

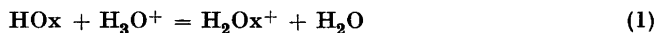
Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. I. Ionization of 8-Quinolinol in Aqueous Solutions of Potassium Chloride

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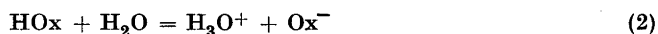
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For an investigation of 8-quinolinol chelates of metals in aqueous salt solutions reliable values for the ionization constants of 8-quinolinol were required. The earlier determinations, however, have been carried out at one ionic strength only. Moreover, the values obtained by different authors are not in good agreement¹. Therefore the determination of these constants was necessary.

In aqueous solutions 8-quinolinol HOx (8-hydroxyquinoline or oxine) reacts as follows:



and



The law of mass action gives

$$[\text{H}^+] [\text{HOx}] / [\text{H}_2\text{Ox}^+] = K_1 \quad (3)$$

and

$$[\text{H}^+] [\text{Ox}^-] / [\text{HOx}] = K_2 \quad (4)$$

where the symbols in brackets denote concentrations (in this paper moles per liter solution). K_1 and K_2 are concentration dissociation constants of the acids H_2Ox^+ and HOx. In the present paper also the "mixed" constants:

$$(\text{H}^+) [\text{HOx}] / [\text{H}_2\text{Ox}^+] = K'_1 \quad (5)$$

and

$$(\text{H}^+) [\text{Ox}^-] / [\text{HOx}] = K' \quad (6)$$

are needed. Here (H^+) denotes the activity of hydronium ion. The thermodynamic constants are defined as follows:

$$K_{1,0} = (f_H + f_{HOx} / f_{H_2Ox^+}) K_1 = (f_{HOx} / f_{H_2Ox^+}) K'_1 \quad (7)$$

and

$$K_{2,0} = (f_H + f_{Ox^-} / f_{HOx}) K_2 = (f_{Ox^-} / f_{HOx}) K'_2 \quad (8)$$

where f 's are the activity coefficients. In addition the constant

$$[OH^-] [HOx] / [Ox^-] = K_w / K_2 = K_{2b} \quad (9)$$

was used. Here K_w is the ionic product of water.

Two potentiometric and one spectrophotometric methods were used:

The first potentiometric method was the familiar one, in which equations (5) and (6) are used. These equations give

$$pK'_1 = pH - \log ([HOx] / [H_2Ox^+]) \quad (10)$$

and

$$pK'_2 = pH - \log ([Ox^-] / [HOx]) \quad (11)$$

When the quotients $[HOx] / [H_2Ox^+]$ and $[Ox^-] / H[Ox^-]$ do not differ too much from unity we can write with sufficient accuracy

$$[HOx] / [H_2Ox^+] = (c_B + c_{Ox} - c_A + [H^+]) / (c_A - c_B - [H^+]) \quad (12)$$

and

$$[Ox^-] / [HOx] = (c_B - c_A - [OH^-]) / (c_A + c_{Ox} - c_B + [OH^-]) \quad (13)$$

where c_B is the stoichiometric concentration of added sodium hydroxide, c_A that of a strong acid (hydrochloric acid in this study), and c_{Ox} that of 8-quinolinol. The experimental procedure comprises the preparation of a solution in which the quotient (12) or (13) does not differ too much from unity and the measurement of pH of this solution.

The second potentiometric method is based on the determination of the buffer capacity at the inflection points which occur about where $c_A - c_B = c_{Ox}$ and $c_B - c_A = c_{Ox}$. The determination of the buffer capacity was performed according to Näsänen's² method, using the equations derived by him:

$$\begin{aligned} \frac{dE}{dm} = \Delta E_{\max} + \frac{1}{6} \{ (\Delta E_{\max} - \Delta E_1) + (\Delta E_{\max} - \Delta E_2) \} \\ - \frac{(\Delta E_{\max} - \Delta E_1) (\Delta E_{\max} - \Delta E_2)}{2 (\Delta E_{\max} - \Delta E_1) + (\Delta E_{\max} - \Delta E_2)} \end{aligned} \quad (14)$$

and

$$P = \frac{\Delta V C k}{V dE/dm} \quad (15)$$

where ΔE_1 , ΔE_{\max} and ΔE_2 are the three successive potential jumps of which ΔE_{\max} is the greatest, m is the number of equal increments of the titrating reagents (in this case a solution of hydrochloric acid), $k = 2.303 RT/nF$, ΔV is the volume of an incre-

ment, V is the volume of the titrated solution, C the concentration of the titrating reagent and P the buffer capacity. The dissociation constant can be calculated by means of the equation ^{2, 3}

$$x = \sqrt{Kc (1-K/x) / (1 + K/x)^3} \quad (16)$$

$$K = (0.434 P - x) (x + K)^2 / xc \quad (17)$$

by the iterative method. In these equations c denotes the total concentration of the weak acid or base. By means of this method the constants K_1 and K_{2b} can be determined. In the first case $x = [H^+]$ and in the second case $x = [OH^-]$.

