

**Potentiometric and Spectrophotometric Studies on
8-Quinolinol and Its Derivatives. XIII. Solubility and Ultra-
violet Spectra of Some Metal Chelates of 7-Nitro-
8-Quinolinol-5-Sulphonic Acid**

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The ultraviolet spectra of the three species of 7-nitro-8-quinolinol-5-sulphonic acid and some of its metal chelates have been measured. The solubility products of the chelates of this reagent with eleven divalent metals have been determined and the effect of ionic strength on the solubility investigated. The results are compared with the corresponding results on 8-quinolinol and on some of its derivatives as studied previously by us.

In a previous paper by the present authors¹ the ionization of 7-nitro-8-quinolinol-5-sulphonic acid and the stability of its metal chelates in aqueous solutions were treated. In the present paper the ultraviolet spectra of 7-nitro-8-quinolinol-5-sulphonic acid and those of its metal chelates are dealt with. Like 8-quinolinol-5-sulphonic acid, its 7-nitro derivative has two types of sparingly soluble metal chelates: $M(HA)_2$ and MA . In the first case only the solubility products of $Ba(HA)_2$, $Sr(HA)_2$ and $Ca(HA)_2$ could be determined. In the second case the solubility products of eleven metal chelates were determined.

RESULTS AND DISCUSSION

In Fig. 1 the spectra of the three species of the reagent are represented. In the spectrum of H_2A the peak at $365\text{ m}\mu$ ($\epsilon = 4\,200$) obviously corresponds to the peak at $353\text{ m}\mu$ ($\epsilon = 2\,700$) in the spectrum of the corresponding species of 8-quinolinol-5-sulphonic acid². This peak occurs in the case of 7-iodo-8-quinolinol-5-sulphonic acid² at $353\text{ m}\mu$ ($\epsilon = 3\,420$), in the case of 8-quinolinol³ at $356\text{ m}\mu$ and in the case of 5,7-dichloro-8-quinolinol⁴ at $368\text{ m}\mu$. The double maximum at $305\text{--}325\text{ m}\mu$ which is seen in the spectra of many other derivatives of 8-quinolinol and which can be attributed to the pyridine nucleus,

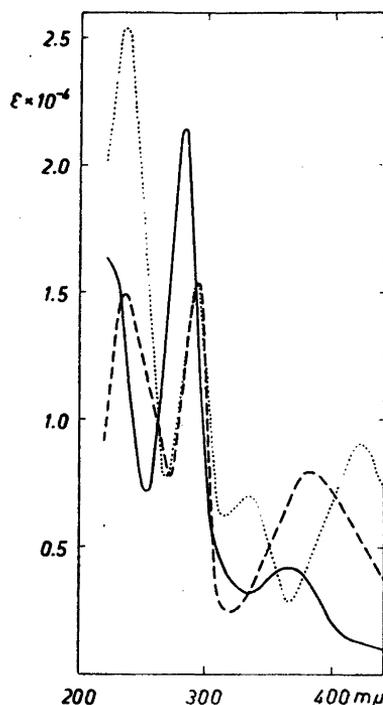


Fig. 1. The ultraviolet absorption spectra of 7-nitro-8-quinolinol-5-sulphonic acid. H_2A , full line, 2 M HCl. HA^- , broken line, pH = 4. A^- , dotted line, 0.1 M NaOH.

is not distinctly visible in the present case. The maximum at 284 $m\mu$ ($\epsilon = 22\,800$) may correspond to the peak of the spectrum of 5,7-dichloro-8-quinolinol⁴ at 260 $m\mu$ (ϵ about 39 000). The other derivatives have peaks at about the same wavelength. The shift to longer wavelengths is thus in the latter case considerable while the peak at 365 $m\mu$ has been displaced less.

