Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. IV. 8-Quinolinol Chelates of Cadmium, Zinc and Copper in Aqueous Solutions

REINO NÄSÄNEN and URHO PENTTINEN

Laboratory of Physical Chemistry, Institute of Technology, Helsinki, Finland

In the two preceding papers [2,3] the 8-quinolinol chelates of the alkaline earth metals have been dealt with. These chelates cannot be precipitated until the pH is so high that the 8-quinolinol in the solution exists mainly in the neutral form, HOx[1]. The chelates of the other divalent metals, however, can be precipitated at a pH so low that the main constituent is the positive ion H_2Ox^+. This fact leads to a somewhat different treatment of the solubility equilibria in the two cases.

The essence of the method used in both cases is to regulate the pH to such a value that, whilst a sufficient amount of the precipitate is formed, the solution contains amounts of 8-quinolinol and metal ions such that the concentrations of all the constituents can be calculated accurately from the stoichiometric concentrations, from the pH measured and from dissociation constants of 8-quinolinol [1]. The pH may be regulated by adding sodium hydroxide or perchloric acid.

The solubility equilibria can be represented at higher pH's by

$$MOx_2(s) + 2\ H^+ = M^{++} + 2HOx \tag{1}$$

and at lower pH's by

$$MOx_2(s) + 4H^+ = M^{++} + 2H_2Ox^+ \tag{2}$$
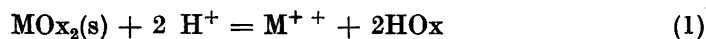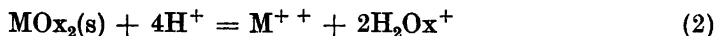
In the latter case, dealt with in the present paper, the law of mass action gives

$$\frac{[M^{++}][H_2Ox^+]^2}{(H^+)^4} = K_s' \tag{3}$$

One can easily see that[2]

$$K'_s = S/K'^2_1 K'^2_2 \tag{4}$$

where S is the solubility product,

$$S = [M^{++}][Ox^-]^2 \tag{5}$$

and K'_1 and K'_2 are the dissociation constants of 8-quinolinol [1].

The complexes between metal ions and the ligand Ox^- display a great stability. Their role in the solubility equilibria is, however, slight beacause of the very low concentration of the ligand. Only the first complex MOx^+ is of any significance. The equilibrium in question can be represented at higher pH's by

$$MOx^+ + H^+ = M^{++} + HOx \tag{6}$$

and at lower pH's by

$$MOx^+ + 2H^+ = M^{++} + H_2Ox^+ \tag{7}$$

In the latter case the law of mass action gives

$$\frac{[MOx^+]\ (H^+)^2}{[M^{++}][H_2Ox^+]} = k''_1 \tag{8}$$

One can easily see that [2]

$$k''_1 = k_1 K'_1 K'_2 \tag{9}$$

where

$$k_1 = [MOx^+]/[M^{++}][Ox^-] \tag{10}$$

For the calculation of the solubility equilibrium the following equations were obtained:

$$[H_2Ox^+] = \frac{c_{Ox} + c_A - c_B + [OH^-] - [H^+]}{2 + K'_1/(H^+)} \tag{11}$$

$$c'_{Ox} = c_{Ox} - [H_2Ox^+]\{1 + K'_1/(H^+) + K'_1 K'_2/(H^+)^2\} \tag{12}$$

$$\frac{1}{K'_s} = \frac{(H^+)^4}{(c_M - 0.5\ c'_{Ox})[H_2Ox^+]^2} + \frac{0.5\ (H^+)^2\ k''_1}{(c_M - 0.5\ c'_{Ox})[H_2Ox^+]} \tag{13}$$

(For an explanation of the notation see refs. 1, 2, 3.) The second term on the right hand side of equation (13) was generally negligible.

The pH was generally measured but in the case of copper chelate, it was so low, (about 2) that the spectrophotometric determination of $[H_2Ox^+]$ gave better results. This analysis was carried out as follows: A sample of clear equilibrium solution was diluted to a suitable concentration with a 0.1 molar solution of perchloric acid and the extinction was measured at 365 mμ.

From the total concentration obtained, the concentration of H_2Ox^+ was calculated and thence, using equation (11), the concentration of hydrogen ion.