The spectrophotometric method is based on the general equation

$$\varepsilon - \varepsilon_{HOx} + (\varepsilon - \varepsilon_{H_2Ox+}) (H^+) / K'_1 + (\varepsilon - \varepsilon_{Ox-}) K'_2 / (H^+) = 0 \quad (18)$$

where $\varepsilon = e/c$. Here e is the extinction of a c molar 8-quinolinol solution as a 1 cm layer (in the reference cell the same solution without 8-quinolinol), and ε 's are molar extinction coefficients. In a sufficiently acidic medium $\varepsilon_{H_2Ox+} = \varepsilon$, in a sufficiently alkaline medium $\varepsilon_{Ox-} = \varepsilon$ and near the isoelectric point approximately $\varepsilon_{HOx} \sim \varepsilon$, as is seen from equation (18). By the measurement of ε in sufficiently acidic and alkaline solution of 8-quinolinol it is thus possible to obtain the values of ε_{H_2Ox+} and ε_{Ox-} . By measurement of ε near the isoelectric point the approximate value of ε_{HOx} is obtained. The measurement of ε at pH ~ 5 gives K'_1 and the measurement at pH ~ 10 gives K'_2 . In the first case the term containing K'_2 and in the second case the term containing K'_1 can be neglected. Now it is possible to calculate a more accurate value for ε_{HOx} as well as for ε_{H_2Ox+} and ε_{Ox-} if necessary. Thereafter the calculation of K'_1 and K'_2 is repeated *etc.*

EXPERIMENTAL

The potentiometric measurements were performed in a water thermostat controlled with an accuracy of $\pm 0.01^\circ \text{C}$. A glass electrode (Beckman types 4990, 42 and E) and a saturated calomel electrode were used. A Radiometer PHM3 potentiometer was used. The glass electrode was standardized against 0.05 molar solutions of potassium acid phthalate or sodium tetraborate. The titration vessel was carefully sealed and provided with a cover, which has holes for the electrodes, the stirrer, the inlet and outlet of nitrogen as well as the addition of reagents.

The chemicals used were the best obtainable. Since 8-quinolinol dissolves slowly and relatively poorly in water, it was generally dissolved in an equivalent amount of a dilute solution of hydrochloric acid. In the spectrophotometric investigation hydrochloric acid, acetate, phosphate and borate buffers were used. The pH of the solutions were calculated and in addition the values obtained were checked by measurement with a glass electrode.

The measurement of the light absorption was carried out with a Beckman Model DU spectrophotometer with 1 cm silica cells. The measurements were performed in a constant temperature room. Temperature of the mounting block of the spectrophotometer was also regulated with a thermostat.

RESULTS

The results by the first potentiometric method are summarized in Table 1. Each value for the dissociation constant is a mean value of four measurements. The concentration of 8-quinolinol c_{Ox} was never higher than about

Table 1. Determination of the dissociation constant K'_1 at 20° C and K'_2 at 25° C in the aqueous solutions of potassium chloride.

\sqrt{I}	pK'_1	\sqrt{I}	pK'_2
0.095	5.056	0.0984	9.765
0.168	5.084	0.168	9.726
0.402	5.164	0.398	9.663
0.696	5.221	0.685	9.610
0.971	5.268	0.985	9.579
1.251	5.309	1.226	9.558
1.524	5.340	1.503	9.548
1.772	5.351	1.746	9.553

0.005 because it was observed that the pH was anomalous too near the saturation point. In most experiments the quotients $[\text{HOx}] / [\text{H}_2\text{Ox}^+]$ and $[\text{Ox}^-] / [\text{HOx}]$ were unity but some other values were also used. The results can be presented by Debye-Hückel equation. The calculation by means of the method of least squares gave

$$p(f_{\text{H}_2\text{Ox}^+} / f_{\text{HOx}}) = \frac{0.505\sqrt{I}}{1 + 0.907\sqrt{I}} \quad (19)$$

$$p(f_{\text{Ox}^-} / f_{\text{HOx}}) = \frac{0.509\sqrt{I}}{1 + 1.018\sqrt{I}} - 0.022 I \quad (20)$$

and

$$pK_{1,0} = 5.011 \text{ (20°)}, pK_{2,0} = 9.805 \text{ (25°)}.$$

The results for the constant K_1 obtained by the second potentiometric method are recorded in Table 2. Equation (7) can be written in the form

$$pK_1 = pK_{1,0} + p(f_{\text{H}_2\text{Ox}^+} / f_{\text{HOx}}) - pf_{\text{H}^+} \quad (21)$$

Table 2. Potentiometric determination of dissociation constant K_1 in potassium chloride solutions at 20° C.