The spectrum of the species HA^- has three peaks: 238 $m\mu$ ($\epsilon = 14\,900$), 293 $m\mu$ ($\epsilon = 15\,300$) and 381 $m\mu$ ($\epsilon = 7\,950$). The first peak obviously corresponds, for instance, to that of 2-methyl-8-quinolinol⁵ at 243 $m\mu$ ($\epsilon = 35\,300$) and to that of 5,7-dichloro-8-quinolinol⁴ at 247 $m\mu$. The second peak at 294 $m\mu$ probably corresponds to that of 5,7-dichloro-8-quinolinol at 277 $m\mu$ ($\epsilon \approx 8\,300$) and to that of 7-iodo-8-quinolinol-5-sulphonic acid² at 284 $m\mu$ ($\epsilon = 20\,800$). The third peak has obviously no counterparts in the spectra of the other derivatives and this may be attributed to the nitro group. On the other hand the peak at about 300 $m\mu$ in the case of many other derivatives has no counterpart in the present spectrum. It may be mentioned that 7-iodo-8-quinolinol-5-sulphonic acid also lacks this peak.

The spectrum of the species A^- has four maxima. The first at 235 $m\mu$ ($\epsilon = 25\,600$) obviously corresponds, for instance, with that of 2-methyl-8-quinolinol⁵ at 256 $m\mu$ ($\epsilon = 33\,000$) and with that of 7-iodo-8-quinolinol-5-sulphonic acid² at 260 $m\mu$ ($\epsilon = 38\,000$). The second peak at 294 $m\mu$ ($\epsilon = 15\,200$) seems to have no counterpart in the spectra of the other 8-quinolinol derivatives. The third maximum at 334 $m\mu$ corresponds to the peak at

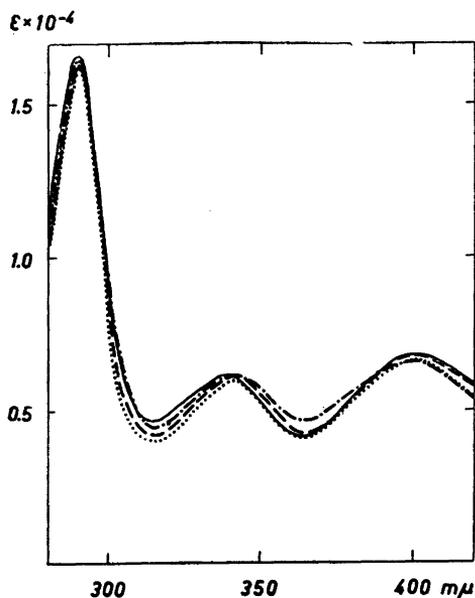


Fig. 2. The ultraviolet absorption spectra of some metal chelates of 7-nitro-8-quinolinol-5-sulphonic acid. Full line: Mn. Broken line: Cd. Dotted line: Zn. Dot- and -dash line: Pb.

335 $m\mu$ of the spectrum of 8-quinolinol³ or to that at 355 $m\mu$ in the same spectrum. The fourth peak at 420 $m\mu$ ($\epsilon = 9\,000$) has no counterpart in the spectra of the other derivatives.

The spectra of the reagent studied here thus show many peaks which may obviously be attributed to the peaks of the spectra of 8-quinolinol and its other derivatives. However some new peaks also occur.

In Figs. 2 and 3 the spectra of some metal chelates are presented. All the spectra are very similar showing peaks at 290—291 $m\mu$, 340—345 $m\mu$ and 395—403 $m\mu$. These spectra are thus rather similar to the spectrum of the ligand A^- , which has maxima at 293, 333, and 420 $m\mu$. On the basis of the above, it seems obvious that the bond between metal and ligand is chiefly ionic.

The potentiometric method used here for the determination of the solubility products has been previously described^{2,6}. As in the case of 8-quinolinol-5-sulphonic acid⁶, difficulties arose because of a great tendency to supersaturation. On the other hand the supersaturation makes possible the determination of the stability constants of alkaline earth metal chelates which are very sparingly soluble. A spectrophotometric method was also used. These measurements were made at so high a pH that, according to the values of the stability constants, practically all the reagent was in the form MA. Then the concentration of MA was determined spectrophotometrically using molar extinction coefficients of MA as determined above.

