

SHORT NOTES

Spectrophotometric Study of the Complex Formation between Uranyl Ions and β -Resorcylic Acid

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Complexes of β -resorcylic acid with titanium¹, ferric²⁻³, mercuric⁴, and aluminium⁷ ions have been studied. No work appears to have been done on the complex formation of uranyl ions with β -resorcylic acid. This communication deals with a spectrophotometric study of the complex formation of uranyl ions with β -resorcylic acid.

Procedure.—Standard solutions of uranyl nitrate were prepared by direct weighing of analysed sample of uranyl nitrate (A.R.). Uranium content was estimated gravimetrically⁸. β -Resorcylic acid, prepared from resorcinol by the potassium bicarbonate method, was recrystallised from water and dried. The individual solutions and mixtures were kept immersed in T & M thermostat at $25^\circ \pm 0.1^\circ$ for $\frac{1}{2}$ hr. (ca) to attain equilibrium. The absorption spectra were recorded on a Unicam SP 500 spectrophotometer. All pH measurements were made with a Beckman pH-meter, model H-2. The pH was adjusted by adding suitable amounts of a dilute NaOH solution. The composition of the complex was studied by Job's method⁹, mole-ratio method¹¹, and slope-ratio method¹².

Nature of the Complexes Formed.—Mixtures containing 1:1, 1:2, and 1:3 ratios of uranium to BRA were prepared at pH 4.2, keeping the total volume 50 ml in each case. In each case the maximum absorbance was found between 454 m μ and 478 m μ and minimum absorbance at 462 m μ . The isoabsorptive region of (454 m μ to 478 m μ) of maximum absorbance clearly indicates that in the colour system under investigation, the reagent forms only one complex in solution with uranyl ion under the conditions of study.

Influence of H-ion Concentration on the Stability of the Complex.—The absorbance of mixtures containing uranyl nitrate and the reagent in 1:1 ratio at different pHs were measured at 478 m μ . The maximum absorbance was at pH 4.2. The complex is sensitive even to a small change in pH.

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Composition of the Complex

Job's Method.—Optical densities of the solutions (*pH* 4.2), prepared by mixing *x* ml of 0.01*M*-BRA solution with (12−*x*) ml of 0.01*M* uranyl nitrate solution were determined at 452 *mμ*, 478 *mμ*, and 500 *mμ* against corresponding strength of uranyl nitrate solutions of *pH* 4.2. The final volume of the mixture was made to 50 ml with distilled water. Absorbance values were plotted against the ratios of concentrations of uranyl ion to the total concentration of the reagent and uranyl ion showed maximum at the ratio of 0.5, indicating the formation of 1:1 complex. With 0.005 *M* solutions of the reactants, the same conclusion was arrived at. Results obtained are shown in Fig. 1.

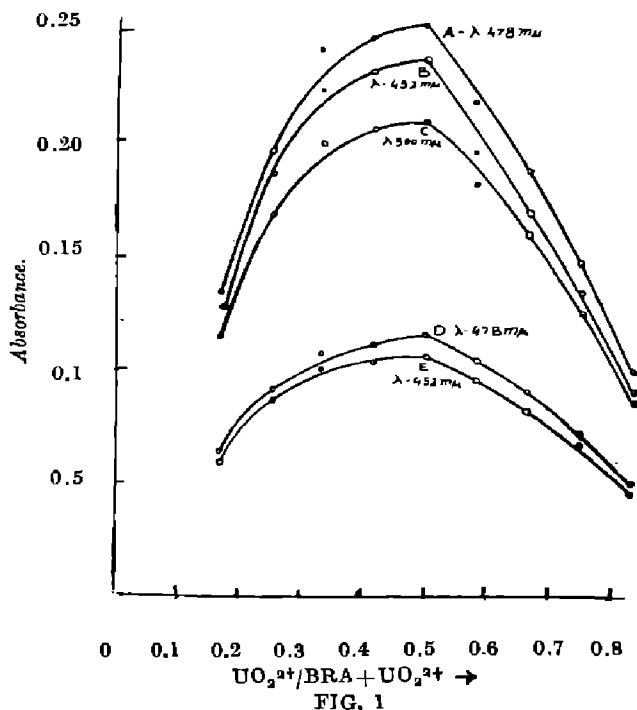


FIG. 1

Each curve has a broad maximum which is indicative of appreciable dissociation of the complex.

Slope-ratio Method.—The absorbance of the solutions of both series was determined at *pH* 4.2 and at 478 *mμ* and 500 *mμ* against corresponding solutions of uranyl nitrate of *pH* 4.2. Results obtained are shown in Fig. 2. Curves obtained are parallel to each other, thus having the same value for the slopes showing that the molar composition is 1:1.

Mole-ratio Method.—Employing equimolar solutions of the reagent and uranium, a series of solutions having the ratio of uranium to the reagent varying from 1:0.2 to 1:12

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were prepared (pH 4.2) and their optical densities measured at 478 m μ and curves shown in Fig. 3, show a break at the mol ratio of 1:1.

