

## Potentiometric and Spectrophotometric Studies on 8-Quinolol and Its Derivatives. III. 8-Quinolol Chelates of Barium, Strontium and Magnesium in Aqueous Solutions

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The method used for the investigation of calcium chelate<sup>1</sup> has also been used in this study. In deriving the equations for the calculation of the equilibrium constants, however, some approximations, which were quite permissible, but not inevitable, were made and the exact equations are now given. The stability constants of the complexes may be calculated by means of the following equations (for an explanation of the notation, see ref. 1).

$$\sum i k'_i ([\text{HOx}]/(\text{H}^+))^{i-1} - c'_{\text{Ox}} (\text{H}^+)/[\text{M}^{++}][\text{HOx}] = 0 \quad (1)$$

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

$$[\text{HOx}] = (c_{\text{Ox}} + c_{\text{A}} - c_{\text{B}} + [\text{OH}^-] - [\text{H}^+]) / (1 + 2 (\text{H}^+)/K'_1) \quad (3)$$

$$[\text{M}^{++}] = c_{\text{M}} / (1 + \sum k'_i ([\text{HOx}]/(\text{H}^+))^i) \quad (4)$$

From equations (1) and (4) we obtain:

$$\sum (i - c'_{\text{Ox}}/c_{\text{M}}) ([\text{HOx}]/(\text{H}^+))^i k'_i - c'_{\text{Ox}}/c_{\text{M}} = 0 \quad (5)$$

For the calculation of the solubility equilibria the following equation is needed:

$$[\text{M}^{++}] = (2c_{\text{M}} - c'_{\text{Ox}}) / (2 + \sum (2 - i) ([\text{HOx}]/(\text{H}^+))^i k'_i) \quad (6)$$

The concentration  $[\text{HOx}]$  may be calculated from equation (3) and thus the constant

$$K_{\text{S}} = S/K'_2 = [\text{M}^{++}][\text{HOx}]^2/(\text{H}^+)^2 \quad (7)$$

may be calculated from the known values of the stoichiometric concentrations, the dissociation constants of 8-quinolinol, the constants  $k'_i$ , and the pH of the solution.

Of the constants  $k'_i$ , only the first,  $k'_1$  can be calculated accurately, because the last term in equation (1) is, within the experimental error, independent of the quotient  $[\text{HOx}]/(\text{H}^+)$  when the latter is varied from  $0.987 \cdot 10^5$  to  $7.05 \cdot 10^5$ . Thus in equation (1) the term including the constants  $k'_i$  ( $i > 1$ ) are negligible. Under the conditions prevailing in the cases investigated here the first complex is the only one of importance. The higher complexes would be expected to play a more important role at higher ligand concentrations, which are possible only at a high pH. Under such conditions, however, the potentiometric method is useless, and the spectrophotometric method is unsuitable because of the very low solubilities of the 8-quinolinolates in question.

The values obtained for the constant  $k'_1$  are recorded in Table 1.

Table 1. Potentiometric determination of the constants  $k'_1$  in barium, strontium and magnesium chloride solutions at 20° C.

$\sqrt{I}$	log $F$	Barium complex		Strontium complex		Magnesium complex	
		$pk'_1$	$pk'_{1,0}$	$pk'_1$	$pk'_{1,0}$	$pk'_1$	$pk'_{1,0}$
0.115	0.148	7.98	7.83	7.48	7.33	5.31	5.16
0.196	0.228	8.06	7.83	7.58	7.34	5.38	5.17
0.320	0.324	8.16	7.84	7.67	7.35	5.47	5.15
0.720	0.509	8.33	7.82	7.85	7.34	5.65	5.14
1.000	0.596	8.41	7.81	7.92	7.32	—	—
		mean value	7.83		7.34		5.16

