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Stability Constants of Uranyl Chelates with Nuclear-Substituted Salicylic Acids

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The formation of an orange-red coloured water soluble chelate between uranyl ion and *p*-aminosalicylic acid with maximum absorption at 460 mμ is reported. The colour of the complex is fairly stable and attains maximum intensity at a pH 4.5. The composition of the complex has been evaluated by Job's and mole ratio methods employing absorbance data and has been found to be 1 : 1 with respect to metal and ligand. The stability constants of the uranyl chelates of certain nuclear substituted salicylic acids, such as, 3-nitrosalicylic, 5-sulphosalicylic, β-resorcylic and *p*-aminosalicylic acids have been determined and the validity of the linear relationship between ligand basicity and the metal chelate stability studied. Based on pH and adsorption studies, tentative structures for the above uranyl chelates have also been proposed.

The complex formation of substituted salicylic acids, such as amino-, alkyl-, chloro-, and nitrosalicylic acids, has been studied in detail with ferric and aluminium ions. It was observed by Foye et al.[1] that the sequence of stabilities with both the metals was parallel to the ionisation constants of the ligands. However, no such studies of the stability constants of uranyl chelates with nuclear-substituted salicylic acids have been carried out.

Baiulescu[2] has introduced a new method for the colorimetric determination of *p*-aminosalicylic acid based on the facts that the above ligand develops a characteristic orange-red colour with uranyl ions and that the complex obeys Beer's law. However, no details regarding the stoichiometry and stability constant have been reported. Recently, Rajam and Martell[3] have studied the formation of a 1 : 1 uranyl-5-sulphosalicylate employing the pH-titration technique; they reported its stability constant (log K) to be 10.62. The formation of a red water-soluble chelate between uranyl ions and β-resorcylic acid[4] with a metal-ligand ratio of 1 : 1, which is also confirmed by the present authors, has been studied by spectrophotometric methods, but no data regarding the stability constant have been presented. While studying the chelate formation of 3-nitrosalicylic acid with ferric ions, the present authors have observed spectrophotometrically and potentiometrically that 3-nitrosalicylic acid forms a 1 : 1 chelate with uranyl ions.[5]

The present communication will describe the

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[1] O. F. William and J. G. Turcotte, *J. Pharma. Sci.*, **51**, 329 (1962).

[2] Gh. Baiulescu, *Acad. rep. popular Romine, Studii Cercetari Chim.*, **6**, 433 (1958); *Chem. Abstr.*, 12931d, (1959).

[3] K. S. Rajam and A. E. Martell, *J. Inorg. Nucl. Chem.*, **26**, 789 (1964).

[4] M. N. Desai and B. M. Desai, *Curr. Sci.*, **34**, No. 8, 244 (1965).

[5] J. M. Rao and U. V. Seshayya, unpublished work.

studies in the complex formation of uranyl ions with *p*-aminosalicylic acid in some detail, as well as the evaluation and comparison of the stability constants of uranyl *p*-aminosalicylate, β-resorcylate and 3-nitrosalicylate chelates. Spectrophotometric, pH and ion exchange methods were employed in the studies of the above systems. pH titrations of the uranyl ion-5-sulphosalicylic and salicylic acids with the metal-ligand ratio of 1 : 1 were also carried out, and the stability constants were evaluated for purposes of comparison.

Experimental

A standard solution of uranyl nitrate was prepared from a B. D. H. Analar sample by direct weighing; the uranium content was gravimetrically confirmed as uranium oxide. For spectrophotometric studies, an uranyl perchlorate solution was prepared by dissolving the uranium hydroxide, precipitated from a known volume of a standard uranyl nitrate solution, in dilute perchloric acid. Fresh solutions of ligands, *p*-aminosalicylic (PAS), β-resorcylic (RA), 3-nitrosalicylic (NSA), 5-sulphosalicylic (5-SSA), and salicylic (SA) acids were prepared by direct weighing and were standardised potentiometrically and titrimetrically.

All the spectrophotometric measurements were carried out by means of a UNICAM SP 600 spectrophotometer. pH titrations were carried out with the help of a Ludwig pH meter, type-12.

Results and Discussion

The development of an orange-red colour when sodium *p*-aminosalicylate was mixed with uranyl ions is almost instantaneous and is pH-dependent. The absorbance of the mixture containing uranyl perchlorate and *p*-aminosalicylic acid in the ratio of 1 : 3 attains a maximum intensity at pH=4.5.