The results on the solubility products

$$[M^{++}] [HA^-]^2 = S_1 \quad (1)$$

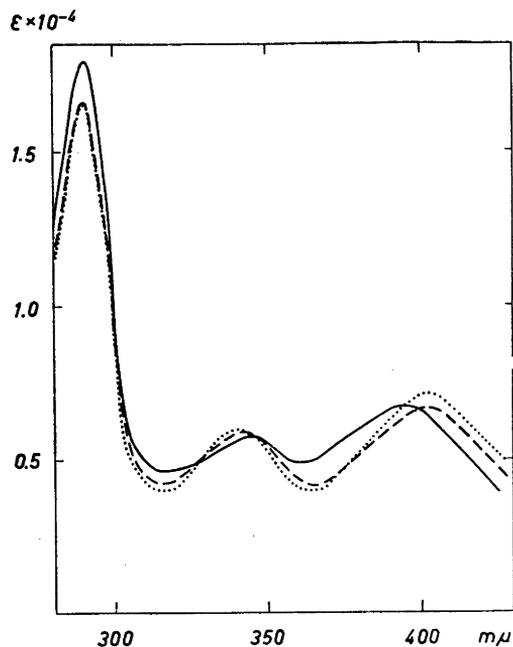


Fig. 3. The ultraviolet absorption spectra of some metal chelates of 7-nitro-8-quinolinol-5-sulphonic acid. Full line: Cu. Broken line: Co. Dotted line: Ni.

are presented in Table 1. Here c_B , c , c_M are the total concentrations of sodium hydroxide, reagent and metal ions, respectively. In Tables 1 and 2 the results concerning the solubility products

$$[M^{++}] [A^-] = S_2 \quad (2)$$

are given. The results obtained by the spectrophotometric method are presented in Table 3.

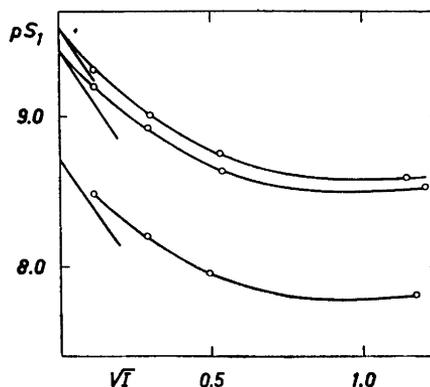


Fig. 4. Solubility products $[Ba^{++}][HA^-]^2$ (lower curve), $[Sr^{++}][HA^-]^2$ (middle curve) and $[Ca^{++}][HA^-]^2$ (upper curve) as a function of ionic strength in solutions of potassium chloride.

Table 1. Potentiometric determination of the solubility products of the barium, strontium and calcium chelates of 7-nitro-8-quinolinol-5-sulphonic acid at 25° C. $S_1 = [M^{++}][HA^-]^2$. $S_2 = [M^{++}][A^-]$.

Ba(HA) ₂ KCl	pH	\sqrt{I}	pS ₁	BaA KCl	pH	\sqrt{I}	pS ₂
$c = 2.18 \cdot 10^{-3}$	2.735	0.103	8.49	$c = 2.02 \cdot 10^{-3}$	3.687	0.155	7.21
$c_B = 0.00$	2.760	0.288	8.21	$c_B = 3.02 \cdot 10^{-3}$	3.803	0.292	6.95
$c_M = 3.22 \cdot 10^{-3}$	2.769	0.487	7.96	$c_M = 7.46 \cdot 10^{-3}$	4.015	0.497	6.58
	2.729	1.170	7.82		4.167	0.732	6.34
					4.241	1.030	6.22
Sr(HA) ₂ KCl	2.718	0.103	9.20	SrA KCl	3.581	0.155	7.36
$c = 2.18 \cdot 10^{-3}$	2.755	0.279	8.93	$c = 2.02 \cdot 10^{-3}$	3.736	0.296	7.04
$c_B = 0.00$	2.780	0.532	8.64	$c_B = 3.02 \cdot 10^{-3}$	3.842	0.495	6.79
$c_M = 3.22 \cdot 10^{-3}$	2.700	1.197	8.54	$c_M = 7.45 \cdot 10^{-3}$	3.952	0.666	6.60
					3.986	0.881	6.52
Ca(HA) ₂ KCl	2.718	0.101	9.30	CaA KCl	3.276	0.150	8.97
$c = 2.18 \cdot 10^{-3}$	2.757	0.294	9.03	$c = 2.02 \cdot 10^{-3}$	3.335	0.300	8.72
$c_B = 0.00$	2.780	0.520	8.75	$c_B = 3.02 \cdot 10^{-3}$	3.438	0.505	8.45
$c_M = 3.05 \cdot 10^{-3}$	2.710	1.142	8.61	$c_M = 6.94 \cdot 10^{-3}$	3.479	0.704	8.30
					3.462	0.930	8.27

