Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. X. Solubility of Some Metal Chelates of 8-Quinolinol-5-Sulphonic Acid in Aqueous Solution

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In the preceding paper of the present authors [1] the stability of some metal chelates of 8-quinolinol-5-sulphonic acid in aqueous solutions was investigated. The results demonstrated that the sulphonic acid group has practically no effect on the stability. On the other hand, it is well known that the metal chelates of this reagent are more soluble than those of 8-quinolinol [2]. The solubility of metal chelates of 8-quinolinol-5-sulphonic acid, however, seem not to have been determined before.

As a dibasic acid, 8-quinolinol-5-sulphonic acid (H_2A) has two types of sparingly soluble metal chelates: $M(HA)_2$ and MA as was observed by Claus and Posselt [3] long ago. We have observed, however, that although it is obviously possible to precipitate $M(HA)_2$ between pH's 4—8 this requires an excess of reagent, so rendering the potentiometric method useless for the determination of the solubility product. Therefore we have investigated only chelates of the type MA, except in the case of barium and strontium where the conditions required were attainable.

RESULTS

The potentiometric method used has been recently described by Ekman and Näsänen [4]. Equilibrium was frequently reached after one day but in some cases a very great tendency to supersaturation existed and precipitation occasionally only began after one week. In this respect, cobalt chelate, espesially, offered difficulties. In connection with cobalt chelate a slow darkening of the solution was observed when sodium hydroxide was added in excess. The maximum at about 360 mμ was shifted towards longer wavelengths and the maximum extinction increased considerably. Generally the measurements are made after 1—2 weeks' standing.

In some cases the precipitate was so soluble that the potentiometric method gave very inaccurate results. This was especially true in the case of copper
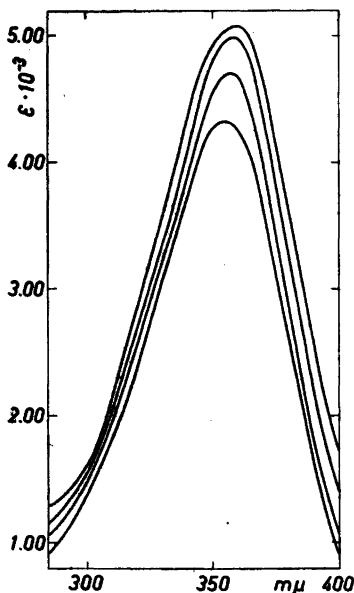
Fig. 1. Molar extinction coefficients of 8-quinolinol-5-sulphonic acid chelates of the alkaline earth metals. From the highest curve downwards: $c_{BaCl_2} = 0.0999$. $pH = 10.5$. $c_{SrCl_2} = 0.0998$. $pH = 10.6$. $c_{CaCl_2} = 0.0945$. $pH = 10.5$. $c_{MgCl_2} = 0.0929$. $pH = 9.6$. $c = 1.48 \cdot 10^{-4}$.

chelate. Therefore we also used a spectrophotometric method for checking. In these measurements the metal ion concentration and pH used were so high that, according to the values of the stability constants, practically all the reagent was in the form MA, and sufficient reagent was added to produce precipitation. When equilibrium was reached the ultraviolet spectrum of the saturated solution was measured. If dilution for extinction measurement was necessary, this was made with a solution of the metal salt in question in such a manner that the metal ion concentration remained constant. The pH of the saturated solution was checked and the effect of addition of sodium hydroxide studied. Thus determination of the concentration of MA was possible if the molar extinction coefficient was known. These were determined in mixed solutions of metal salt and reagent. The pH and the concentration of metal ion were so high that practically all the reagent was present as the chelate MA. The concentration of the reagent was so low that no precipitation occurred.

