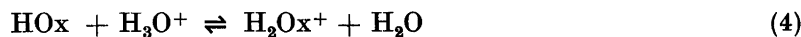
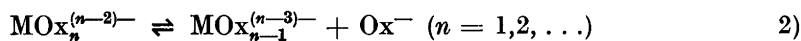
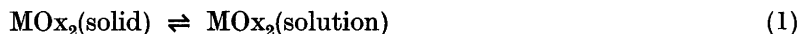


Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. II. 8-Quinolinol Chelate of Calcium in Aqueous Solution

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The equilibria of 8-quinolinol chelates of divalent metals in aqueous solution can obviously be represented as follows:¹



The law of mass action gives

$$[\text{M}^{++}][\text{Ox}^-]^2 = S \quad (5)$$

$$[\text{MOx}_n^{(n-2)-}]/[\text{M}^{++}][\text{Ox}^-]^n = k_n \quad (n = 1, 2, \dots) \quad (6)$$

$$(\text{H}^+)[\text{Ox}^-]/[\text{HOx}] = K_2' \quad (7)$$

$$(\text{H}^+)[\text{HOx}]/[\text{H}_2\text{Ox}^+] = K_1' \quad (8)$$

In the case of chelates which are soluble already in slightly acidic media, it is more convenient to use the equations:

$$[\text{M}^{++}][\text{HOx}]^2/(\text{H}^+)^2 = S/K_2'^2 = K_s \quad (9)$$

$$[\text{MOx}_n^{(n-2)-}](\text{H}^+)^n/[\text{M}^{++}][\text{HOx}]^n = k_n K_2'^n = k_n' \quad (10)$$

which are obtained by combining (7) with the other equations.

When alkali hydroxide is added to a solution of 8-quinolinol, the pH of the solution is changed in a way represented in Fig. 1 by the highest curve. If the solution of 8-quinolinol contains calcium salt the course of the titration curve is changed in the way represented by the other curves in Fig. 1. This effect of the calcium salt is obviously due to the formation of CaOx^+ and to some extent to the formation of CaOx_2 . From the measured pH values and stoichiometric concentrations it is possible to calculate the equilibrium constants k'_1 and k'_2 . For this purpose the following equations are required. From the stoichiometric equations

$$c_M = [\text{M}^{++}] + [\text{MOx}^+] + [\text{MOx}_2] \quad (11)$$

$$c_{\text{Ox}} = [\text{Ox}^-] + [\text{H}_2\text{Ox}^+] + [\text{HOx}] + [\text{MOx}^+] + 2[\text{MOx}_2] \quad (12)$$

where c_M and c_{Ox} are stoichiometric concentrations, the former that of metal salt, the latter that of 8-quinolinol, and from equations (7), (8), (10) we obtain

$$k'_1 + 2([\text{HOx}]/(\text{H}^+)) k'_2 - c'_{\text{Ox}} (\text{H}^+)/[\text{M}^{++}][\text{HOx}] = 0 \quad (13)$$

where

$$c'_{\text{Ox}} = c_{\text{Ox}} - [\text{HOx}](1 + K'_2/(\text{H}^+) + (\text{H}^+)/K'_1) \quad (14)$$

The electroneutrality gives

$$2[\text{M}^{++}] + [\text{MOx}^+] + [\text{H}_2\text{Ox}^+] + c_B = [\text{OH}^-] + [\text{Ox}^-] + 2 c_M + c_A \quad (15)$$

where c_B and c_A are stoichiometric concentrations, the former that of sodium hydroxide and the latter that of a strong acid. From equations (7), (8), (11), (12) and (15) we obtain

$$[\text{HOx}] = (c_{\text{Ox}} + c_A + [\text{OH}^-] - c_B)/(1 + 2(\text{H}^+)/K'_1) \quad (16)$$

and from equations (10) and (11)

$$[\text{M}^{++}] = c_M / \{ (1 + k'_1[\text{HOx}]/(\text{H}^+) + k'_2[\text{HOx}]^2/(\text{H}^+)^2) \} \quad (17)$$