The constants k_1'' were determined spectrophotometrically, using the equation

$$\varepsilon k_1'' - \varepsilon_{MOx^+} k_1'' + \{(\varepsilon - \varepsilon_{H_2Ox^+})(H^+)^2 + (\varepsilon - \varepsilon_{HOx})K_1'(H^+)\}/[M^{++}] = 0 \qquad (14)$$

In this equation $\varepsilon = e/c_{Ox}$ (e the extinction when 10 mm cells were used), ε_{MOx^+}, $\varepsilon_{H_2Ox^+}$, ε_{HOx} are molar extinction coefficients as indicated. The values of K_1', $\varepsilon_{H_2O^+}$ and ε_{HOx} have been determined previously [1]. The wavelength range 340 mμ—380 mμ was used. The conditions were not very favourable because the light absorption of H_2Ox^+ at this wavelength range is relatively large but the other methods seemed to be still worse. From a definite pH value upwards practically all the 8-quinolinol exists as MOx^+ if the metal salt is in excess. On the other hand from a definite pH value downwards the complex ions practically vanish from the solution. The measurements must therefore be made over a relatively narrow pH range characteristic of each chelate. Generally four or five pH values were used. For each pH an equation (14) was obtained. These equations were then solved by the method of least squares. The desired pH's were obtained by adding perchloric acid or sodium hydroxide.

The results relating to the complex equilibria are recorded in Table 1.

Table 1. Spectrophotometric determination of equilibrium constants k_1'' for $CdOx^+$, $ZnOx^+$ and $CuOx^+$ at 20° C.

pH	350 mμ	360 mμ	370 mμ	380 mμ	
4.739	1530	1540	1460	1195	$c_{Cd} = 4.79 \cdot 10^{-3}$
4.983	1595	1650	1560	1310	$c_{Ox} = 2.00 \cdot 10^{-4}$
5.462	1910	2050	1990	1690	$\sqrt{I} = 0.127$
6.978	2175	2358	2265	1935	$pk_1'' = 7.35$

pH	350 mμ	355 mμ	360 mμ	365 mμ	
4.417	1715	1760	1750	1700	$c_{Zn} = 4.20 \cdot 10^{-3}$
4.744	1890	1940	1940	1910	$c_{Ox} = 2.00 \cdot 10^{-3}$
6.265	2140	2235	2260	2235	$\sqrt{I} = 0.115$
7.444	2180	2270	2325	2275	$pk_1'' = 6.56$

pH	530 mμ	355 mμ	360 mμ	365 mμ	370 mμ	
2.31	1735	1790	1815	1770	1700	$c_{Cu} = 5.00 \cdot 10^{-3}$
2.39	1715	1790	1810	1790	1710	$c_{Ox} = 2.00 \cdot 10^{-4}$
2.68	1790	1885	1940	1960	1900	$\sqrt{I} = 0.123$
3.59	1940	2080	2160	2200	2100	$pk_1'' = 2.550$
5.88	1975	—	2190	2215	—	

For extrapolation to zero ionic strength the equation

$$pk''_{1.0} = pk''_1 - \frac{2.02\sqrt{I}}{1 + a\sqrt{I}} \qquad (15)$$

was used. The value $a = 1.54$, obtained previously for $CaOx^+$, was used [2]. The extrapolation gave

	$CdOx^+$	$ZnOx^+$	$CuOx^+$
$pk''_{1.0}$	7.135	6.363	2.361

Using the values $pK_{1.0} = 5.02$ and $pK_{2.0} = 9.90$, obtained previously [1], we obtained from equation (9) the complexity consants of MOx^+. With the complexity constants of the alkaline earth metals, previously determined [2,3], we obtain the following summary:

	$BaOx^+$	$SrOx^+$	$CaOx^+$	$MgOx^+$	$CdOx^+$	$ZnOx^+$	$CuOx^+$
$\log k_{1.0}$	2.07	2.56	3.27	4.74	7.78	8.56	12.56

