Fig. 5. Relationship between pH and log K. at 25°C, μ = 0.1.

In Fig. 5, the value of log K' is plotted against the pH value. The experimental data obtained are in good agreement with the curve whose slope was 1. This supports the assumption of the above equation, that only a $\mathrm{UO_2HR}^{2-}$ chelate is formed. Above pH 4.8, uranyl hydroxide begins to precipitate, so the value of log K' gradually becomes smaller.

The Formation Constant. The formation constant of the uranyl chelate, K, was represented as follows:

$$K = [\mathrm{MHR}]/[\mathrm{M}][\mathrm{HR}] \qquad (8)$$

$$K = K'\alpha_\mathrm{M}\alpha_\mathrm{H} \qquad (9)$$

where:

$$\alpha_M = 1 + [OH][M]K^{OH}_{M_2(OH)} + [OH]^2[M]K^{2OH}_{M_2(OH)_2} \quad (10)$$

$$\alpha_H = 1 + K_{a_2}/[H] + K_{a_1}K_{a_2}/[H]^2 \quad (11)$$

As to α_M, the second and third terms of Eq. (10) can be neglected when the pH value is lower than 4.5 ($\alpha_M=1$), but they cannot be neglected above pH 4.5, as the hydroxo uranyl complexes $M_2(OH)$ and $M_2(OH)_2$ are formed. Therefore, the values of α_M above pH 4.5 were calculated from Eq. (10) using the values of $K^{OH}_{M_2(OH)}=1.2\times10^{10}$ and $K^{2OH}_{M_2(OH)_2}\times1.0\times10^{22}$.[5]

α_H was calculated from Eq. (11), using the values of $K_{a1}=1.002\times10^{-3}$ and $K_{a2}=1.738\times10^{-10}$.[2]

Thus, the values of the formation constant were calculated from Eq. (9). They are also listed in Table 1. The average value of the constant is found to be 1.25×10^{10}.

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5) S. Ahrland, S. Hietanen, L. G. Sillen, *Acta Chem. Scand.*, **9**, 177 (1955).