The Composition of the Complex.—The method of Voshburg and Cooper⁶⁾ was employed to determine the nature of the complex formed in the solution. All the mixtures, containing metal-ligand in ratios of 1 : 1, 1 : 2, and 1 : 3, showed a maximum absorption at 460 mμ; this isoabsorptive point suggests the formation of only one complex in solution. Job's continuous variation⁷⁾ and mole ratio methods⁸⁾ were employed to establish the stoichiometry of the complex.

In Job's continuous variation method, equimolecular aqueous solutions (1×10^{-3} M) of the metal and ligand were mixed in complementary quantities and the absorption was measured at 460 mμ and at pH=4.5. The Job curve (Fig. 1, curve A) obtained by plotting the optical densities against the composition of the coloured solutions has shown a peak at the mole fraction of 0.5 of the metal to the ligand, indicating the formation of 1 : 1 complex.

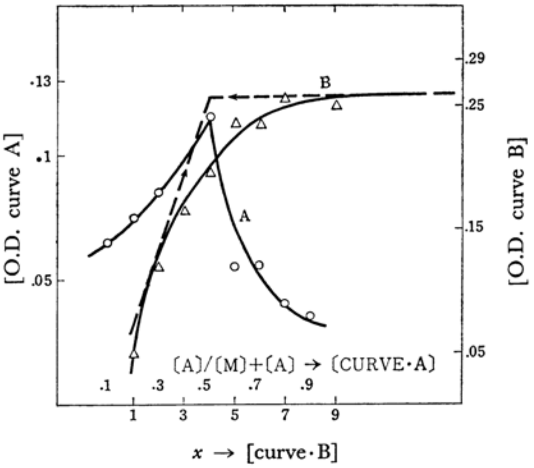

Fig. 1. Composition of the complex by Job's method and mole ratio methods.
A, [A]/([M]+[A])=mole fraction; B, x=ml. of 5×10^{-3} M ligand added to 4 ml. of 5×10^{-3} M uranyl solution. Total volume=20 ml. pH=4.5; λ=460 mμ

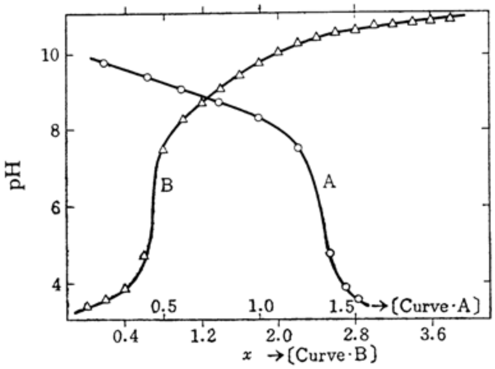

Fig. 2. Curve A, Formation of β-resorcylic acid. $\bar{n}$=Average number of protons held per mole of anion residue; ($x=\bar{n}$)
Curve B, Potentiometric titration of resorcylic acid in 0.10 M KNO_3 at 28°C with 0.05 M NaOH. ($x=a$, equivalents of base added.)

In the mole ratio method too, the plot of the optical densities against the amount of ligand added to the metal shows a clear break at one equivalent of the ligand, confirming the 1 : 1 ratio of the metal to the ligand in the complex.

The Interaction of Uranyl Ions with Nuclear-Substituted Salicylic Acids.—Potentiometric titrations for the 1 : 1 ratio of uranyl ions to various ligands were performed at the same ligand concentration. The results of the experimental measurements are presented in Fig. 3, curves A, B, C, D, and E. The titration curves indicate qualitatively the relative magnitudes of the stabilities of

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6) W. C. Voshburg, and C. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).
7) P. Job, *Ann. Chim.*, **11**, 97 (1936).
8) A. E. Harvey, and D. L. Manning *J. Am. Chem. Soc.*, **72**, 4488 (1950).

the uranyl chelates. Precipitations were found at the end of the titrations; they were probably caused by disproportionation to the metal hydroxide or by the hydrolysis of the 1 : 1 chelate.

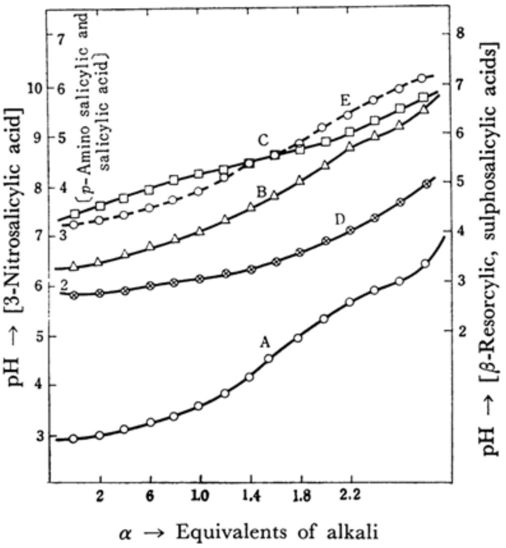

Fig. 3. Potentiometric titration of uranyl chelates of substituted salicylic acids in 0.10 M KNO_3 at 28°C with molar ratio 1:1 of ligand to uranyl ions.
A, 3-nitrosalicylic acid; B, resorcylic acid; C, *p*-aminosalicylic acid; D, 5-sulphosalicylic acid; and E, salicylic acid.

