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SPECTROPHOTOMETRIC INVESTIGATION OF COMPLEX FORMATION

Part I. UO_2^{2+} Complexes of Some Substituted Salicylic Acids in Aqueous Solution.

By

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ABSTRACT

A study of the interaction of uranium as uranyl ion with salicylic acid and 5-methoxy, 5-chloro, 5-nitro, 4-methyl and 4-iodo salicylic acids have been carried out spectrophotometrically. It was found that UO_2^{2+} forms 1:1 complex only under our experimental conditions. Stability constants have been determined at 25°C in aqueous solution. The results also include the correlation of the stability of these complexes with those of respective proton complexes.

INTRODUCTION

Salicylic acid and its substitutes (H_2L) can form strong chelate compounds with metal ions, and by using Bjerrum method (1) Perrin (2) reported the stability constants of many metal complexes. UO_2^{+2} ion is known to form complexes with salicylic acid and its derivatives and use of this tendency has been applied in analytical chemistry (3). Complex formation between UO_2(II), Cu(II), Ni(II), Co(II) and Be(II) with 2,4-and 2,5-dihydroxy benzoic acid have been studied in aqueous-dioxan medium, and observed a linear relationship between the logarithm of stabilities of metal ligand and proton ligand complexes (12). Foley and Anderson (13) have shown the existence of only a 1:1 uranyl-sulphosalicylate complex in aqueous solution. Same conclusion has been reached by Rajan and Martell (14) for the same complex.

In the case of free ligand an intramolecular hydrogen bonding is expected (intermolecular hydrogen bonding should not be excluded). Branch and Yabroff (4) suggested that hydrogen bonding stabilize the anion much more than the undissociated molecule, and it requires coplanarity with the benzen ring for its existence (5). Accordingly, hydrogen bond would increase the acidity of the ligand, and on the other hand it would hinder the interaction with the UO_2^{2+} ion in chelation. Another factor which affects the acidity of the ligands, is due to the electron withdrawing properties of the carboxylic group (9). In other words, the acidic hydrogen of carboxylic group which released from dissociation would tend to interact with the hydroxy group, weaking the coordination (11).

THEORETICAL

The expected equilibrid to be occurred in the solution are:

$$H_2L \rightleftharpoons HL^- + H^+$$

$$HL^- \rightleftharpoons L^{2-} + H^+$$

$$UO_2^{2+} + H_2L \rightleftharpoons UO_2L + 2H^+$$

$$UO_2^{2+} + HL^- \rightleftharpoons UO_2L + H^+$$

$$UO_2^{2+} + L^{2-} \rightleftharpoons UO_2L$$

The above equilibria can be described in terms of thermodynamic equilibrium constants:

$$K_1 = f_1^2 (HL^-) (H^+) \ / \ (H_2L) \qquad (1)$$

$$K_2 = f_2 (L^{2-}) (H^+) \ / \ (HL^-) \qquad (2)$$

$$F_1 = f_1^2 (UO_2^{+2}) (H^+)^2 \ / \ f_2 (UO_2^{2+}) (H^2L) \qquad (3)$$

$$F_2 = (UO_2L) (H^+) \ / \ f_2 (UO_2^{2+}) (HL^-) \qquad (4)$$

$$S = (UO_2L) \ / \ f_2^2 (UO_2^{2-}) (L^{2-}) \qquad (5)$$

where f_1, f_2 are the activity coefficients of the singly and doubly charged species. The above equilibrium constants can be related to each other by the following equations:

$$F^1 = F_2 \, X \, K^1 \qquad (6)$$

$$F_2 = S \, X \, K_2 \qquad (7)$$

$$S = F^1 / K^1 K_2 \qquad (8)$$

Let:

m = The total concentration of $UO_2(CH_3COO)_2$

a = The total concentration of H_2L (Ligand)

h = The concentration of free hydrogen ion (H^+)

C = The concentration of the complexed uranyl ion (UO_2L)

Then we have:

$$m = (UO_2^{2+}) + C \qquad (9)$$

$$a = (H_2L) + (HL^-) + C \qquad (10)$$

(L^{1-}) is negligible in the (pH) range studied.