In the spectrophotometric method described above, a high pH value of the equilibrium solution is necessary. The determination of solubility products at lower pH's by spectrophotometry is also possible. We have used this method in case of the lead chelate. The method was as follows. To the solution of the reagent an about 1.1-fold amount of lead nitrate was added. When the equilibrium was reached, the pH of the solution was determined and the total concentration of reagent in the solution was determined spectrophotometrically as PbA. It was possible to bring all the reagent to PbA by adding sodium hydroxide and lead nitrate in such quantities and as such dilute solutions that precipitation did not occur. The concentration of PbA in the equilibrium solu-

Table 2. Potentiometric determination of the solubility products of the 7-nitro-8-quinolinol-5-sulphonic acid chelates of some divalent metals at 25° C. $S_2 = [M^{++}][A^-]$.

MgA KCl	pH	\sqrt{I}	pS ₂	MnA KCl	pH	\sqrt{I}	pS ₂
$c = 13.0 \cdot 10^{-3}$	3.462	0.374	5.56	$c = 2.02 \cdot 10^{-3}$	3.395	0.157	7.67
$c_B = 20.2 \cdot 10^{-3}$	3.868	0.797	5.00	$c_B = 3.02 \cdot 10^{-3}$	3.631	0.430	7.09
$c_M = 46.5 \cdot 10^{-3}$	4.063	1.110	4.76	$c_M = 7.71 \cdot 10^{-3}$	3.716	0.760	6.87
	4.307	1.530	4.61				
CdA NaNO ₃	3.141	0.151	8.45	ZnA NaNO ₃	2.710	0.233	8.40
$c = 2.02 \cdot 10^{-3}$	3.242	0.374	7.96	$c = 5.00 \cdot 10^{-3}$	2.761	0.507	8.00
$c_B = 3.02 \cdot 10^{-3}$	3.293	0.770	7.70	$c_B = 7.50 \cdot 10^{-3}$	2.765	0.873	7.82
$c_M = 7.15 \cdot 10^{-3}$				$c_M = 17.1 \cdot 10^{-3}$			
CoA NaNO ₃	2.388	0.356	8.16				
$c = 10.74 \cdot 10^{-3}$	2.650	0.680	7.84				
$c_B = 16.11 \cdot 10^{-3}$	2.274	1.360	8.14				
$c_M = 39.75 \cdot 10^{-3}$							

Table 3. Spectrophotometric determination of the solubility products of some metal chelates of 7-nitro-8-quinolinol-5-sulphonic acid at 25° C. $S_2 = [M^{++}] [A^-]$.

	$c \cdot 10^3$	$c_M \cdot 10^3$	$[MA] \cdot 10^3$	\sqrt{I}	pS_2
MnA	2.077	30.80	0.604	0.304	7.24
KCl	2.077	30.80	0.960	0.610	6.81
CdA	2.077	29.50	0.234	0.295	8.09
NaNO ₃	2.077	29.50	0.244	0.525	7.80
ZnA	2.079	2.840	0.947	0.410	8.15
NaNO ₃	9.000	12.29	1.020	0.607	7.89
	9.000	12.29	1.370	0.842	7.85
CoA	1.985	73.5	1.621	0.542	7.86
NaNO ₃	7.507	277.7	2.490	0.910	7.73
	7.507	277.7	2.940	1.055	7.84
NiA	3.079	2.998	2.691	0.400	8.75
NaNO ₃	9.000	12.98	3.862	0.625	8.45
	9.000	12.98	4.803	0.833	8.42
CuA	2.077	29.23	1.050	0.296	11.07
NaNO ₃	2.077	29.23	1.059	0.428	10.89
	2.077	29.23	1.600	0.782	10.66
PbA	2.077	30.40	0.061	0.302	9.36
NaNO ₃					

Table 4. Spectrophotometric determination of the solubility product of lead chelate in acidic medium. 25° C. Added electrolyte NaNO₃.

$c \cdot 10^3$	$c_M \cdot 10^3$	pH	$[A^-]$	$[Pb^{++}]$	\sqrt{I}	pS_2
5.432	5.975	2.252	$1.13 \cdot 10^{-7}$	$0.81 \cdot 10^{-3}$	0.160	10.03
5.432	5.975	2.304	$5.20 \cdot 10^{-7}$	$1.21 \cdot 10^{-3}$	0.515	9.20

Table 5. Thermodynamic values of solubility products, respective B values and solubilities.

