

Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. VIII. Calcium Chelates of 7-Iodo-8-Quinolinol-5-Sulphonic Acid

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The 7-iodo-8-quinolinol-5-sulphonic acid (ferron, loretin, yatren, chiniofon) forms two calcium compounds¹ which are both sparingly soluble in water. If we formally write its formula as H_2A , the formulae of these calcium compounds are $Ca(HA)_2$ and CaA without water of hydration. The aim of this study was to determine the solubility products of these compounds. In addition it was necessary to investigate the ionization of this acid and the stability of the chelates in solution.

The ionization of the reagent was investigated previously by us², and the results obtained were generally confirmed in the present study, except for the first ionization constant in high ionic strength ($I > 1$) for which we have now obtained somewhat greater values. This was due to a glass electrode used at that time which gave distinctly wrong values at high ionic strengths, as was later observed. The corrected values may be obtained from

$$pK_1' = 2.514 - \frac{0.509\sqrt{I}}{1 + 1.44\sqrt{I}} + 0.13 I \quad (1)$$

The chelates in solution were of the type CaA and $CaA_2^{=}$. We were not able to establish the existence of complexes such as $CaHA^+$ and $Ca(HA)_2$. Their absence is also proved spectrophotometrically, as is seen in Fig. 1, where the effect of calcium ions on the ultraviolet spectrum of the reagent at different pH's is presented. No effect can be observed at pH's where the HA^- ion concentration is high but the concentration of $A^{=}$ still very small. With increasing $[A^{=}]$ the effect is gradually heightened. The second curve from the top is obviously the spectrum of CaA . This spectrum very much resembles that of the ligand $A^{=}$, as in the case of oxine³.

The determination of the stability constants

$$k_1 = [MA] / [M^{++}][A^{=}] \quad (2)$$

and

$$k_2 = [MA_2^{=}] / [M][A^{=}]^2 \quad (3)$$

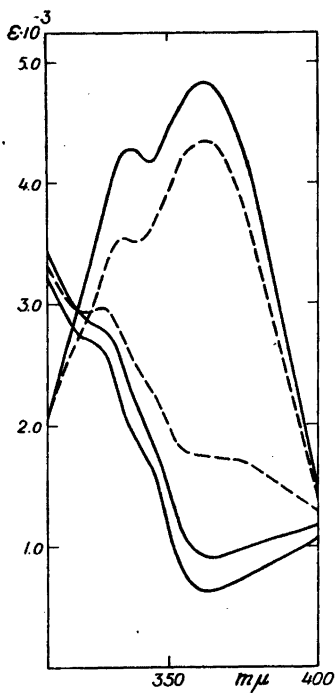


Fig. 1. Effect of calcium ions on the ultra-violet spectrum of 7-iodo-8-quinolinol-5-sulphonic acid at several pH's. From the highest curve downwards: $c = 10^{-4}$, $c_{Ca} = 0$, $pH = 9$. $c = 10^{-4}$, $c_{Ca} = 0.91$, $pH = 9$. $c = 10^{-4}$, $c_{Ca} = 0.51$, $pH = 6$. $c = 10^{-4}$, $c_{Ca} = 0$, $pH = 6$. $c = 10^{-4}$, $c_{Ca} = 0$, $pH = 4$ (the lowest curve) and $c = 10^{-4}$, $c_{Ca} = 0.91$, $pH = 4$ (the lowest curve).

was carried out by the usual titration method³. The equations used are as follows:

$$[HA^-] = (2c - c_B - [H^+]) / (1 + 2(H^+) / K_1') \quad (4)$$

$$c' = c - [HA^-] \left\{ 1 + (H^+) / K_1' + K_2' / (H^+) \right\} \quad (5)$$

$$k_1' + k_2' \frac{x(2c_M - c)}{c_M - c'} - \frac{c'}{x(c_M - c')} = 0 \quad (6)$$

where

$$x = [HA^-] / (H^+) \quad (7)$$

$$k_1' = k_1 K_1' \quad (8)$$

$$k_2' = k_2 K_2'^2 \quad (9)$$

$$K_1' = (H^+) [HA^-] / [H_2A] \quad (10)$$

$$K_2' = (H^+) [A^{2-}] / [HA^-] \quad (11)$$

The symbols are those used previously^{2,3}.

The results concerning complex equilibria are recorded in Table 1. The data of the table are mean values of several measurements. The thermodynamic constant $k_{1,0}$ was calculated by means of

Table 1. First stability constant of calcium chelate in solutions of potassium chloride at 25° C.