Acid Dissociation Constants of *β*-Resorcylic Acid.—The step-by-step ionisation of *β*-resorcylic acid with its step constants can be expressed as follows:

$$H_3A \leftrightarrows H_2A^- + H^+; \quad k_1 = \frac{(H_2A^-)(H\cdot)}{(H_3A)}$$

$$H_2A^- \rightleftarrows HA^{2-} + H^+; \; k_2 = \frac{(HA^{-2})(H\cdot)}{(H_2A^-)}$$

$$HA^{2-} \rightleftarrows A^{3-} + H^+; \quad k_3 = \frac{(A^{3-})(H\cdot)}{(HA^{2-})}$$

where the parentheses indicate the concentrations of the respective ions.

The values of k_1 and k_2, the first and the second acid dissociation constants, of the *β*-resorcylic acid (H_3A) were determined by titrating the free acid in the presence of mineral acid (HNO_3) with standard, carbon dioxide-free sodium hydroxide (Fig. 2B). Various values of $\bar{n}$, the average number of protons held per anion residue, calculated from the following equations[9] have been plotted against the pH (Fig. 2A):

$$\bar{n} = \frac{(H_2A^-)+2(H_3A)}{C_A}; \; (H_2A^-) = aC_A + (H\cdot)$$

and $(H_3A) = C_A - (H_2A^-)$ in low-buffer regions and $(H_2A^-) = (a-1)C_A - (OH^-)$; $(HA^{2-}) = C_A - (H_2A^-)$ in higher buffer regions.

where a = equivalents of base added, and
C_A = total anion concentration.

The third dissociation constant, k_3, has been evaluated from the potentiometric data, using the algebraic method of Schwarzenbach et al.[10]:

$$(HA^{2-}) = (a-2)C_A - (OH^-);$$

$$(A^{3-}) = C_A - (HA^{2-}); \; k_3 = \frac{(A^{3-})(H\cdot)}{(HA^{2-})}$$

The present value of $k_1 = 2.2 \times 10^{-4}$ slightly differs from the reported value of 4.73×10^{-4}[11] obtained conductometrically. The values of k_2 and k_3 have been worked out to be 4.5×10^{-10} and 1.16×10^{-11} respectively. The literature, however, does not reveal any values for these two constants for purposes of comparison.

The Stability Constants of the Chelates.— The equilibrium involved in the metal chelate formation of a 1 : 1 system (metal-ligand) may be expressed as:

$$UO_2{}^{2+} + A^{2-} \rightleftarrows UO_2A; \quad K = \frac{(UO_2A)}{(UO_2{}^{2+})(A^{2-})}$$

where K is the stability constant of the chelate. The stability constants of the complexes have been evaluated employing Bjerrum's method as modified by Chaberek and Martell.[12] In the case of a 1 : 1 complex, the various factors involved in the K of the chelate are obtained by using the following equations:

$$(A^{2-}) = \frac{(2-a)C_A - (H\cdot) + (OH^-)}{\dfrac{2(H\cdot)^2}{k_1k_2} + \dfrac{(H\cdot)}{k_2}}$$

$$K = \frac{C_A - x(A^{2-})}{(A^{2-})[C_M + x(A^{2-}) - C_A]}$$

where

$$x = \frac{(H\cdot)^2}{k_2k_1} + \frac{(H\cdot)}{k_2} + 1$$

where k_1 and k_2 are the suitable acid dissociation constants of the ligands, and where C_M = the total metal ion concentration.

The values of the stability constants of the uranyl chelates (Table I) indicate a gradual increase in the stability of the chelates as the basic nature of the donor group of the ligand increases. The stabilities of the uranyl chelates were found to increase in the sequence; 3-nitrosalicylic < 5-sulphosalicylic < *β*-resorcylic < salicylic < *p*-aminosalicylic acids. Moreover, as was predicted by the thermodynamically-derived equation of Ernst and

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[9] S. Chaberek, Jr., and A. E. Martell, ibid., **74**, 5052 (1952).