By means of equations (13), (14), (16) and (17) we obtain on the basis of the titration curves of Fig. 1 the constants k'_1 and k'_2 . Each curve refers to one ionic strength. The results are recorded in Table 1. Each value of k'_1 is calculated by the

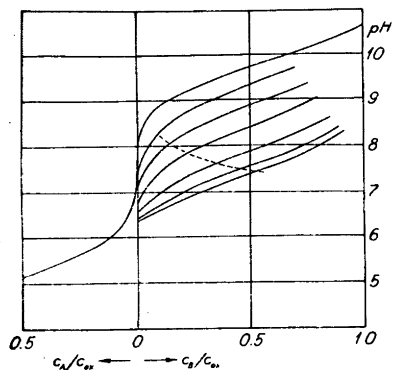


Fig. 1. Effect of calcium chloride on the neutralization curve of 8-quinolinol. $c_{\text{Ox}} = 3.38 \cdot 10^{-3} - 3.66 \cdot 10^{-3}$. From the highest curve downwards: $c_{\text{Ca}} = 0, 0.0027, 0.0087, 0.35, 0.173, 0.46, 0.81$.

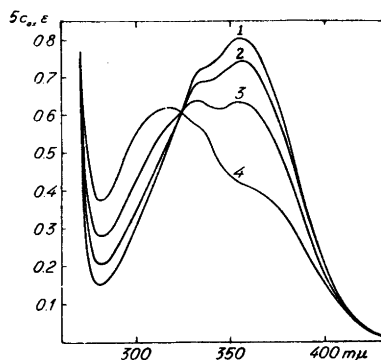


Fig. 2. Ultraviolet absorption spectra of a mixed solution of 8-quinolinol and calcium chloride at some pH values. $c_{\text{Ox}} = 6.67 \cdot 10^{-5}$. $c_{\text{Ca}} = 5.03 \cdot 10^{-2}$. $\sqrt{I} = 0.4$. Curve 1, pH = 9.65. Curve 2, pH = 9.04. Curve 3, pH = 8.69. Curve 4, pH = 8.12.

Table 1. Potentiometric determination of the constant k'_1 in calcium chloride solutions at 20° C.

$c_{\text{Ox}} \cdot 10^3$	$c_{\text{Ca}} \cdot 10^2$	\sqrt{I}	pk'_1
3.61—3.66	0.273—0.276	0.109	6.775
3.40—3.45	0.855—0.865	0.171	6.842
3.39—3.44	3.41—3.47	0.328	6.955
3.38—3.45	17.0—17.3	0.720	7.135
3.40—3.45	45.5—46.3	1.18	7.260
3.40—3.44	79.6—81.0	1.55	7.335

method of least squares from six points of the respective titration curve. For k'_2 only an approximate value ($k'_2 = 10^{-14}$) was obtained. The results can be presented by the Debye-Hückel equation

$$\text{pk}'_1 = \text{pk}'_{1,0} + \frac{1.514\sqrt{I}}{1 + \alpha\sqrt{I}} \quad (18)$$

The method of least squares gave for the parameters the values:

$$\text{pk}'_{1,0} = 6.63 \text{ and } \alpha = 1.54 \text{ (20° C)}$$

Using the value $\text{pK}'_{2,0} = 9.90$ of Näsänen, Lumme and Mukula¹ we obtain:

$$\log k_{1,0} = \text{pK}'_{2,0} - \text{pk}'_{1,0} = 3.27 \text{ (20° C)}$$

Similarly we obtain

$$\log k_{2,0} = 2 \text{p}K'_{2,0} - \text{p}K'_{2,0} \sim 6$$

The complex CaOx^+ was also investigated spectrophotometrically. In Fig. 2 the spectrum (270—430 $m\mu$) of an 8-quinolinol solution containing calcium chloride is presented at certain pH's. Ammonia-hydrochloric acid buffer solutions were used. The constant k'_1 can be calculated from the values of the molar extinction coefficient ϵ . For the calculation the equation