\sqrt{I}	pk_1'	pK_2'	$\log k_1$
0.173	4.65	7.22	2.57
0.269	4.78	7.14	2.36
0.524	4.89	7.00	2.11
0.935	4.90	6.90	2.00
1.370	4.70	6.87	2.17

$$\log k_1 = \log k_{1,0} - \frac{4.027 \sqrt{I}}{1 + a\sqrt{I}} + BI \quad (12)$$

The calculation gave

$$\log k_{1,0} = 3.07, a = 2.0 \text{ and } B = 0.28$$

For the second constant we obtained $k_2 \sim 10^4$.

The solubility equilibria were studied by the same method as before³, but the case is now more complicated on account of the two solid components. In the "point titration" method^{3,4} used, the calcium concentration was always kept greater than or equal to the concentration of the chelating agent. Equilibrium was reached after two days but the pH was generally measured after one week at the earliest. From Fig. 2 we see the effect of calcium ions on the titration curve when precipitation occurs. By means of the pH values belonging to the lower part, the solubility product

$$[M^{++}] [HA^-]^2 = S_1 \quad (13)$$

may be calculated. From the higher part analogously, the solubility product

$$[M^{++}] [A^{=}] = S_2 \quad (14)$$

is obtained. The equations needed in the first case are:

$$[H_2A] = (c - c_B - [H^+]) / \{1 - K_1'K_2' / (H^+)^2 - K_1'k_1'[M^{++}] / (H^+)^2\} \quad (15)$$

$$c' = c - [H_2A] (1 + K_1' / (H^+) + K_1'K_2' / (H^+)^2) \quad (16)$$

$$[M^{++}] = (c_M - 0.5c') / (1 + 0.5 k_1'K_1'[H_2A] / (H^+)^2) \quad (17)$$

$$[HA^-] = [H_2A] K_1' / (H^+) \quad (18)$$

In the second case, analogously:

$$[HA^-] = (2c - c_B - [H^+]) / (1 + 2(H^+) / K_1') \quad (19)$$

$$c = c - [HA^-] (1 + (H^+) / K_1' + K_2' / (H^+)) \quad (20)$$

$$[M^{++}] = (c_M - c') / (1 - k_2' [HA^-]^2 / (H^+)^2) \quad (21)$$

$$[A^{=}] = K_2'[HA^-] / (H^+) \quad (22)$$

The point where the precipitation of $M(HA)_2$ begins may be calculated from equations (13) and from the equations for complex equilibria. The point where $M(HA)_2$ begins to change to MA is calculated from equations (13), (14), (15), (16), (17), and (18). The point where all $M(HA)_2$ is changed to MA is obtained from (13), (14), (19), (20), (21), and (22). When two solid phases exist, we obtain from (13) and (14)

$$[HA^-] = S_1K_2 / S_2(H^+) \quad (23)$$

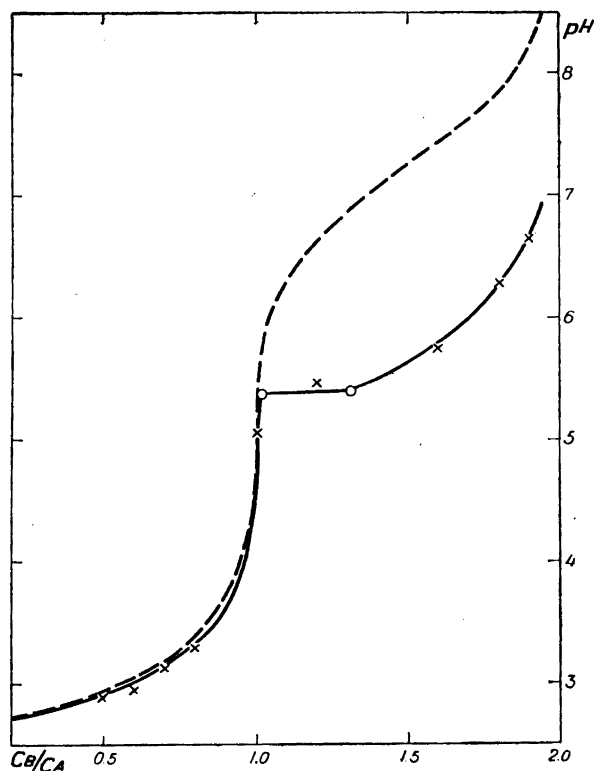


Fig. 2. Titration curve when precipitation of $\text{Ca}(\text{HA})_2$ and CaA occurs. $c = 5 \cdot 10^{-3}$, $c_{\text{Ca}} = 6 \cdot 10^{-3}$. Between the points \circ both the sparingly soluble compounds exist. The dotted line represents the titration curve of the reagent. Experimental points: \times .