[10] G. Schwarzenbach, E. Kampitsch and R. R. Steiner, *Helv. Chem. Acta*, **28**, 837 (1945).

[11] J. E. F. Dippy, *J. Chem. Soc.*, **1959**, 1717.

[12] S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

TABLE I. STABILITY CONSTANTS OF URANYL CHELATES OF SALICYLIC ACIDS

Temperature $=28\pm0.1$°C
Ionic strength $(\mu)=0.10$ M (KNO_3)

Sl. No.	Ligand	pk_1	pk_2	pk_1k_2	log K
1*	3NSA	1.90	10.33	12.23	8.57
2*	5SSA	2.50	11.75	14.25	10.70
3	RA	3.65	10.94	14.61	11.98
4*	SA	2.98	13.59	16.57	13.12
5*	PAS	4.08	13.75	17.82	14.41

* The values of the acid dissociation constants have been abstracted from earlier works.

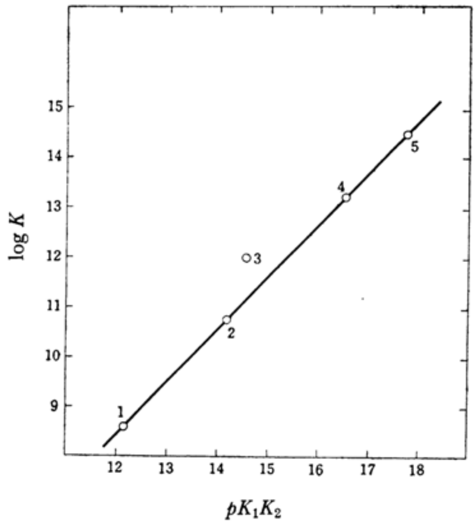
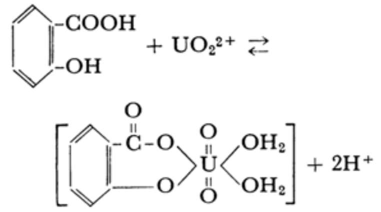


Fig. 4. Linear relationship of log K vs. $p(K_1K_2)$. (1) 3-nitrosalicylic acid (2) sulphosalicylic acid (3) β-resorcylic acid (4) salicylic acid (5) p-aminosalicylic acid.

Menashi,[13] and as has been proposed by many workers,[14-16] the plot of $\log_{10}K$ against $p(k_1k_2)$ yields a straight line, as is shown in Fig. 4, for the complexes of the uranyl ions with both salicylic and substituted salicylic acids.

Under the experimental conditions, it seems that all the above ligands react with uranyl ions in 1 : 1 ligand-metal ratio, liberating two protons; the adjacent carboxylic and the phenolic groups seem to be responsible for the binding of the metal atom in the complexes. The structure with the reactive moiety may be tentatively represented as:



Similar structures have been assigned to the ferric complexes of p-aminosalicylate,[17] 5-sulphosalicylate,[18] β-resorcylate[19] and o-cresotate[20] by earlier workers. Further, the non-ionic nature of all the chelates, uranyl-3-nitrosalicylic, β-resorcylic and p-aminosalicylic acids was confirmed by their non-adsorption on both cation exchange resin, Rexyn 102(H), and anion exchange resin, Rexyn AG-7(Cl-SO_4).

Summary

1) The composition of the uranyl p-aminosalicylic acid chelate was found by spectrophotometric methods to be 1 : 1 with respect to the metal-ligand ratio.

2) The stability constants of uranyl-salicylate and substituted salicylate chelates were determined, and the validity of the linear relationship between the ligand basicity and the metal chelate stability was studied.

3) The second and third acid dissociation constants of β-resorcylic acid were determined from potentiometric data.

4) The stabilities of uranyl chelates were found to increase in the sequence:

3-nitrosalicylic acid < 5-sulphosalicylic < β-resorcylic < salicylic < p-aminosalicylic acids.

5) Substituents were found to play an important role in this case.

The authors are grateful to Professor N. V. Subba Rao for his keen interest in their investigations.

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13) Z. L. Ernst and J. Menashi, *Trans. Faraday Soc.*, **59**, 2838 (1963).

14) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

15) D. D. Perrin, *J. Chem. Soc.*, **1958**, 3125

16) S. P. Datta, R. Leberman and B. R. Rabin, *Trans. Faraday Soc.*, **55**, 1982, 2141 (1959).

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19) M. L. N. Reddy and U. V. Seshayya, *J. Indian Chem. Soc.*, **41**, 289 (1964).

20) K. G. Divekar, *J. Sci. Ind. Res.*, **21B**, 309 (1962).