For the complexes of the alkaline earth metals the absorption spectra (280—400 mμ) were obtained indirectly. The spectra of the cadmium, zinc and copper complexes, on the contrary, have been obtained directly because of the very much greater complex formation. The absorption spectra of the latter (300—400 mμ) are shown in Fig. 1. The maxima at about 360 mμ obviously correspond to the maximum of Ox^- at 355 mμ [1]. A shoulder at about 330 mμ in the spectra of $ZnOx^+$ and $CdOx^+$ obviously corresponds to the maximum at 335 mμ in the spectrum of Ox^-. Another shoulder occurs in the spectra of the cadmium and zinc complexes near 315 mμ, at which H_2Ox^+ has a maximum. The same maximum and the two shoulders also occur in the spectra of the complexes of the alkaline earth metals but the shoulders do not occur in the spectrum of the copper complex. In terms of the structures of 8-quinolinol HOx, its positive ion H_2Ox^+ and its negative ion Ox^-, as reported in the literature [4], the following structures may be suggested for MOx^+

| I | II | III |
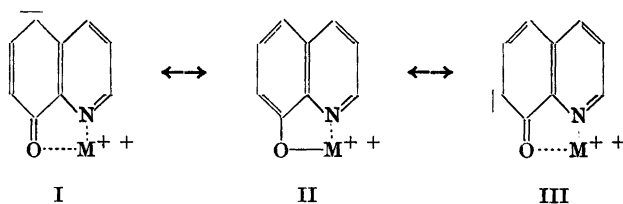
The polar structure I probably corresponds to the maximum at about 360 mμ. Thus this structure seems to be predominant. The structures II and III
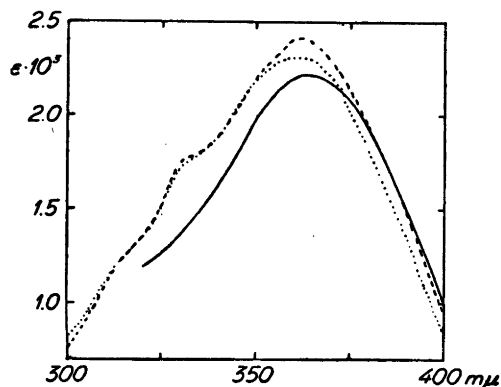
Fig. 1. Molar extinction coefficients of MOx+. CdOx+ – – –, ZnOx+ . . . ., CuOx+ ——.

probably corresponding to the shoulders at 315 mμ and 335 mμ, are of little significance.

We have assumed above that the higher complexes, particularly MOx$_2$, do not make any contribution to the equilibrium. In actual fact the spectrophotometric data show that this is true, as can easily be understood in view of the very low concentration of the ligand Ox$^-$ at the pH's in question.

The results relating to the solubility equilibria of cadmium, zinc and copper chelates in sodium perchlorate solutions are recorded in Table 2. The measurements are performed at 2—4 ionic strengths. The values quoted for log K_s' are mean values.

Table 2. Solubility equilibria of cadmium, zinc and copper chelates in sodium perchlorate solutions.

$\sqrt{I}$	$(c_A \cdot 10^3)$ $c_{Ox} \cdot 10^3$	CdOx$_2$ (25° C) $c_{Cd} \cdot 10^3$	$c_B \cdot 10^3$	pH	log K_s'
0.145	3.62—3.70	6.92—7.09	2.04—6.12	3.835—4.173	7.88
0.506	3.43—3.49	6.57—6.68	1.92—4.71	4.004—4.190	8.54
1.010	3.68—3.71	7.05—7.10	2.04—3.04	4.085—4.186	9.07

$\sqrt{I}$	$(c_A \cdot 10^3)$ $c_{Ox} \cdot 10^3$	ZnOx$_2$ (20° C) $c_{Zn} \cdot 10^3$	$c_B \cdot 10^3$	pH	log K_s'
0.104	4.87—4.96	2.42—2.47	1.58—4.28	3.306—3.434	5.65
0.142	9.01—9.62	4.50—4.81	1.58—4.27	3.040—3.812	5.73
0.266	4.86—9.60	2.42—4.80	1.58—15.81	3.363—3.854	6.00
0.413	4.84—9.57	2.41—4.78	1.57—15.76	3.411—3.886	6.25