From equation (9)

$$(UO_2^{2-}) = m - C \qquad (11)$$

Combining equations (9), (10) with equations (1), (4) gives

$$(HL^-) = K_1\,(a\text{-}C) / (hf_1^2 + K_1) \qquad (12)$$

$$(H_1L) = hf_1^2(a\text{-}C) / (hf_1^2 + K_1) \qquad (13)$$

$$a / C = 1 + h\,(hf_1^2 + K_1) / F_2K_1f_2(m\text{-}C) \qquad (14)$$

From Lambert-Beer law, and for cell of a 1cm path length:

$$D / 1 = EUO_2\,(UO_2^{2+}) + E_{H2L}\,(H_2L) + E_{HL}\,(HL^-) + EC \qquad (15)$$

where D is the optical density of the solution, and E is the molar extinction coefficient of the complex and other species.

Substitution of (UO_2^{2+}), (H_2L) and (HL^-) from the above equations into (15) and simplifying:

$$D / 1 = mE_{UO2} + au + C\,(E\text{-}E_{UO2} - u) \qquad (16)$$

$$\text{where } u = (E_{H2L}\,bf_1^2 + E_{HL}\,K_1) / (hf_1^2 - K_1) \qquad (17)$$

The optical density was measured at a certain wavelength where the complexes absorb, and in this case $EUO_2 = u = 0$, and equation (16) can be reduced to:

$$D / 1 = EC \qquad (18)$$

By substituting C from equation (18) into equation (14) and simplifies:

$$m / D = 1 / E1 + 1 / E1F_1\,(h(hf_1^2 + K_1) / f_2(a\text{-}D / El) \qquad (19)$$

In the determination of stability constants the variables, h, l, m and a were arraanged in such a way to maximize the accuracy in the optical measurements.

RESULTS AND DISCUSSION

The formation of a complex between UO_2^{2+} and salicylic acid was confirmed by the change in colour. The solutions used were very diluted, so the formation of any polynuclear species could be ignored (16). The 1:1 complex was formed in the pH range (3-4.7) where there is no precipitation or hydrolysis been observed. There was no precipitate formed in the metal complex titration in similar studies (17). Also no hydrolysis has been reported up to pH 9 by Banks and Sing in UO_2-5- sulphosalicylic acid system (18).

A certain quantity of standard solution of a given salicylic acids were mixed with different amounts of solutions of CH_3COOH, NaOH and CH_3COONa. A fixed excess of a standard solution of $(CH_3COO)_2UO_2$ were added together with the required quantity of water in order to keep the ionic strength constant. The optical densities of the solutions were measured at wavelength (475 mn).

By assuming that b = (NaOH), p = (CH_3COOH) and q = (CH_3COONa), then (CH_3COO^-) = 2m + p + q and (Na^+) + b + q. By applying the electroneutrality principle and providing that both (OH^-) and (L^{2-}) are negligible then:

$$(HL^-) + 2m + p + q = h + b + q + 2\,(UO_2^{2+}) \qquad (20)$$

combining equations (11), (12), (18) and (20) yield:

$$h^2 f_1^2 + h\,(K_1 + f_1^2\,(b\text{-}p\text{-}2D\,/\,E_1)) + K_1\,(b\text{-}p\text{-}a\text{-}D\,/\,E1) = 0 \qquad (21)$$

value of h can be determined from above equation. The ionic strength can be calculated by:

$$I = h + b + q + 3\,(m\text{-}D\,/\,E1) \qquad (22)$$

Davies equation (19) was used in the estimation of activity coefficient

$$\text{-}\log_{10} fz = 0.5Z^2\,((I^{0.5}\,/\,(1+I^{0.5})) - 0.3\ I) \qquad (23)$$

Equation (19) can be solved by means of the method of least squares for the approximate values of E and F_1, where the expression (a-D / El) was initially replaced by a. Approximate values of D / El and a -D / El were found, and an accurate values of h and E computed by means of equations (21) and (19) respectively.

Table (1) shows the result of calculation for the uranyl 5-methoxysalicylate complex. The other constants for all six complexes calculated in the same way and summarized in table (2).