In Fig. 1 we see the molar extinction coefficients of the alkaline earth metal chelates between 290—400 mμ and in Figs. 2 and 3 those of the other metal chelates investigated. When the concentration of MA in saturated solution is known, we obtain the solubility product from the equation

$$S_2 = [M^{++}] \, [A^=] = [MA] / k_1 \tag{1}$$

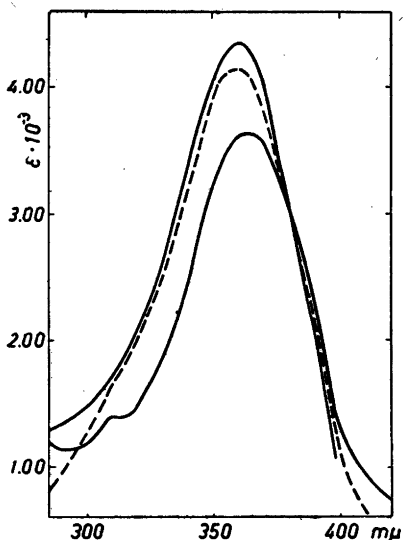where the values of the stability constants k_1 may be obtained from the preceding paper of the present authors [1].

Fig. 2. Molar extinction coefficients of 8-quinolinol-5-sulphonic acid chelates of some divalent metals. Upper full line: $c_{Co(NO_3)_2} = 0.00975$. $pH = 7.3$. Lower full line: $c_{Cu(ClO_4)_2} = 0.0095$. Broken line: $c_{NiCl} = 0.00974$. $pH = 7.4$.
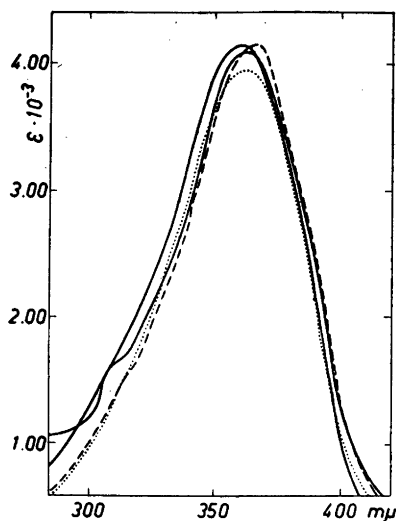
Fig. 3. Molar extinction coefficient of 8-quinolinol-5-sulphonic acid chelates of some divalent metals. Upper full line: $c_{MnCl_2} = 0.01$. $pH = 8.2$. Lower full line: $c_{Cd(ClO_4)_2} = 0.00958$. $pH = 8.0$. Broken line: $c_{Pb(NO_3)_2} = 0.00990$. $pH = 7.5$. Dotted line: $c_{Zn(NO_3)_2} = 0.00922$. $pH = 7.2$.

The analysis of the precipitates obtained gave the formula $M(HA)_2$ or MA without water of hydration. The chelates investigated were of the colours (without drying):

Ba(HA)$_2$	white	CdA	yellowish
BaA	yellowish	ZnA	»
Sr(HA)$_2$	white	CoA	brownish yellow
SrA	yellow	NiA	greenish
CaA	»	CuaA	»
MgA	yellowish	PbA	yellowish
MnA	»		

The potentiometric results are presented in Table 1, where c_M is the stoichiometric concentration of the metal ion, c that of the reagent and c_B that of the sodium hydroxide added. The electrolyte added is signified after the symbol of the chelate.

Table 1. Potentiometric determination of the solubility product of some metal chelates of 8-quinolinol-5-sulphonic acid at 25° C. $S_1 = [M^{++}][HA^-]^2$. $S_2 = [M^{++}][A^=]$.