$$k'_1 \epsilon_{\text{CaOx}^+} - \epsilon k'_1 - \{(\epsilon - \epsilon_{\text{HOx}})(\text{H}^+) + (\epsilon - \epsilon_{\text{Ox}^-})K'_2\} / [\text{Ca}^{++}] = 0 \quad (19)$$

was derived. In this equation the ϵ 's are molar extinction coefficients as indicated. The values of ϵ_{HOx} and ϵ_{Ox^-} were obtained from the paper of Näsänen, Lumme and Mukula¹, the value of K'_2 from the equation¹

$$\text{p}K'_2 = 9.90 - \frac{0.509\sqrt{I}}{1 + 1.018\sqrt{I}} + 0.022I \quad (20)$$

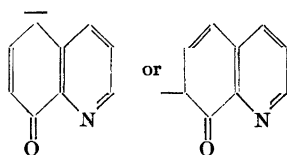
The results are recorded in Table 2. For the calculation of k'_1 the range 340—385 $m\mu$ was used. In this case the concentration of 8-quinolinol is so small that the complex CaOx_2 can be neglected. The results agree very well with the

Table 2. Spectrophotometric determination of the constant k'_1 at 20° C. $\sqrt{I} = 0.40$.
 $c_{\text{Ox}} = 6.67 \cdot 10^{-5}$. $c_{\text{Ca}} = 5.03 \cdot 10^{-2}$. $K'_2 = 1.77 \cdot 10^{-10}$.

λ	$\epsilon \cdot 10^{-3}$	pH	$\text{p}k'_1$
340	1.86	8.69	7.01
	2.08	9.04	
345	1.87	8.69	7.03
	2.13	9.04	
350	1.90	8.69	7.02
	2.20	9.04	
355	1.91	8.69	7.00
	2.23	9.04	
360	1.88	8.69	7.03
	2.22	9.04	
365	1.81	8.69	7.00
	2.13	9.04	
370	1.69	8.69	6.99
	1.98	9.04	
375	1.53	8.69	7.00
	1.79	9.04	
380	1.33	8.69	7.01
	1.56	9.04	
385	1.11	8.69	6.99
	1.30	9.04	
		mean value	7.01

potentiometric results, as is seen from Fig. 3 where pk'_1 is represented as a function of ionic strength.

By means of equation (19) the molar extinction coefficient of CaOx^+ can also be calculated. In Fig. 4 this quantity as well as these of HOx and Ox^- are compared at the range 280–400 $m\mu$. The spectra of CaOx^+ and Ox^- show a certain similarity but both differ distinctly from that of HOx . The following structure for Ox^- has been suggested²



The peaks at 335 $m\mu$ and 355 $m\mu$ may be assigned to these 7,8 and 5,8 keto-tautomers. The peak at 355 $m\mu$ also appears in the spectrum of CaOx^+ . The maximum at 335 $m\mu$ appears in the spectrum of CaOx^+ as a shoulder. This resemblance of the spectra of CaOx^+ and Ox^- seems to point to a certain similarity of structures.

The results obtained for the solubility equilibria are recorded in Table 3. In Fig. 1 the broken line represents the pH at which precipitation should begin. This system has however a very great tendency to supersaturation and therefore the parts of the curves in Fig. 1 above this limits correspond to a homogenous equilibrium. Before long, however, precipitation begins and the pH suddenly falls. Generally the solubility equilibrium is reached four hours after the beginning of precipitation. However, an interval of about twenty hours was allowed to elapse before the pH was measured.

Table 3. Solubility equilibria of calcium chelate in potassium chloride solutions at 20° C.

