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

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In a previous paper [1] from this laboratory the ionization of 8-quinolinol-5-sulphonic acid was studied. We have now completed this investigation by the determination of the concentration constants of this dibasic acid using cells without liquid junction:

H_2 or glass electrode / H_2A, HA^-, K^+, Cl^- / AgCl-Ag
H_2 or glass electrode / H_2A, HA^-, $A^=$, K^+, Cl^- / AgCl-Ag

The previous data for the mixed constants were checked, too, by the same method as before.

For the above cell we obtain

$$-\log [H^+] = (E^\circ - E) / 2.303\ RT + \log [Cl^-] + 2 \log f \pm \qquad (1)$$

For E° the value 222.3 mV was used [2]. The activity coefficient $f\pm$ was considered to be that of the pure hydrochloric acid in potassium chloride solution and its values were obtained from a paper of Harned and Hamer [3]. The values of E° and $f \pm$ were checked occasionally. The medium effect of the acid studied was neglected because of its low concentration. After the hydrogen ion concentration has been determined, the ionization constant is obtained in the usual way.

When a glass electrode was used, the standard potential E° was determined before and after each measurement, using a dilute hydrochloric acid solution as reference.

The silver-silver chloride electrode was prepared by the method of Shedlovsky and MacInnes [4]. In other respects the experimental procedures were the same as before.

The stability constants were determined by the same method as before [5]. In the case of oxine, the ligand was a univalent anion, but in the present case the ligand is a divalent anion. Therefore the equations used for the calculation of the stability constants undergo a slight modification. The equation

$$k'_1 + \Sigma x k'_n\ (nc_M - c') / (c_M - c') - c' / x\ (c_M - c') = 0 \qquad (2)$$

was used at higher pH's and the equation

$$k''_1 + \Sigma y k''_n\ (nc_M - c'') / (c_M - c'') - c''/x\ (c_M - c'') = 0 \qquad (3)$$

at lower pH's. In these equations

$$k'_n = k_n K'^n_2 \text{ and } k''_n = k_n K'^n_1 K'^n_2. \qquad (4)$$

Further,

$$x = [\mathrm{HA}^-] / (\mathrm{H}^+),\ y = [\mathrm{H_2A}] / (\mathrm{H}^+)^2, \qquad (5)$$

$$c' = c - [\mathrm{HA}^-]\ (1 + K'_2 / (\mathrm{H}^+) + (\mathrm{H}^+) / K'_1 \qquad (6)$$

$$c'' = c - [\mathrm{H_2A}]\ (1 + K'_1 / (\mathrm{H}^+)) + K'_1 K'_2 / (\mathrm{H}^+)^2) \qquad (7)$$

$$[\mathrm{HA}^-] = (2c - c_\mathrm{B} - [\mathrm{H}^+] + [\mathrm{OH}^-]) / (1 + 2\ (\mathrm{H}^+) / K'_1) \qquad (8)$$

$$[\mathrm{H_2A}] = (2c - c_\mathrm{B} - [\mathrm{H}^+] + [\mathrm{OH}^-]) / (2 + K'_1 / (H^+)) \qquad (9)$$

Here c is the stoichiometric concentration of the chelating agent, c_M that of the metal salt and c_B that of sodium hydroxide. The stability constants

$$k_n = [\mathrm{MA}_n^{(2n-2)-}] / [\mathrm{M}^{++}]\ [\mathrm{A}^=]^n \qquad (10)$$

are calculated by means of the relations (4) from the values of k'_n or k''_n. In the present case, $n = 2$.

RESULTS

In the measurement of the ionization constants, the silver-silver chloride electrode, the hydrogen electrode, the glass electrode and the calomel electrode (the last through a junction of saturated potassium chloride solution) were dipped in the same solution simultaneously. The potential differences $E_\mathrm{H,S}$ (hydrogen and silver chloride), $E_\mathrm{G,S}$ (glass and silver chloride), $E_\mathrm{H,C}$ (hydrogen and calomel) and $E_\mathrm{G,C}$ (glass and calomel) where then measured. The results are recorded in Tables 1 and 2, and can be represented by the following equations:

Table 1. Determination of the first ionization constant of 8-quinolinol-5-sulphonic acid at 25° C.