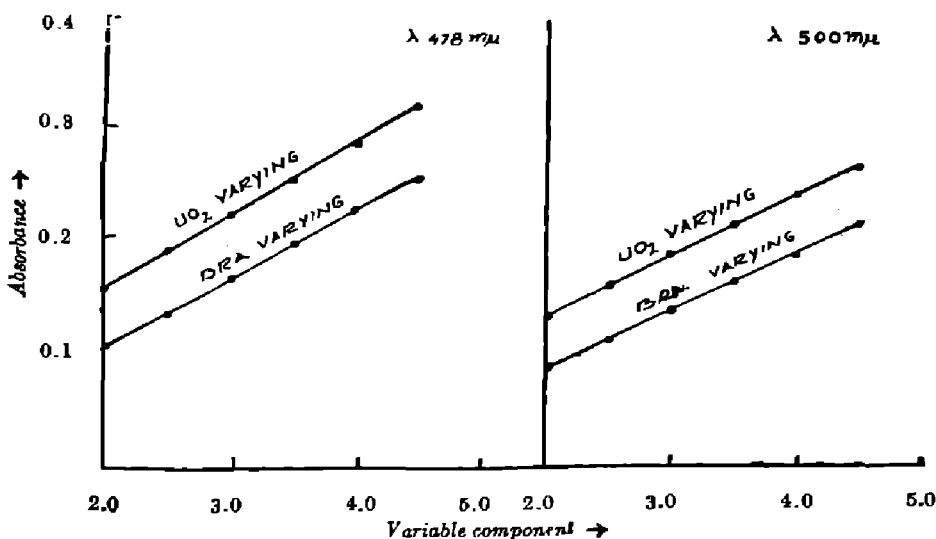


FIG. 2

0.01M Uranyl sol'n. (2-4.5 ml) added to 10.0 ml of 0.05M-BRA (total volume=50.0 ml).
 0.01M-BRA soln. (2-4.5 ml) added to 0.05M uranyl sol'n. (total volume=50.0 ml).

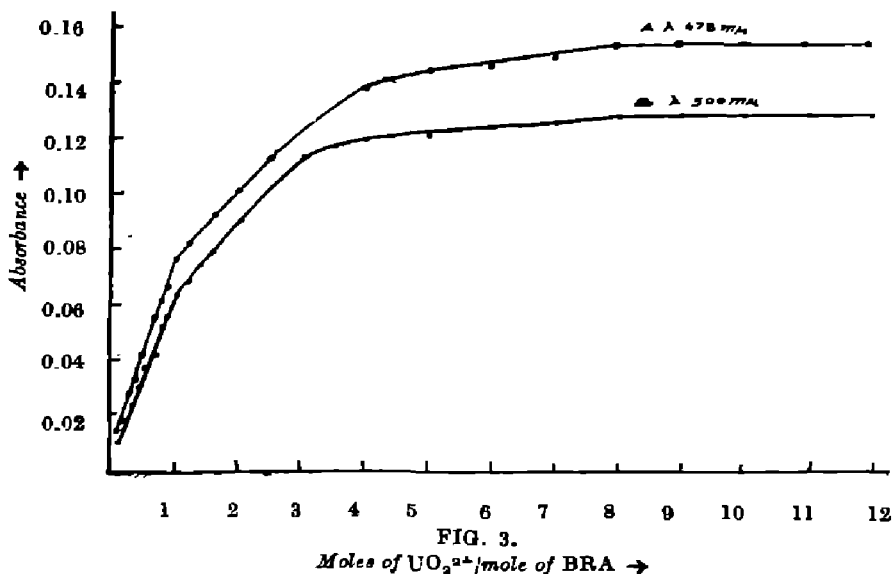
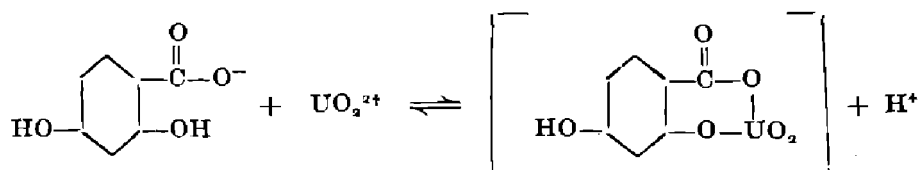


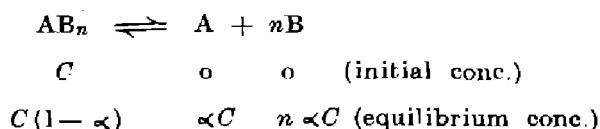
FIG. 3.

β -Resorcylic acid can be used for the estimation of uranyl ion, but as shown by Vivarelli³, the disadvantage is the interference by Ag, Al, Bi, Co, Cr, Cu, Hg, Ni, Pb, Sb, Sn, Ti, Zn, citrate, tartrate, oxalate, phosphate, cyanide and nitrite. Moreover, the complex is highly sensitive even to a small change in pH.

The *pH* of β -resoreylic acid solution (50 ml of 0.01 *M*; *pH* 2.85) was found to decrease to 2.0 when one equivalent of 0.1 *M* (5 ml, *pH* 2.45) uranyl nitrate was added, thus indicating an increase in the H^+ -ion concentration of the mixture, possibly to the displacement of the phenolic OH by the uranyl ion. The reaction of the formation of the complex can be represented by



If the dissociation of the complex be represented by



the dissociation constant may be written as

$$K_\alpha = \frac{(\alpha\text{C})(n\alpha\text{C})^n}{\text{C}(1-\alpha)}$$

The value n for the complex having been determined, the value of α may be obtained from Fig. 3 by the relation:

$$\alpha = \frac{E_m - E_s}{E_m}$$

where E_m and E_s have the usual significance.

$$\text{Thus, } \alpha = \frac{0.152 - 0.076}{0.152} = 0.50$$

$$\therefore K'_\alpha = 2.0 \times 10^{-4}$$

The same value is arrived at from Fig. 3 at 500 $m\mu$. The stability constant K' is equal to 5.0×10^3 .

The standard free energy of formation of the complex is calculated from the relation $\Delta F^\circ = RT/\ln k$ and comes out to be -5.07 kcal./mole at 25°.

Molecular extinction coefficient, ϵ , is equal to the slope of the straight line (UO_2^{2+} varying, 478 $m\mu$) in Fig. 2 and is equal to 3.33×10^2 .

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