\sqrt{I}	$c_{\text{Ox}} \cdot 10^3$	$c_{\text{Ca}} \cdot 10^3$	$c_{\text{A}} \cdot 10^3$	$c_{\text{B}} \cdot 10^3$	pH	$\log K_s$
0.085	3.41	1.61	3.41	5.50	8.94	8.90
0.092	3.84	1.94	3.84	6.27	8.87	8.91
0.117	6.55	3.09	6.55	11.20	8.74	8.93
0.124	3.41	2.73	3.41	5.50	8.61	8.97
0.178	3.41	3.43	3.41	5.55	8.71	9.00
0.269	3.41	3.43	3.41	5.55	8.75	9.08
0.461	3.41	3.43	3.41	5.55	8.78	9.17
0.782	3.41	3.43	3.41	5.55	8.81	9.21
0.952	3.41	3.43	3.41	5.55	8.80	9.20
1.004	3.41	3.43	3.41	5.55	8.78	9.16
1.180	3.41	3.43	3.41	5.55	8.77	9.13

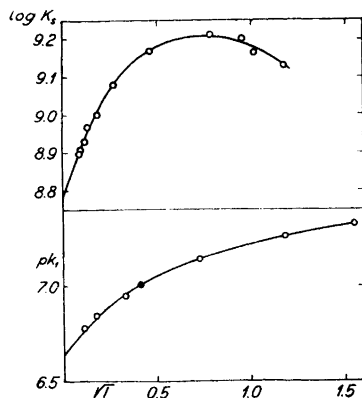


Fig. 3. Constant k'_1 in calcium chloride solutions and constant K_s in potassium chloride solutions as a function of ionic strength. ● spectrophotometric, ○ potentiometric method.

For the calculation of K_s the following equations were required. The stoichiometric equations are in this case

$$c_{\text{Ca}} = [\text{Ca}^{++}] + [\text{CaOx}^+] + [\text{CaOx}_2] + x \quad (21)$$

$$c_{\text{Ox}} = [\text{Ox}^-] + [\text{HOx}] + [\text{H}_2\text{Ox}^+] + [\text{CaOx}^+] + 2[\text{CaOx}_2] + 2x \quad (22)$$

where x is the decrease in total calcium concentration owing to precipitation. Combining these equations with the electroneutrality equation (15) we obtain also in this case equation (16). From equations (7), (8), (10), (21) and (22) we obtain

$$[\text{Ca}^{++}] = \frac{2c_{\text{Ca}} - c_{\text{Ox}} + [\text{HOx}](1 + (\text{H}^+) / (K'_1 + K'_2 / (\text{H}^+)))}{2 + k'_1 [\text{HOx}] / \text{H}^+} \quad (23)$$

The results can be presented by the Debye-Hückel equation

$$\log K_s = \log K_{s,0} + \frac{2.018\sqrt{I}}{1 + \alpha\sqrt{I}} - BI \quad (24)$$

The calculation by the method of least squares gave

$$\log K_{s,0} = 8.76, \quad \alpha = 2.24 \text{ and } B = 0.203 \text{ (20}^\circ\text{C)}$$

For the solubility product of calcium chelate we thus obtain (*cf.* equations (5) and (9))

$$\text{pS}_0 = 2 \text{pK}_{2,0} - \log K_{s,0} = 11.12 \text{ (20}^\circ\text{C)}$$

In Fig. 3 $\log K_s$ is represented as a function of ionic strength.

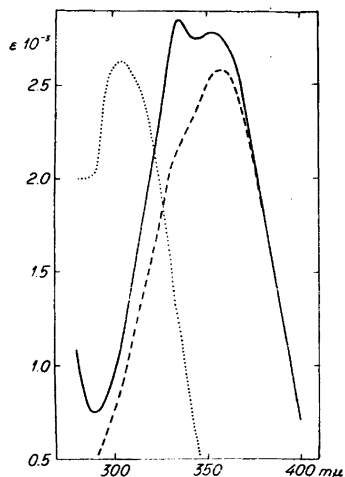


Fig. 4. Molar extinction coefficients of Ox^- , HOx and $CaOx^+$ at the range 280–400 $m\mu$.