	pH	$\sqrt{I}$	pS		pH	$\sqrt{I}$	pS
Ba(HA)₂.				Sr(HA)₂.			
KCl.	3.71	0.44	6.26	KCl.	3.98	0.44	5.69
$c = 1.17 \cdot 10^{-2}$	3.74	0.50	6.17	$c = 1.17 \cdot 10^{-2}$	3.99	0.49	5.65
$c_B = 5.86 \cdot 10^{-3}$	3.76	0.66	6.12	$c_B = 5.86 \cdot 10^{-3}$	4.02	0.74	5.58
$c_M = 6.24 \cdot 10^{-3}$.	3.82	0.86	6.02	$c_M = 6.24 \cdot 10^{-3}$.	4.08	0.96	5.51
	3.86	1.05	5.98		4.10	1.16	5.52
	3.84	1.29	6.11		4.08	1.38	5.66
BaA.	7.96	0.14	5.59	SrA.	6.97	0.14	6.62
KCl.	8.46	0.14	5.60	KCl.	7.57	0.14	6.61
$c = 2.49 - 2.67 \cdot 10^{-3}$	8.47	0.46	5.06	$c = 2.49 - 2.67 \cdot 10^{-3}$.	7.48	0.30	6.19
$c_B = 3.56 - 4.68 \cdot 10^{-3}$	8.65	0.70	4.76	$c_B = 3.56 - 4.42 \cdot 10^{-3}$	7.74	0.71	5.73
$c_M = 5.94 - 11.22 \cdot 10^{-3}$.	8.65	0.75	4.74	$c_M = 6.96 - 11.21 \cdot 10^{-3}$.	7.91	1.10	5.48
					8.02	1.56	5.31
CaA.	6.51	0.14	7.09	MgA.	7.11	0.43	6.58
KCl.	7.12	0.34	6.53	KCl.	6.52	0.69	6.22
$c = 2.49 - 2.67 \cdot 10^{-3}$	7.34	0.53	6.21	$c = 2.50 - 31.3 \cdot 10^{-3}$	6.17	0.89	6.07
$c_B = 3.56 - 4.42 \cdot 10^{-3}$	7.60	0.84	5.85	$c_B = 3.74 - 46.9 \cdot 10^{-3}$	5.92	1.19	5.79
$c_M = 5.93 - 11.06 \cdot 10^{-3}$	7.64	1.25	5.74	$c_M = 4.63 - 58.1 \cdot 10^{-3}$.	5.51	1.52	5.76
MnA.	4.78	0.33	8.75	CdA.	3.41	0.19	10.90
MnCl₂.	4.59	0.70	8.20	NaNO₃.	3.77	0.37	10.36
$c = 2.68 \cdot 10^{-3}$				$c = 2.74 - 2.80 \cdot 10^{-3}$.	3.45	0.50	10.24
$c_B = 5.10 \cdot 10^{-3}$.				$c_B = 3.75 - 4.94 \cdot 10^{-3}$	3.48	0.70	10.09
$c_M = 0.036 - 0.167$.				$c_M = 1.21 - 2.39 \cdot 10^{-3}$.	3.49	0.94	10.01
ZnA.				CoA.			
NaNO₃.	3.50	3.48	10.89	Co(NO₃)₂.	3.91	0.523	10.52
$c = 1.67 \cdot 10^{-3}$.	3.68	3.68	10.83	$c = 2.90 \cdot 10^{-2}$	3.85	0.710	10.34
$c_B = 3.56 \cdot 10^{-3}$.	3.86	3.86	10.27	$c_B = 5.50 \cdot 10^{-2}$.			
$c_M = 5.60 \cdot 10^{-3}$.	3.87	3.87	10.08	$c_M = 0.169$.			
	3.92	3.92	9.92				
NiA.	3.26	0.14	11.76	PbA.	2.41	0.13	13.58
KCl.	3.62	0.45	10.97	NaNO₃.	2.46	0.29	13.18
$c = 2.49 \cdot 10^{-3}$	3.65	0.71	10.81	$c = 2.61 \cdot 10^{-3}$.	2.51	0.40	12.83
$c_B = 4.42 \cdot 10^{-4}$.	3.67	1.06	10.73	$c_B = 0.00$.	2.59	0.81	12.30
$c_M = 1.09 \cdot 10^{-2}$.	3.58	1.58	10.90	$c_M = 5.82 \cdot 10^{-3}$.	2.62	1.16	12.11

The spectrophotometric results are presented in Table 2. In those cases where the agreement with the potentiometric results was good only one experiment was made. In the case of MnA and CoA the agreement was inferior. In the case of CuA the potentiometric method was useless. Therefore in those cases several measurements were made.