and

$$[\text{M}^{++}] = S_2^2 (\text{H}^+)^2 / S_1 K_1'^2 \quad (24)$$

The principle of electroneutrality gives

$$c_{\text{B}} = 2c_{\text{M}} - 2[\text{M}^{++}] - [\text{H}^+] + [\text{HA}^-] + 2[\text{A}^-] + 2[\text{MA}_2^-] \quad (25)$$

Thus this portion of the curve may be easily constructed. The amounts of $\text{M}(\text{HA})_2$ (y_1) and MA (y_2) precipitated may be calculated from

$$c_{\text{M}} = [\text{M}^{++}] + [\text{MA}] + [\text{MA}_2^-] + y_1 + y_2 \quad (26)$$

and

$$c = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^-] + [\text{MA}] + 2[\text{MA}_2^-] + y_1 + 2y_2 \quad (27)$$

The results relating to the solubility equilibria are recorded in Tables 2 and 3. The thermodynamic constants were calculated according to

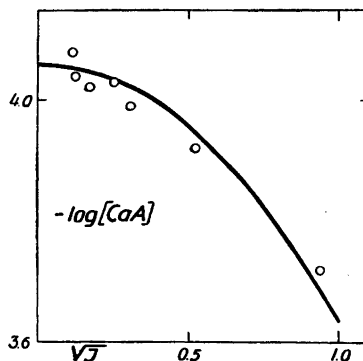


Fig. 3. Solubility of CaA in water at 25° C.

Table 2. Solubility product of $\text{Ca}(\text{HA})_2$ in potassium chloride solutions at 25° C.

$c \cdot 10^3$	$c_B \cdot 10^3$	$c_{\text{Ca}} \cdot 10^3$	c_{KCl}	pH	\sqrt{I}	pS_1
4.57	3.20	5.56	—	3.107	0.121	7.35
4.59	2.75	5.51	—	2.949	0.126	7.31
4.55	3.64	5.54	—	3.294	0.127	7.34
4.61	2.30	5.61	—	2.887	0.127	7.30
4.55	3.64	5.54	0.0732	3.347	0.302	7.04
4.27	3.42	10.41	0.2292	3.396	0.513	6.81
3.35	2.68	27.21	0.7192	3.518	0.897	6.58

Table 3. Solubility product of CaA in potassium chloride solutions at 25° C.

$c \cdot 10^3$	$c_B \cdot 10^3$	$c_{\text{Ca}} \cdot 10^3$	c_{KCl}	pH	\sqrt{I}	pS_2
4.33	8.23	5.27	—	6.641	0.113	6.83
4.35	7.83	5.30	—	6.291	0.117	6.76
4.41	6.61	5.37	—	5.720	0.128	6.69
4.27	6.41	5.21	0.0688	5.952	0.307	6.32
4.26	6.39	5.19	0.228	6.119	0.503	5.91
4.17	6.26	5.08	0.894	6.251	0.955	5.79

$$pS_1 = pS_{1,0} - \frac{3.054 \sqrt{I}}{1 + \alpha \sqrt{I}} + BI \quad (28)$$

and

$$pS_2 = pS_{2,0} - \frac{4.072 \sqrt{I}}{1 + \alpha \sqrt{I}} + BI \quad (29)$$

The following values were obtained:

	pS_0	α	B	
$\text{Ca}(\text{HA})_2$	7.64	1.68	0.03	(25° C)
CaA	7.13	1.81	—	(25° C)

From equations (2) and (9) we obtain

$$[\text{MA}] = k_1 S_2 \quad (30)$$

valid in a saturated CaA solution. The dependence on the ionic strength may be presented by

$$-\log [\text{MA}] = 4.06 - 0.43 I \quad (31)$$

In Fig. 3 this quantity is represented as a function of ionic strength. This result was confirmed spectrophotometrically in a solution with high pH and high calcium concentration. In such a saturated solution nearly all the reagent is in the form of CaA.

7-Iodo-8-quinolinol-5-sulphonic acid has been used for the gravimetric determination of calcium as $\text{Ca}(\text{HA})_2^5$. We see from Fig. 2 that the best pH for precipitation is about 4—5. The relatively high value of the solubility product necessitates the use of an excess of reagent.

These solubility and complex equilibria seem not have been studied previously.

SUMMARY

The complex and solubility equilibria of the calcium chelates of 7-iodo-8-quinolinol-5-sulphonic acid (H_2A) have been investigated. The complexes in the solution are of the type CaA and CaA_2^- . The first stability constant has been determined and the second roughly estimated. The solubility products of the two sparingly soluble compounds $\text{Ca}(\text{HA})_2$ and CaA have been determined. The ultraviolet spectrum of CaA in solution is given. No complexes of the type CaHA^+ or $\text{Ca}(\text{HA})_2$ have been detected in the solution.

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