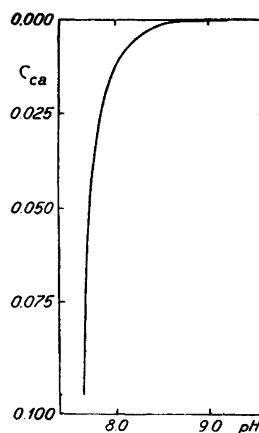


Fig. 5. Beginning of precipitation. $c_{Ox} = 3.78 \cdot 10^{-3}$, $\sqrt{I} = 0.4$.

By means of the values of the equilibrium constants it is now possible to calculate the pH at which the precipitation begins. This value is not constant but is dependent on the calcium and 8-quinolol concentration (and to a lesser extent also on ionic strength). Neglecting complex formation and H_2Ox^+ , which have a relatively slight effect, we obtain from equations (7), (9) and (12)

$$(H^+) = c_{Ox} \sqrt{c_{Ca} / K_s} - K'_2 \quad (25)$$

The exact calculation is possible by means of the following equations:

$$(H^+) = [HOx] \sqrt{[Ca^{++}] / K_s} \quad (26)$$

$$[HOx] = c_{Ox} / \left\{ 1 + K'_2 / (H^+) + (H^+) / K'_1 + k'_1 [Ca^{++}] / (H^+) + 2k'_2 [HOx][Ca^{++}] / (H^+)^2 \right\} \quad (27)$$

$$[Ca^{++}] = c_{Ca} / \left\{ 1 + k'_1 [HOx] / (H^+) + k'_2 [HOx]^2 / (H^+)^2 \right\} \quad (28)$$

When $K'_2 > (H^+)$ all terms in the denominators of (27) and (28) except the first and second terms can generally be neglected. In this case we obtain

$$(H^+) = c_{Ox} \sqrt{[Ca^{++}] / K_s} - K'_2 \quad (29)$$

and

$$[Ca^{++}] = c_{Ca}^2 / (2 c_{Ca} + k'_1{}^2 K_s - [Ca^{++}]) \quad (30)$$

Using the values obtained above for the equilibrium constants, we have calculated for some values of c_{Ox} and c_{Ca} the pH values at which precipitation begins. These results are represented in Fig. 5. According to Irving, Ewart and Wilson³ the solubility of 8-quinolinol in pure water is 3.78 g-mol/l at 20° C. When precipitation begins near the isoelectric point c_{Ox} cannot be higher than this value. From Fig. 5 we see that when $c_{\text{Ox}} = 3.78 \cdot 10^{-3}$ and $c_{\text{Ca}} = 0.1$ precipitation begins at pH = 7.7. When $c_{\text{Ca}} = 0.01$ and the 8-quinolinol concentration is the same, precipitation begins at pH = 8.1. The same curve indicates also how complete precipitation is. For instance, the calculation gives that the total calcium concentration of the solution is $1 \cdot 10^{-4}$ when the excess of 8-quinolinol is $3.78 \cdot 10^{-3}$ and the pH is 9.2. With the same excess of 8-quinolinol the total calcium concentration is $1 \cdot 10^{-5}$ if the pH is 11.2. In analytical practice the excess of 8-quinolinol may in these higher pH's, be somewhat greater than in the case treated, because a part of the 8-quinolinol exists as Ox^- .

Concerning experimental details the reader is referred to the paper of Näsänen, Lumme and Mukula¹.

SUMMARY

The equilibria of 8-quinolinol chelate of calcium in aqueous solution has been studied. The complexity constant of the first complex between calcium and 8-quinolinol ions has been determined potentiometrically and spectrophotometrically as a function of ionic strength. For the thermodynamic constant the value $k_{1,0} = 5.4 \cdot 10^3$ at 20° C was obtained. For the complexity constant of the second complex the approximate value $k_2 \sim 10^6$ was obtained. The ultra-violet spectrum of the first complex has been determined. It shows a similarity to that of the 8-quinolinol ion, pointing to a certain resemblance of structures. The solubility product of calcium chelate has been determined in solutions of potassium chloride as a function of ionic strength. For the thermodynamic solubility product of calcium chelate the value $S_0 = 6.0 \cdot 10^{-12}$ (20° C) was obtained.

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