DISCUSSION

The maxima of the spectra of MA in the case of the alkaline earth metals seem to change regularly from about 354 mμ for MgA towards longer wavelengths, being 356 mμ for CaA, 358 mμ for SrA and 359 mμ for BaA. The maximum value of the molar extinction coefficient increases in the same order. For the other chelates the maximum occurs at about 262 mμ for Cd, Co and

Table 2. *Spectrophotometric determination of the solubility products of some metal chelates of 8-quinolinol-5-sulphonic acid at 25° C.* $S_2 = [M^{++}][A^=]$.

	$c \cdot 10^3$	c_M	$[MA] \cdot 10^3$	$\sqrt{I}$	pS_2
BaA	2.23	0.151	0.217	0.67	4.81
SrA	2.23	0.151	0.077	0.67	5.73
CaA	2.23	0.143	0.194	0.66	6.00
MgA	2.28	0.169	3.81	0.72	6.11
MnA	2.68	0.0363	1.25	0.33	8.90
»	2.68	0.0363	1.27	0.33	8.90
»	2.68	0.167	2.12	0.70	8.30
»	23.1	0.231	2.55	0.83	8.20
CdA	2.68	0.0348	0.168	0.32	10.60
PbA	2.68	0.0359	0.0074	0.33	12.80
ZnA	2.68	0.0335	1.06	0.32	10.49
CoA	2.90	0.092	2.51	0.52	10.40
»	2.90	0.169	2.69	0.71	10.32
»	3.85	0.233	3.38	0.84	10.25
»	7.16	0.288	3.56	0.95	10.27
NiA	2.38	0.185	8.00	0.75	10.86
CuA	2.68	0.0345	1.45	0.32	13.50
»	2.68	0.0950	1.69	0.53	13.17
»	2.68	0.159	2.14	0.68	13.00
»	2.68	0.220	2.19	0.81	12.98

Zn and at about 265 mμ for Ni and Cu. The maximum value of the molar extinction coefficient increases, however, in the order Cu, Zn, Cd, Pb, Mn, Ni, Co.

The results of Table 1 can be represented by the equation:

$$pS_1 = pS_{1,0} - \frac{3.05 \sqrt{I}}{1 + a \sqrt{I}} + BI \qquad (2)$$

or

$$pS_2 = pS_{2,0} - \frac{4.07 \sqrt{I}}{1 + a \sqrt{I}} + BI \qquad (3)$$

Using the reasonable value $a = 1.5$, we have calculated the parameters by the method of least squares. These data are presented in Table 3. The values for copper, cobalt and manganese chelates are obtained from spectrophotometric measurements.

Table 3. *The thermodynamic solubility products of 8-quinolinol-5-sulphonic acid chelates of some divalent metals at 25° C.*

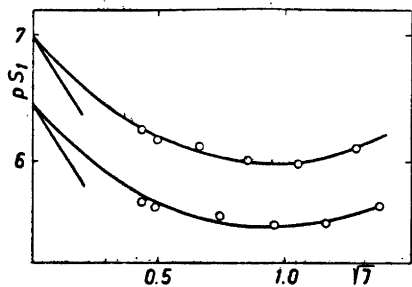|	$pS_{1,0}$	B	$pS_{2,0}$	B	Added electrolyte
Ba	6.99	0.26	6.09	0.151	KCl
Sr	6.45	0.30	7.10	0.068	»
Ca	—	—	7.47	− 0.035	»
Mg	—	—	7.60	—	»
Mn	—	—	9.79	− 0.14	MnCl$_2$
Cd	—	—	11.39	0.21	NaNO$_3$
Zn	—	—	11.30	0.25	»
Co	—	—	11.46	0.44	Co(NO$_3$)$_2$
Ni	—	—	12.10	0.28	KCl
Cu	—	—	14.34	0.15	Cu(ClO$_4$)$_2$
Pb	—	—	13.96	− 0.13	NaNO$_3$

