

Uranium (VI)-5-Iodo-8-Hydroxyquinoline-7-Sulfonic Acid Chelate

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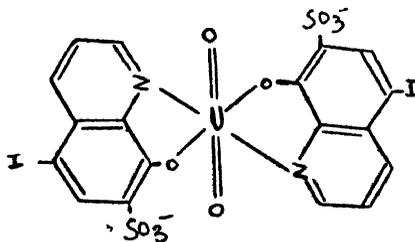
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In recent communications from these laboratories, the authors reported the characteristics of the uranium chelates of 8-hydroxyquinoline-7-sulfonic acid and some of its derivatives¹⁻³. The present work deals with the detailed investigation of the orange red complex formed between uranyl ion and 5-iodo-8-hydroxyquinoline-7-sulfonic acid (abbreviated as IHQS) in aqueous medium regarding composition, stability and thermodynamic parameters like ΔG , ΔH and ΔS , associated with the complex formation, by spectrophotometric method.

The solution of 5-iodo-8-hydroxyquinoline-7-sulfonic acid was prepared as described earlier⁴. A solution of uranyl nitrate (BDH) was prepared in double distilled water and standardised. The instruments used for the pH and absorbance measurements were the same as mentioned before⁵. Sodium acetate—acetic acid buffer was used to maintain the pH of the solutions and the ionic strength was adjusted with sodium perchlorate.

The method of Vosburgh and Cooper⁶ was adopted for the investigation of the nature of the complex formed in solution. The results indicate the formation of only one complex under the conditions of study. The empirical formula of the complex formed in solution has been determined by the three different methods⁷⁻⁹ and was found to be $UO_2(IHQS)_2$. Assuming that the phenolic hydrogen is replaced by the uranyl ion, which in turn is coordinated through the adjacent nitrogen, the structure of the complex may be represented as :



The values of apparent stability constant K (See Table 1), under the above conditions, were calculated from the absorbance data by the method of Banerji and Dey¹⁰, mole ratio method⁸ and the method using molecular extinction coefficient data. The values of $\log K$, so obtained are tabulated in Table 1.

For the determination of the thermodynamic equilibrium constant of the complex, the stability constants at different ionic strengths have been determined. The results, as

TABLE 1

Apparent stability constant of the chelate

Method	pH	log K (25°)
Mole ratio method	5.8±0.1	8.8±0.01
Method of Banerji and Dey	5.8±0.1	8.5±0.50
Method using molecular extinction coefficient data	5.8±0.1	8.8±0.02

obtained by the method using molecular extinction coefficient data have been represented in Table 2.

TABLE 2

Stability constants at different ionic strengths

(pH = 5.8±0.1; Temp. = 25°; Cell width = 1 cm)

Ionic strength	Stability constant
0.02	(6.70±0.04) × 10 ⁸
0.05	(6.31±0.02) × 10 ⁸
0.10	(5.76±0.05) × 10 ⁸
0.15	(5.20±0.03) × 10 ⁸
0.20	(4.75±0.02) × 10 ⁸
0.30	(4.29±0.01) × 10 ⁸
0.40	(4.00±0.03) × 10 ⁸
0.50	(4.01±0.02) × 10 ⁸

By the method of extrapolation, using log K values¹¹, the thermodynamic stability constant at zero ionic strength was found to be 7.0×10^8 at 25°. It was observed that the addition of the neutral salt increases the extent of dissociation of the complex. The ionic atmosphere about the complex ions are denser in salt solution. They screen the interaction between the ions of the complex and reduce their rate of recombination¹². But, beyond ionic strength 0.3, the value of the K remains almost constant, probably due to the fact that the activity coefficient of an ion passes through the minima as the ionic strength increases.

The thermodynamic parameters of the complex have been determined by the method mentioned earlier¹³ and the results obtained have been presented in Table 3.

TABLE 3

Log K, ΔG, ΔH and ΔS at various temperatures

(Ionic strength = 0.05; pH = 5.8±0.1; Cell-width = 1 cm; Wavelength = 470 nm)

Temperature	25°	30°	35°	40°	45°
Log K	8.80	8.85	8.89	8.94	8.98
—ΔG (kcal/mole)	12.08	12.35	12.61	12.88	13.15
ΔH (kcal/mole)	4.00	3.98	4.02	4.01	3.99
ΔS (e.u.)	53.98	53.93	53.94	53.96	53.94

The fact that the stability constant increases with an increase in the temperature clearly indicates that the reaction is endothermic. The entropy change relates to the

amount of the order in the products, compared to that in the reactants. When ΔS is positive, it contributes to a negative free energy change which accounts for the stability of the complex.