The stability constant of a first (1:1) metal ligand complex can be related to the logarithm of the acid dissociation constant pK of the corresponding ligand (22), (23). The general form:

Table 1. Stability constant of uranyl 5-Methoxy Salicylate

$\lambda = 475$ nm, $l = 1$ cm, $a = 1.787 \times 10^{-3}$ mole / l,

$m \times 10^3$ (mole / l)	D	$h \times 10^5$ (g. ion / l)	$X \times 10^5$	$Y \times 10^3$
1.224	0.452	3.137	5.159	2.708
1.071	0.420	3.201	4.926	2.550
0.918	0.380	2.717	3.862	2.415
0.765	0.332	2.650	3.466	2.303
0.612	0.273	2.469	2.946	2.241
0.306	0.150	2.095	2.109	2.039
0.152	0.078	2.093	1.936	1.945

$S = 7.4066 \times 10^{12}$ $\log S = 12.867 + 0.058$

$\sigma = \mp 0.003$ $E = 562 \mp 4$

$$X = \frac{(hf_1^2 + K_1)}{f_2\,(a\text{-}D / El)} \qquad Y = m / D$$

$$\log S = ApK + B \tag{24}$$

where A and B constants, which first used by Bjerrum (10) and much discussed by Martell and Calvin (24). The above linear relation has been found by many workers (25-27), (6) to hold for metal complexes of a series of closely related ligands. Bartusk (16) has drawn linear plots between formation constants of uranyl complexes and the acidity of phenolic ligands. Equation (24) has no general validity, where ligands of different character are compared; and in most cases the slopes differ from unity. The slope could be in unity if the changes in partial molar free energies of the metal-ligand and proton-ligand complexes compensated one another exactly. The deviation from unit slope can also be explained in term of π- bonding (15), (25). The slopes will be greater than unity of the metal ion has π-acceptor properties, and smaller than unity if it has π-donor properties.

Figure (1) shows a fairly satisfactory linear relation, (whose slope is 1.04) this was obtained by using the method of least squares to the data given in table 2. Since the slope is approximately unity, it is indicated that the metal complexes and the proton complexes have been affected to the same extent by substitution.

Table 2

No	Complex	$K_1 \times 10^{-3}$	K_2	$(F_1 \pm \sigma F_1) \times 10^5$	$(F_2 \pm \sigma F_2) \times 10^2$	$(E \pm \sigma E)$	$\text{LogS} \pm \sigma\text{logS}$	pK_2
1	UO_2-salicylate	1.50	2.028×10^{-14}	2.098 ± 0.4	1.88 ± 0.3	712 ± 16	11.910 ± 0.062	13.693
2	UO_2-5 methoxysalicylate	1.234	$1.429 \times 10^{1-4}$	10.7 ± 0.1	8.64 ± 0.6	562 ± 4	12.867 ± 0.058	13.845
3	UO_2-5 chlorosalicylate	2.263	1.130×10^{-13}	6.799 ± 0.5	2.89 ± 0.2	746 ± 8	11.271 ± 0.04	12.947
4	UO_2-5 nitrosalicylate	7.815	4.539×10^{-11}	20.7 ± 0.3	2.99 ± 0.3	590 ± 7	8.959 ± 0.08	10.343
5	UO_2-4 methylsalicylate	0.649	5.768×10^{-15}	2.053 ± 0.3	3.40 ± 0.1	487 ± 9	13.177 ± 0.08	14.239
6	UO_2-4 iodosalicylate	2.14	2.244×10^{-13}	18.5 ± 0.1	8.11 ± 0.3	438 ± 10	11.702 ± 0.03	12.649

Values of ionization constants are taken from ref. (17) (20) and (21)

EXPERIMENTAL

All chemicals such acetic acid, sodium hydroxide, and sodium acetate were of analytical reagent grade. Salicylic acid and 5-methoxy, 5-chloro, 5-nitro and 4-methyl salicylic acids were obtained from (Aldrich), and 4-iodo salicylic acid was synthesized from 4-amino salicylic acid using (Sandmayer-reaction) (7). All the substituted salicylic acids were recrystalized and their purity was checked before their use. Standard solutions of acetic acid were prepared and standardized against sodium hydroxide (8). Uranyl acetate was supplied by (Merck). Measurements of optical density at $25^{o}C$ were made with a Pye-unicam SP-8800 spectrophotometer.

ÖZET

Uranil (UO_2^{+2}) iyonunun, salisilik asit ve 5-metoksi, 5-kloro, 5-nitro, 4-metil ve 4-iyodo salisilik asitlerle etkileşimi, spektrofotometrik olarak incelendi. Çalışma şartlarımızda UO_2^{2+}'in yalnız 1:1 komplekslerinin oluştuğu bulundu. Kararlılık sabitleri 25°C'de, sulu çözeltide tayin edildi. Sonuçlar bu komplekslerin kararlılıklarının, ilgili proton komplekslerinin kararlılıklarıyla karşılaştırılmalarını da içermektedir.

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