Fig. 4. Solubility products [Ba++] [HA⁻]²
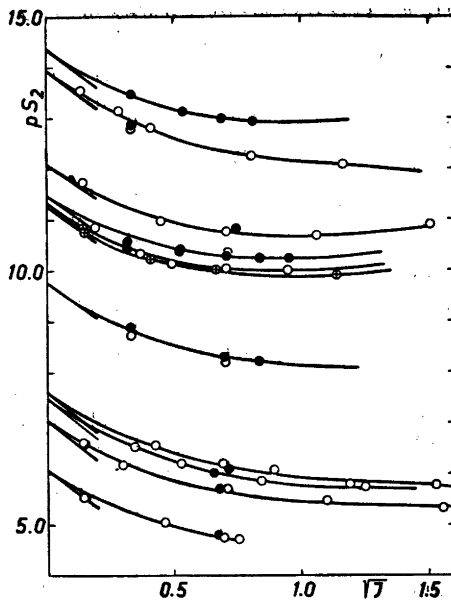(upper curve) and [Sr++] [HA⁻]² (lower
curve) as functions of ionic strength.

Fig. 5. Solubility products ([M++] [A⁼])
as functions of ionic strength. From the top:
BaA, SrA, CaA, MgA, MnA, ZnA, CdA,
CoA, NiA, PbA, CuA. Spectrophotometric:
●. Potentiometric: ○.

In Figs. 4 and 5 the solubility products are represented as functions of ionic
strength. We see from Fig. 5 that the potentiometric and spectrophotometric
results agree relatively well. The smaller differences may in part be due to the
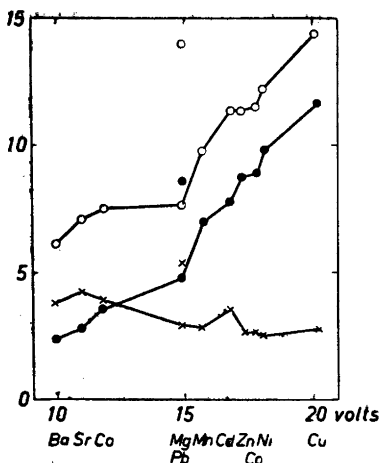different composition of the medium.

Fig. 6. Ionization potential of gaseous
metal atom and $pS_{2,0}$ (○), $logk_{1,0}$ (●),
and log [MA]₀ (×).

In Fig. 6 log $k_{1,0}$, $pS_{2,0}$ and log [MA] ($I = 0$) are represented as functions of the second ionization potential of gaseous metal atoms. As is seen from the figure, and still better from Table 2, the solubility [MA] of different metal chelates varies considerably and does not seem to be a simple function of the ionization potential. Therefore in this case the solubility product is not quite parallel with the stability constant.

Some of these chelates are recommended for the gravimetric analysis of metals in question [5]. Although our analyses show definite composition for these compounds (at about 170° C they seem to lose all water of hydration) they have hardly any importance in this respect because of their slow and frequently incomplete precipitation [5]. In the latter respect, only lead chelate is a total exception as may be seen from Table 2. It must also be observed that in all our measurements an excess of metal salt has been present.

SUMMARY

The solubility products of certain 8-quinolinol-5-sulphonic acid chelates of some divalent metals have been determined. Also the concentration of the chelate molecule in saturated solution has been determined spectrophotometrically. The ultraviolet spectra of the chelates have been determined. The solubility products decrease in the order: Ba, Sr, Ca, Mg, Mn, Cd, Zn, Co, Ni, Cu, but the concentration of the neutral molecule in saturated solution does not follow the same order.

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