KCl 2.837 M, ml	$\sqrt{I}$	$E_\mathrm{G,S}$ mV	$E_\mathrm{H,S}$ mV	$E_\mathrm{G,C}$ mV	pK_1 G, S	pK_1 H, S	pK'_1 G, C
1.00	0.195	87.2	−553.3	153.6	3.971	3.970	4.025
3.03	0.330	113.9	−526.6	154.6	3.912	3.910	4.001
5.06	0.418	125.5	−514.8	155.6	3.892	3.886	3.978
10.06	0.575	139.8	−500.7	155.9	3.878	3.887	3.969
15.06	0.684	147.7	−492.8	155.8	3.876	3.874	3.968
20.06	0.770	152.8	−487.8	155.7	3.880	3.880	3.970
30.09	0.895	159.4	−481.1	154.8	3.910	3.908	3.981
50.15	1.062	165.5	−474.9	152.9	3.979	3.976	4.012
70.20	1.166	169.5	−471.0	152.1	4.006	4.000	4.020

75.07 ml 0.002954 M $\mathrm{H_2A}$.
1.125 ml 0.0985 M NaOH
$E^\circ_\mathrm{G,S} = 419.0$ mV. $E^\circ_\mathrm{H,S} = -222.3$ mV. $E^\circ_\mathrm{G,C} = 395.1$ mV.
$p_{\mathrm{H_2}} = 743$ mm Hg.

Table 2. Determination of the second dissociation constant of 8-quinolinol-5-sulphonic acid at 25° C.

KCl 2.837 M, ml	$\sqrt{I}$	$E_{G,S}$ mV	$E_{H,S}$ mV	$E_{G,C}$ mV	$E_{H,C}$ mV	pK_2 G,S	H,S	G,C	H,C	pK'_2 G,C	H,C
1.00	0.242	−164.3	−804.8	−104.7	−744.1	8.415	8.413	8.383	8.365	8.450	8.433
3.03	0.401	−131.5	−771.5	− 97.5	−737.7	8.262	8.249	8.240	8.238	8.327	8.325
5.06	0.506	−116.7	−757.6	− 93.0	−733.4	8.186	8.191	8.166	8.166	8.252	8.252
10.06	0.680	− 99.4	−740.2	− 90.2	−730.6	8.126	8.128	8.128	8.129	8.205	8.205
15.06	0.799	− 90.4	−730.9	− 88.6	−727.2	8.105	8.103	8.113	8.082	8.178	8.147
20.06	0.890	− 83.4	−723.7	− 86.9	−727.0	8.093	8.087	8.099	8.094	8.149	8.144
30.09	1.021	− 74.6	−715.3	− 86.0	−726.5	8.083	8.089	8.110	8.112	8.134	8.136
50.15	1.178	− 66.3	−706.9	− 84.0	−724.6	8.098	8.097	8.117	8.120	8.101	8.104
90.25	1.342	− 59.2	−699.0	− 83.2	−723.2	8.121	8.107	8.150	8.139	8.086	8.075

75.07 ml 0.002954 M H_2A.
1.125 ml 0.0985 M NaOH.
$E^{\circ}_{G,S} = 419.0$ mV. $E^{\circ}_{H,S} = -222.3$ mV. $E_{G,C} = 395.1$ mV. $E_{H,C} = -246.0$ mV.
$p_{H_2} = 743.0$ mm Hg.

$$pK'_1 = 4.104 - \frac{0.509\sqrt{I}}{1 + 1.16\sqrt{I}} + 0.126\, I \tag{11}$$

$$pK_1 = 4.112 - \frac{1.018\sqrt{I}}{1 + 1.40\sqrt{I}} + 0.251\, I \tag{12}$$

$$pK'_2 = 8.750 - \frac{2.036\sqrt{I}}{1 + 1.41\sqrt{I}} + 0.168\, I \tag{13}$$

$$pK_2 = 8.757 - \frac{2.036\sqrt{I}}{1 + 1.41\sqrt{I}} + 0.168\, I \tag{14}$$

The parameters of these equations are calculated by the method of least squares from the data in Tables 1 and 2.

The results on the chelates of the alkaline earth metals are recorded in Table 3. The thermodynamic constants $k'_{1,0}$ were obtained by extrapolation by means of the Debye-Hückel equation

$$pk'_1 = pk'_{1,0} + \frac{2.545\sqrt{I}}{1 + a\sqrt{I}} - BI \tag{15}$$

The results on the chelates of some other metals are presented in Table 4.

Table 3. Determination of the stability of 8-quinolinol-5-sulphonic acid chelates of alkaline earth metals at 25° C.

Ba($BaCl_2$) $\sqrt{I}$	pk'_1	Sr($SrCl_2$) $\sqrt{I}$	pk'_1	Ca($CaCl_2$) $\sqrt{I}$	pk'_1	Mg($MgCl_2$) $\sqrt{I}$	pk'_1	pk'_2
0.0940	6.598	0.089	6.195	0.082	5.415	0.061	~4.1	~9.3
0.145	6.762	0.143	6.261	0.125	5.493	0.072	4.108	~9.3
0.273	6.760	0.271	6.351	0.215	5.618	0.100	4.183	
0.695	7.037	0.585	6.523	0.413	5.761	0.170	4.209	
1.21	7.078	1.21	6.602			0.320	4.374	
1.54	7.001	1.54	6.515			0.570	4.498	
$pk'_{1,0} = 6.444$		$pk'_{1,0} = 6.000$		$pk'_{1,0} = 5.234$		$pk'_{1,0} = 3.962$		