These can be represented satisfactorily by the equation

$$pk'_1 = pk'_{1,0} + \frac{1.514 \sqrt{I}}{1 + 1.54 \sqrt{I}} \quad (8)$$

obtained previously for calcium chelate<sup>1</sup>. The constants

$$k_{1,0} = \frac{(\text{MOx}^+)}{(\text{M}^{++})(\text{Ox}^-)} \quad (9)$$

may be calculated from the relation

$$\log k_{1,0} = pK_{2,0} - pk'_{1,0} \quad (10)$$

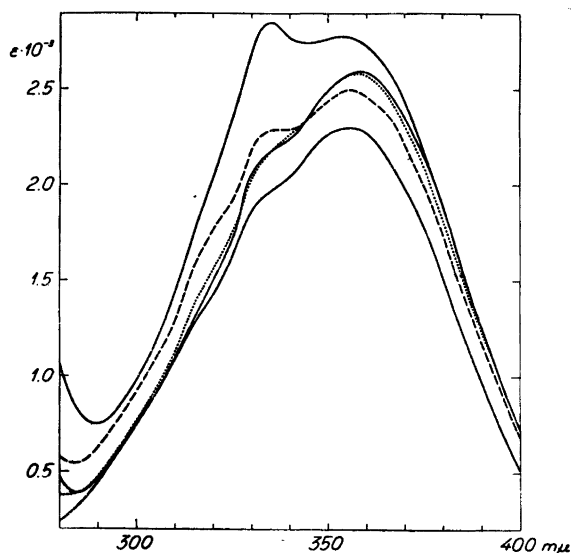


Fig. 1. Ultra-violet absorption spectra of the 8-quinolinol complexes of alkaline earth metals. Upper full line  $Ox^-$ ; middle full line  $CaOx^+$ ; lower full line  $MgOx^+$ ; broken line  $SrOx^+$ ; dotted line  $BaOx^+$ .

Using the value  $pK_{2,0} = 9.90$  of Näsänen, Lumme Mukula<sup>2</sup> we obtain

	$MgOx^+$	$CaOx^{+1}$	$SrOx^+$	$BaOx^+$	
$\log k_{1,0}$	4.74	3.27	2.56	2.07	(20° C)

The results obtained spectrophotometrically using the method used in the study of calcium chelate were consistent with the above. In Fig. 1 the molar extinction coefficients of the complex ion  $MOx^+$ , as well as that of the ligand  $Ox^-$ , are represented over the range 280—400  $m\mu$ . The spectra of the complexes seem to resemble each other and the spectrum of  $Ox^-$  in main features. The relatively small differences are irregular and may in part be due to experimental error. The effect of the latter are relatively great because of the indirect method.

The results relating to the solubility equilibria of magnesium chelate are recorded in Table 2. The constant  $K_s$  may be represented by the equation

$$\log K_s = 4.248 + \frac{2.018 \sqrt{I}}{1 + 1.90 \sqrt{I}} - 0.402 I \quad (20^\circ C) \quad (11)$$

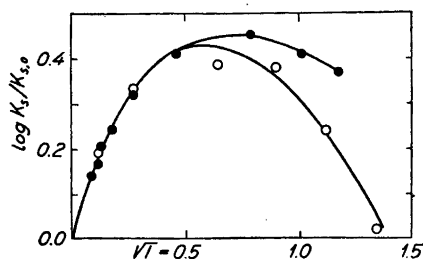


Fig. 2. Solubility products of 8-quinolinol chelates of magnesium and calcium in aqueous solutions of potassium chloride as a function of the ionic strength at 20° C.

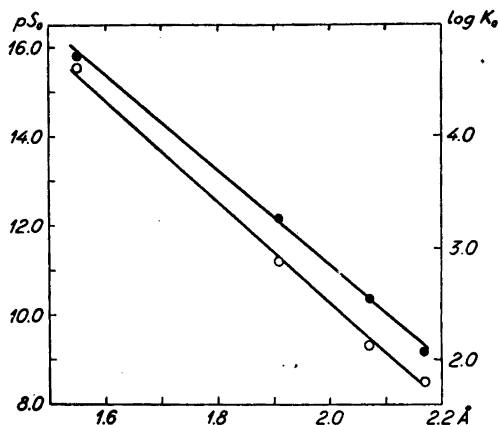


Fig. 3. The thermodynamic solubility product and the complex constant of the chelates of alkaline earth metals as a function of the metallic (octahedral) radius.

Table 2. Solubility equilibria of magnesium chelate in potassium chloride solutions at 20° C.

$$c_{\text{Ox}} = 3.41 \cdot 10^3. \quad c_{\text{Mg}} = 2.81 \cdot 10^3. \quad c_{\text{A}} = 3.41 \cdot 10^3. \quad c_{\text{B}} = 5.55 \cdot 10^3.$$

$\sqrt{I}$	pH	$\log K_s$
0.114	6.53	4.44
0.270	6.60	4.58
0.640	6.63	4.63
0.900	6.63	4.62
1.180	6.57	4.49
1.340	6.48	4.27