	$pS_{1,0}$	B	$pS_{2,0}$	B	pMA_0	Add. electrolyte
Ba	8.75	0.270	7.76	0.133	5.18	KCl
Sr	9.42	0.350	7.86	0.257	5.79	KCl
Ca	9.54	0.229	9.49	0.410	7.23	KCl
Mg			6.50	0.011	3.22	KCl
Mn			8.11	0.242	3.35	KCl
Cd			8.90	0.390	3.73	KCl
Zn			9.08	0.364	3.16	NaNO ₃
Pb			10.35	0.3	4.39	NaNO ₃
Co			8.96	0.510	2.90	NaNO ₃
Ni			9.66	0.318	2.61	NaNO ₃
Cu			11.87	0.410	3.01	NaNO ₃

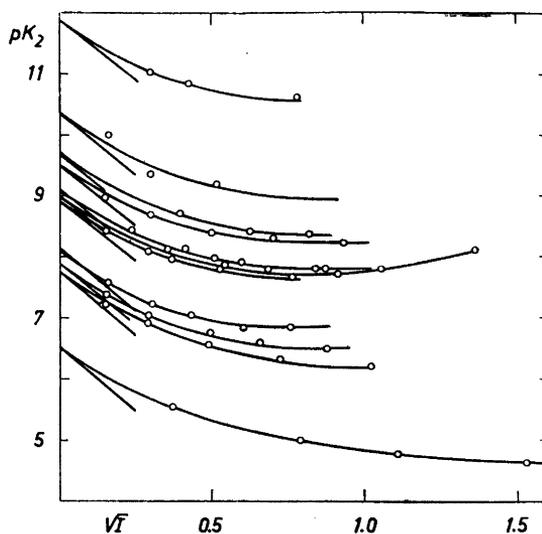


Fig. 5. Solubility products $[M^{++}][A^-]$ as functions of ionic strength. From below: Mg, Ba, Sr, Mn, Cd, Co, Zn, Ca, Ni, Pb, Cu.

tion was obtained by the first spectrophotometric method. Then using the measured pH value of the equilibrium solution and the ionization constant of the reagent, the concentration of A^- was obtained. Also the concentration of lead ion in the solution can now be calculated by subtracting the sum of MA in the solution and the precipitate from the total lead concentration. The values obtained by this procedure are presented in Table 4 and are seen to be in a relatively good agreement with the results in Table 3.

The results on the solubility products can be presented by the equations

$$pS_1 = pS_{1,0} - \frac{3.05 \sqrt{I}}{1 + 1.5 \sqrt{I}} + BI \quad (3)$$

and

$$pS_2 = pS_{2,0} - \frac{4.07 \sqrt{I}}{1 + 1.5 \sqrt{I}} + BI \quad (4)$$

The values of $pS_{1,0}$, $pS_{2,0}$ and corresponding values of B are presented in Table 5. In Figs. 4 and 5 the solubility products are represented as functions of the ionic strength. We see from these figures that the effect of added electrolytes on the solubility products is fairly normal.

From equation (2) and from equation

$$[MA]/[M^{++}][A^-] = k_1 \quad (5)$$

we obtain

$$[MA] = k_1 S_2 \quad (6)$$

In Table 5 the concentration of MA at zero ionic strength ($[MA]_0$) is also given. In the case of 8-quinolinol-5-sulphonic acid this quantity was about 10^{-3} for

most of the metals investigated. Only the chelates of barium, strontium, calcium and lead were less soluble. In the present case the state of things is not very much different except that the barium, strontium and calcium chelates are now about 10^2 — 10^3 times less soluble. Therefore the determination of the stability constants of the chelates of the last mentioned metals were carried out in supersaturated solutions¹. This proved to be possible owing to the rather strong tendency of these metal chelates to supersaturation as mentioned above.

The stability constants of the metal chelates of 8-quinolinol derivatives, studied by us up to now, increase with increasing second ionization potential of gaseous metal atoms as in many other systems⁷. Further the respective solubility products follow the same order. On account of their exceptionally low solubility, the barium, strontium and calcium chelates do not follow this rule in the present case.

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