Before discussing the values of the overall stability of uranium chelates of a group of related ligands, it will be interesting to discuss the effect of substituents on the thermodynamic ionization of these ligands¹⁴. The thermodynamic ionization constants of these related ligands have been determined spectrophotometrically, by the method of Philip¹⁵ and the relevant pK values obtained at 25° have been presented in Table 4.

TABLE 4

Thermodynamic ionization constants of the ligands in aqueous medium

Ligands	pK _{a1}	pK _{a2}	ΔF_1 (kcal/mole)	ΔF_2 (kcal/mole)
8-hydroxy-quinoline.	5.05	9.82	—	—
HQS	3.27	7.76	4.49	10.64
CHQS	2.85	7.44	3.91	10.21
BHQS	3.08	7.58	4.23	10.40
IHQS	3.18	7.65	4.36	10.50

A comparison of the thermodynamic ionization constants of 8-hydroxy quinoline-7-sulfonic acid with that of the parent compound 8-hydroxyquinoline, obtained by Nasanen¹⁶ reveals that the substituent group decreases the pK values, i.e., increases the ionization of the ligand. The sulfonic group is known to be a σ and π electron acceptor. The lower values of the sulfonate derivatives may be considered as a result of electronic interaction of the sulfonate group with the aromatic ring. Although the sulfonic acid group is itself negative, the nature of the interaction is such that the negative charge is withdrawn from the ring.

The halo substituted derivatives are more acidic than 8-hydroxyquinoline-7-sulfonic acid. The ionization of the halo substituted acids is more owing to the inductive electron withdrawing effect of the halogens. Our observations reveal that the halogen substitution affects the ionization only to a small extent, due to the fact that $-I$ and $+T$ effects of halogen oppose each other and as the $-I$ effect predominates over $+T$ effect, there is a small increase in the ionization. The order of the effect is :



A comparison of the values of the overall stability of uranium chelates of a group of related ligands¹⁻³ reveals that the halogen substitution decreases the overall stability constants of the chelates. The halo substituted derivatives are more acidic and form less stable chelates as compared to those of 8-hydroxyquinoline-7-sulfonic acid. It has been observed that the iodo derivative forms more stable chelate than the corresponding bromo derivative; which in turn forms a chelate of greater stability than the chloro derivative. It seems to be quite reasonable in view of the fact that the inductive effects of halogens decrease in the order : $Cl > Br > I$.

A similar relationship is also observed in enthalpy and entropy changes of the complexes (Table 5).

TABLE 5
Thermodynamic constants of the uranium chelates

Chelate	$K_T(25^\circ)$	$-\Delta G(25^\circ)$ (kcal/mole)	ΔH (kcal/mole)	ΔS (e.u.)
UO ₂ (HQS) ₂	8.5×10^8	12.22	4.6	56.5
UO ₂ (IHQS) ₂	7.0×10^8	12.08	4.0	53.9
UO ₂ (BHQS) ₂	4.2×10^8	11.73	3.5	51.1
UO ₂ (CHQS) ₂	3.6×10^8	11.53	3.2	49.4

The symbol HQS stands for 8-hydroxyquinoline-7-sulfonic acid, IHQS stands for 5-iodo-8-hydroxyquinoline-7-sulfonic acid, BHQS stands for 5-Bromo-8-hydroxyquinoline-7-sulfonic acid and CHQS stands for 5-Chloro-8-hydroxyquinoline-7-sulfonic acid in the form of their respective anions.

The complex, uranium(VI)-5-iodo-8-hydroxyquinoline-7-sulfonic acid obeyed Beer's law in the concentration range 10 to 150 ppm. The molar absorptivity and sensitivity of the reaction were found to be 1510 and 0.158 $\mu\text{g}/\text{cm}^2$ at 470 nm (pH 5.8). The diverse ions like Cu²⁺, Pb²⁺, Al³⁺, Mg²⁺, Hg²⁺, Co²⁺, Cd²⁺, Be²⁺, Ca²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Pd²⁺, Cl⁻, NO₃⁻, SO₄²⁻, ClO₄⁻ etc. do not interfere; whereas Fe³⁺, V⁵⁺, Ti⁴⁺, Cr³⁺, F⁻, BO₃³⁻, C₂O₄²⁻ and PO₄³⁻ interfere even when present in small quantities.

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