In Fig. 2,  $\log K_s$  for the magnesium and calcium chelates are plotted against ionic strength. The pH is sensitive to the value of  $K_s$  only when  $c_{\text{B}} < c_{\text{A}} - c_{\text{Ox}}$ . Under these conditions the barium and strontium chelates precipitate only if the metallic ion concentration is considerable. The extrapolation to zero ionic strength in these cases was done by means of the equation

$$\log K_s = \log K_{s,0} + \frac{2.018 \sqrt{I}}{1 + 2.24 \sqrt{I}} - 0.203 I \quad (20^\circ \text{C}) \quad (12)$$

obtained previously for calcium chelate<sup>1</sup>. This calculation gave the values

$$\begin{array}{ccc} \text{SrOx}_2 & \text{BaOx}_2 & \\ \log K_{s,0} & 10.47 & 11.31 \quad (20^\circ \text{C}) \end{array}$$

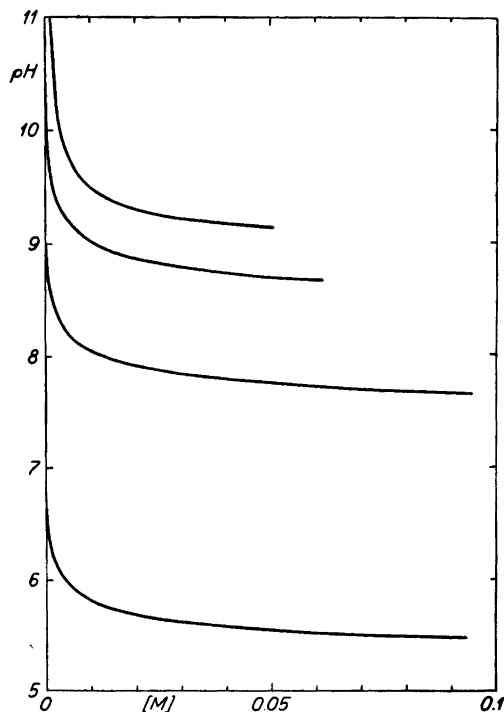


Fig. 4. Precipitation of alkaline earth metals with 8-quinolinol.  $[Ox] = 3.78 \cdot 10^{-3}$ .

From the values of the thermodynamic constants:

	MgOx <sub>2</sub>	CaOx <sub>2</sub>	SrOx <sub>2</sub>	BaOx <sub>2</sub>	
log $K_{s,0}$	4.25	8.76	10.47	11.31	(20° C)

the thermodynamic solubility products

$$S_0 = (M^{++})(Ox^-)^2 \quad (13)$$

may be calculated. Using the relation<sup>1</sup>

$$pS_0 = 2 pK_{2,0} - \log K_{s,0} \quad (14)$$

we obtain

	MgOx <sub>2</sub>	CaOx <sub>2</sub>	SrOx <sub>2</sub>	BaOx <sub>2</sub>	
$pS_0$	15.55	11.22	9.33	8.49	(20° C)

The quantities  $pS_0$  and  $\log k_{1,0}$  seem to vary approximately linearly with the metallic radius<sup>3</sup> as may be seen in Fig. 3.

For the calculation of the total concentration of metal in relation to the pH, the following equations were used:

$$[\text{HOx}] = \frac{[\text{Ox}]}{1 + K'_2/(\text{H}^+) + (\text{H}^+)/K'_1 + k'_1[\text{M}^{++}]/(\text{H}^+)} \quad (15)$$

$$[\text{M}^{++}] = K_s (\text{H}^+)^2/[\text{HOx}]^2 \quad (16)$$

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

where  $[\text{Ox}]$  and  $[\text{M}]$  are the total concentrations of 8-quinolinol and of the metal in the solutions respectively. The results in the case  $[\text{Ox}] = 3.78 \cdot 10^{-3}$  are presented in Fig. 4, where  $[\text{M}]$  is plotted against pH. From this figure the pH at which precipitation begins can be seen. The figure also indicates the completeness of precipitation at different pH's. It must be emphasised, however, that here  $[\text{Ox}] = 3.78 \cdot 10^{-3}$  and that  $[\text{M}]$  is relatively highly dependent on  $[\text{Ox}]$  *i.e.* on the excess of reagent, as is evident from equations (15), (16) and (17).

#### SUMMARY

The equilibria of the 8-quinolinol chelates of the alkaline earth metals in aqueous solution have been investigated. The equilibrium constants of the first complexes have been determined potentiometrically and spectrophotometrically. When the pH is not very high, only the first complexes have any significance. The potentiometric and spectrophotometric results were consistent. The absorption spectra of the first complexes were determined over the range 280—400  $m\mu$ . In main features the spectra are similar to the spectrum of the ligand  $\text{Ox}^-$ . The solubility products of the 8-quinolinolates of alkaline earth metals have been determined.

#### REFERENCES

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