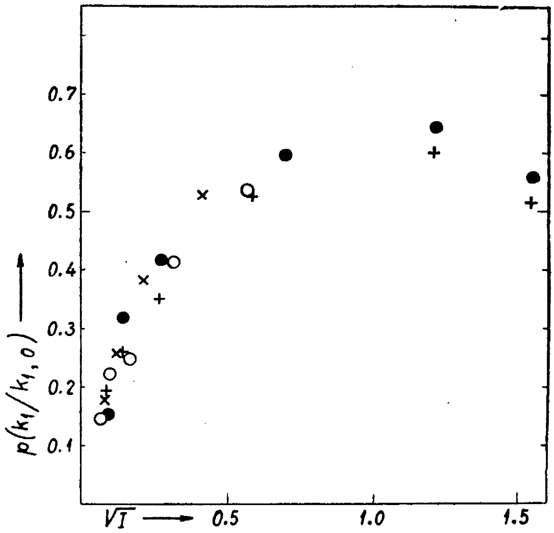

Fig. 1. The effect of ionic strength on the chelate stability. ● *Ba*($BaCl_2$), + *Sr*($SrCl_2$), × *Ca*($CaCl_2$) *and* ○ *Mg*($MgCl_2$).

The thermodynamic constants were now obtained by means of

$$pk''_1 = pk''_{1,0} + \frac{2.036\sqrt{I}}{1 + a\sqrt{I}} - BI \tag{16}$$

The thermodynamic constants $k_{1,0}$ were obtained by means of the relations (4) from the above $k'_{1,0}$ and $k''_{1,0}$ values. These values are presented in Table 5. The values for the second stability constants in the table were calculated by means of the same equation and extrapolated to zero ionic strength by means

Table 4. Determination of the stability of 8-quinolinol-5-sulphonic acid chelates of some divalent metals at 25° C.

Mn($MnCl_2$)		Cd($Cd(ClO_4)_2$)			Pb($Pb(NO_3)_2$)			Zn($Zn(NO_3)_2$)		
$\sqrt{I}$	pk''_1	$\sqrt{I}$	pk''_1	pk''_2	$\sqrt{I}$	pk''_1	pk''_2	$\sqrt{I}$	pk''_1	pk''_2
0.067	5.97	0.045	5.24	~11.3	0.035	4.40	~9.7	0.035	4.25	~9.5
0.137	6.25	0.054	5.27	~11.8	0.050	4.42	~9.5	0.187	4.57	—
0.431	6.44	0.083	5.33	—				0.413	4.77	—
$pk''_{1,0} = 5.93$		$pk''_{1,0} = 5.17$			$pk''_{1,0} = 4.33$			$pk''_{1,0} = 4.21$		

Co($Co(NO_3)_2$)			Ni($NiCl_2$)			Cu($Cu(ClO_4)_2$)		
$\sqrt{I}$	pk''_1	pk''_2	$\sqrt{I}$	pk''_1	pk''_2	$\sqrt{I}$	pk''_1	pk''_2
0.050	4.15	~9.8	0.032	3.12	~7.2	0.059	1.42	~4.1
0.170	4.29	—	0.130	3.39	—	0.123	1.61	—
0.190	4.29	—	0.265	3.43	—			
$pk''_{1,0} = 4.04$			$pk''_{1,0} = 3.11$			$pk''_{1,0} = 1.33$		

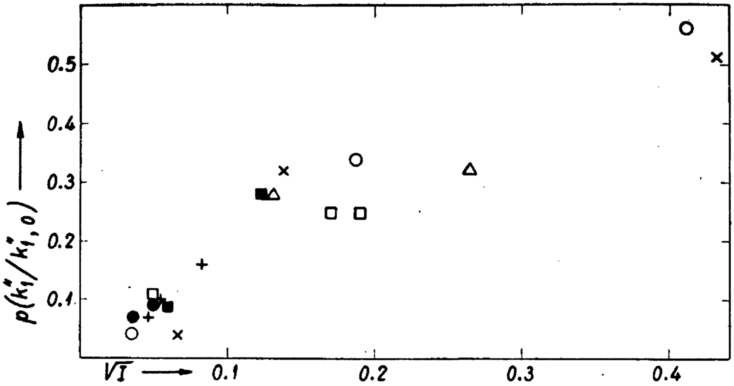

Fig. 2. The effect of ionic strength on the chelate stability. × *Mn*$(MnCl_2)$, + *Cd*$(Cd(ClO_4)_2)$, ● *Pb*$(Pb(NO_3)_2)$, ○ *Zn*$(Zn(NO_3)_2)$, □ *Co*$(Co(NO_3)_2)$, △ *Ni*$(NiCl_2)$, ■ *Cu*$(Cu(ClO_4)_2)$.

of the Debye-Hückel limiting law.