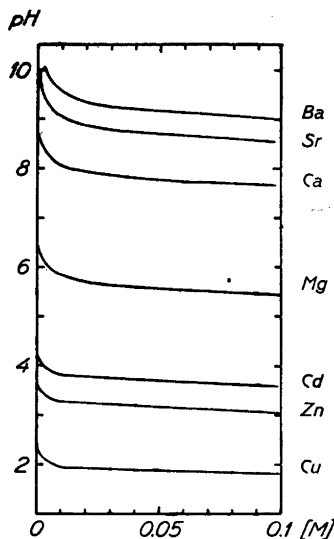| $\sqrt{I}$	$c_{Ox} \cdot 10^3$	CuOx$_2$ (25° C) $c_{Cu} \cdot 10^3$	$c_A \cdot 10^3$	pH	log K_s'
0.176	3.75—4.00	10.59—16.25	6.25—6.67	1.916—2.050	0.342
0.460	3.75	10.00	6.25	2.110	0.870

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Fig. 2. Precipitation of some divalent metals with 8-quinolinol. [Ox] = 3.78 · 10⁻³. $\sqrt{I} = 0.4$.

from 3—6 experiments. The pH's in the measurements of copper chelate were calculated from $[H_2Ox^+]$ measured spectrophotometrically, using equation (11) and the values for the activity coefficient of the hydrogen ion determined previously[1]. The results can be represented by

$$\log K'_s = \log K'_{s,o} + \frac{3.06 \sqrt{I}}{1 + \alpha \sqrt{I}} \tag{16}$$

Calculation by the method of least squares gave

	$CdOx_2$	$ZnOx_2$	$CuOx_2$
$\log K'_{s,o}$	7.49	5.34	—0.125
α	0.95	0.95	0.90

From equation (4) we obtain for the thermodynamic solubility products:

	$CdOx_2(25°)$	$ZnOx_2(20°)$	$CuOx_2(25°)$
pS_o	21.956	24.500	29.571

Recently Phillips and Price[5] have reported values for the solubility products of some 8-quinolinol chelates. These values have been computed from the solubility data available in the literature[6]. Like some other authors[6] they have assumed that the equilibrium in question is represented by (1). Since the data concern solubility in 1 N acetic acid, the pH is generally so low that the equilibrium is represented by (2). Therefore their values are incorrect.

A correct calculation gives solubility product values which are at least of the same order of magnitude as our values.

In Fig. 2 the total concentration of metal in the solution is represented as a function of pH when the excess of reagent is $[Ox] = 3.78 \cdot 10^{-3}$. In the case of cadmium, zinc and copper chelates the following equations were used:

$$[H_2Ox^+] = [Ox]/\left\{1 + K_1'/(H^+) + k_1' \; K_2'/(H^+)^2 + k_1'[M^{++}]/(H^+)^2\right\} \qquad (17)$$

$$[M^{++}] = K_s' \; (H^+)^4/[H_2Ox^+]^2 \qquad (18)$$

$$[M] = [M^{++}](1 + k_1'[H_2Ox^+]/(H^+)^2 \qquad (19)$$

SUMMARY

The equilibria of the 8-quinolinol chelates of cadmium, zinc and copper in aqueous solution have been investigated. The complex formation involved has been studied spectrophotometrically and the complexity constants of the first complexes have been determined. The solubility products of these chelates have been determined potentiometrically. The ultra-violet spectra of the complex ions are discussed.

REFERENCES

1. Näsänen, R., Lumme, P., and Mukula, A. L. *Acta Chem. Scand.* 5 (1951) 1199.
2. Näsänen, R. *Acta Chem. Scand.* 5 (1951) 1293.
3. Näsänen, R. *Acta Chem. Scand.* 6 (1952) 352.
4. Ewing, G. W., and Steck, E. A. *J. Am. Chem. Soc.* 68 (1946) 2181; Stone, K. G., and Friedman, L. 69 (1947) 209; Hearn, J. M., Morton, R. A., and Simpson, J. C. E. *J. Chem. Soc.* (1951) 3318.
5. Phillips, J. P., and Price, H. P. *J. Am Chem. Soc.* 73 (1951) 4414.
6. Treadwell, W. D., and Ammann, A. *Helv. Chim. Acta* 21 (1938) 1249.