Table 5. Stability constants of 8-quinolinol-5-sulphonic acid chelates of some divalent metals at 25° C.

	log $k_{1,0}$	log $k_{2,0}$		log $k_{1,0}$	log $k_{2,0}$
Ba	2.31	—	Pb	8.53	~16.1
Sr	2.75	—	Zn	8.65	~16.2
Ca	3.52	—	Co	8.82	~15.9
Mg	4.79	~ 8.2	Ni	9.75	~18.5
Mn	6.94	—	Cu	11.53	~21.6
Cd	7.70	~14.2			

DISCUSSION

The values obtained by us for the first ionization constant, using cells with ($pK_{1,0} = 4.104$) and without ($pK_{1,0} = 4.112$) liquid junction, are in very satisfactory agreement. The same may be said concerning the values for the second constants, $pK_{2.0} = 8.750$ and 8.757. The agreement is very satisfactory, too, with the values obtained by Näsänen and Ekman [1], $pK_{1,0} = 4.092$ and $pK_{2,0} = 8.776$. At higher ionic strengths (I > 1), however, a correction has been made to the previous values, because a glass electrode used in the previous work gave wrong values in concentrated potassium chloride solution, as was observed later on. From equations (11) and (12) we have calculated that

$$p(K_1/K'_1) = \frac{0.509\sqrt{I}}{1 + 1.95\sqrt{I}} - 0.118\ I \qquad (17)$$

In the case of 8-quinolinol [5], the result was

$$p(K_1/K'_1) = \frac{0.505\sqrt{I}}{1 + 2.20\sqrt{I}} - 0.129\ I \qquad (18)$$

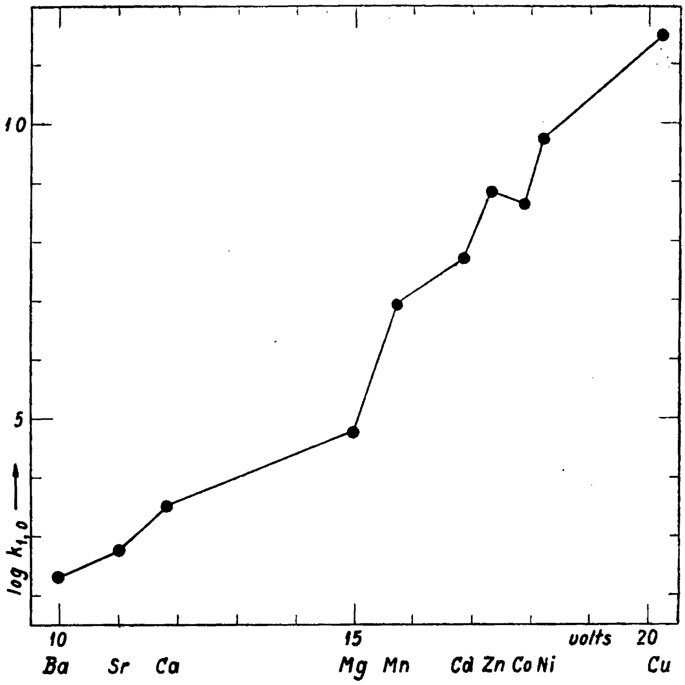

Fig. 3. The chelate stability and the second ionization potential of the gaseous metal atom.

The difference between these two results is 0.026 at $I = 1$. The agreement is thus satisfactory.

In Fig. 1 the quantity p $(k'_1/k'_{1,0})$ is represented as a function of ionic strength in the case of the alkaline earth metals. The stability constants have grouped themselves around the same curve. In Fig. 2, the p$(k''_1/k''_{1,0})$ of the other metal chelates studied is represented. The accuracy is somewhat smaller and the measurements are restricted to a narrower range of ionic strength. The values of the second stability constants are relatively inaccurate. Maley and Mellor [6] have determined the stability constants for zinc, cobalt and copper chelates. Their values for the first stability constants of zinc and copper chelates are in close agreement with our values, but in the case of cobalt a greater difference exists. The second constants differ more.

Recently the relation between the stability of complex compounds and of the ionization potentials of gaseous metal atoms has been discussed by many authors [7]. In Fig. 3 our results are summarized according of these ideas. The figure represents the logarithm of the stability constants as a function of the second ionization potential. The picture is similar to the case of 8-quinolinol [8].

SUMMARY

The stability constants of 8-quinolinol-5-sulphonic acid chelates of eleven divalent metals in aqueous solutions have been determined. The results reveal that the effect of the sulphonic acid group on the chelate stability is generally relatively slight. The ionization constants of 8-quinolinol-5-sulphonic acid have been determined using cells with and without liquid junction.

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