\sqrt{I}	$c \cdot 10^3$	$P \cdot 10^3$	$[H^+] \cdot 10^4$	pK_1
0.0670	3.25	0.768	1.57	5.019
0.0947	6.51	1.087	2.26	5.035
0.169	6.51	1.073	2.23	5.047
0.412	6.48	1.025	2.14	5.086
0.700	6.43	0.933	1.95	5.165
0.985	6.30	0.837	1.77	5.261
1.275	6.21	0.739	1.56	5.360
1.553	6.06	0.640	1.36	5.488
1.818	5.98	0.533	1.16	5.615

When equation (19) was taken into consideration the data of Table 2 gave

$$pI_{H^+} = \frac{0.505 \sqrt{I}}{1 + 2.201 \sqrt{I}} - 0.129 I \quad (22)$$

and

$$pK_{1,0} = 5.025 \text{ (20° C)}$$

The data in Table 2 are mean values obtained from four identical experiments.

In table 3 the results for the constant K_{2b} are summarized. In this case also each P value is a mean value obtained from four identical experiments. The method of least squares gave

$$pK_{2b} = 4.177 + 0.0614 I \quad (23)$$

The thermodynamic constant is thus

$$pK_{2b,0} = 4.177 \text{ (25° C)}$$

Adopting $pK_{w,0} = 13.996$ in accordance with Harned and coworkers⁴ we obtain

$$pK_{2,0} = pK_{w,0} - pK_{2b,0} = 9.819 \text{ (25° C)}$$

The spectrophotometric measurements were made at the wavelengths 350—400 $m\mu$, since at this range the light absorption of HOx is slight but that of the other constituents much greater. This is seen from Fig. 1, in which the extinction of a 0.0003 molar solution of 8-quinolinol is represented as a func-

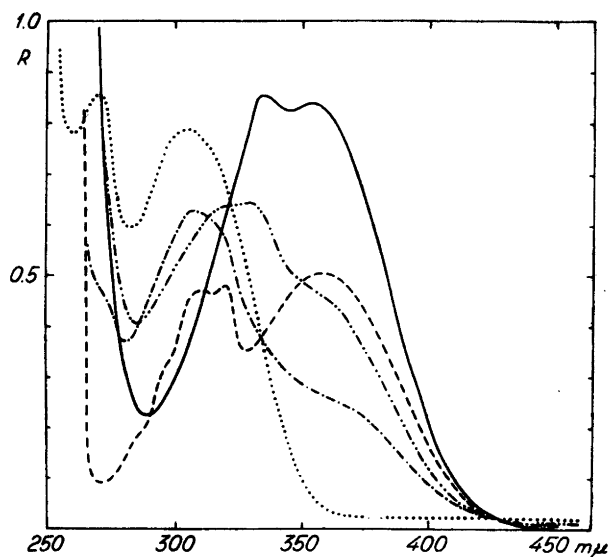


Fig. 1. Ultra-violet absorption spectra of 8-quinolinol in aqueous buffer solutions.
 $\text{pH} = 12.40$ —; $\text{pH} = 9.80$ ·····; $\text{pH} = 6.96$ ·····; $\text{pH} = 5.02$ ·····; $\text{pH} = 1.44$ — — —; $I = 0.04$.

Table 3. Potentiometric determination of dissociation constant K_{2b} in potassium chloride solutions at 25° C.

\sqrt{I}	$c \cdot 10^3$	$P \cdot 10^3$	$[\text{OH}] \cdot 10^4$	$\text{p}K_{2b}$
0.113	5.03	2.323	4.26	4.182
0.180	5.03	2.330	4.26	4.180
0.409	5.01	2.323	4.26	4.180
0.701	4.96	2.250	4.15	4.207
0.976	4.92	2.169	4.02	4.241
1.259	4.80	2.068	3.87	4.272
1.533	4.68	1.959	3.70	4.314
1.779	4.55	1.812	3.45	4.376

tion of wavelength at various pH values. The molar extinction coefficients of the three constituents were obtained by light absorption measurement of the following solutions:

	I	c_{KCl}	pH
$\epsilon_{\text{H}_2\text{Ox}^+}$	0.0025—4.00	0.139—3.89	0.71— 2.67
ϵ_{HOx}	0.0025—4.00	0.139—3.89	6.85— 7.13
ϵ_{Ox^-}	0.04—1.96	0.034—1.90	12.42—12.50

Hydrochloric acid, phosphate and sodium tetraborate-sodium hydroxide buffers were used. In Tables 4 and 5 the results concerning K'_1 and K'_2 are recorded. In these cases acetate and sodium tetraborate-sodium hydroxide buffers were used. The ions of the buffers are seen to represent a high proportion of the ionic strength at low ionic strengths. All light absorption measurements were performed the range 350—400 $m\mu$ at intervals of 5 $m\mu$. The values of the quotients $[HOx] / [H_2Ox^+]$ and $[Ox^-] / [HOx]$ obtained from the spectrophotometric measurements are therefore mean values from eleven experiments. The calculation by means of the method of least

Table 4. Spectrophotometric determination of the constant K'_1 in potassium chloride solutions at 25° C. $c_{Ox} = 3.00 \cdot 10^{-4}$.

I	c_{KCl}	pH	pK'_1
0.0024	0.00029	4.862	4.966
0.0099	0.00549	4.947	4.966
0.0244	0.0109	4.996	4.976
0.0400	0.0156	5.018	5.004
0.0900	0.0371	5.031	5.018
0.250	0.193	5.035	5.060
0.490	0.432	5.014	5.091
1.00	0.948	4.960	5.165
1.96	1.92	4.849	5.203
2.89	2.86	4.747	5.236
4.00	3.98	4.625	5.282

squares gave

$$P(f_{H_2Ox^+} / f_{HOx}) = \frac{0.509\sqrt{I}}{1 + 0.972\sqrt{I}} \quad (24)$$

Table 5. Spectrophotometric determination of the constant K'_2 in potassium chloride solutions at 25° C. $c_{Ox} = 3.00 \cdot 10^{-4}$.

I	c_{KCl}	pH	pK'_2
0.040	0.0061	9.800	9.736
0.090	0.0226	9.822	9.698
0.250	0.132	9.882	9.664
0.490	0.372	9.843	9.621
1.00	0.882	9.797	9.581
1.96	1.84	9.772	9.561

and

$$P(f_{Ox^-} / f_{HOx}) = \frac{0.509\sqrt{I}}{1 + 1.256\sqrt{I}} \quad (25)$$

For thermodynamic constants the values

$$pK_{1,0} = 4.910 \text{ (25° C) and } pK_{2,0} = 9.814 \text{ (25° C)}$$

were obtained with this method.

The effect of temperature on the constant pK'_2 was preliminarily investigated over the range 15°—40° C. The decrease of pK'_2 was on average 0.0179 when temperature was increased one degree.

DISCUSSION

For the thermodynamic constants the following values were thus obtained:

Method	$pK_{1,0}$	(20° C)	$pK_{2,0}$	(25° C)
Potentiometric I	5.011		9.805	
Potentiometric II	5.025		9.819	
Spectrophotometric	(4.910	(25° C)	9.814	
Mean value	5.017	(20° C)	9.813	(25° C)

The agreement of the values obtained by means of the different methods is very satisfactory. The first potentiometric method is based on the pH value of the 0.05 molar acid potassium phthalate for which we have adopted the value $pH = 4.00$ at 20° C or on the 0.05 molar sodium tetraborate solution for which we have adopted the value $pH = 9.18$ at 25° C. The possible liquid junction potentials by using a saturated calomel electrode are neglected⁵. In the second potentiometric method the liquid junction potentials have no significance. In the spectrophotometric method 8-quinolinol is dissolved in buffer solutions. The pH of these must be calculated from the values of dissociation constants and activity coefficients, or determined as in the first potentiometric method, but in addition there are still the spectrophotometric measurements. The significance of this method is that by it the measurements can be carried out in much more dilute solutions than by means of the potentiometric ones.

A comparison of the values obtained by the earlier authors is difficult since ionic strength and temperature are frequently not specified. The reader is referred in this respect to the paper of Irwing, Ewart and Wilson¹, who have given a detailed discussion. On the basis of their own studies the latter authors favour the values $pK_{1,0} = 5.00 \pm 0.10$ and $pK_{2,0} = 9.85 \pm 0.05$ at 20° C. Our values are seen to be within these limits.

The effect of additions of potassium chloride is illustrated in Fig. 2, in which $p(f_{H_2Ox} / f_{HOx})$ and $p(f_{Ox-} / f_{HOx})$ are represented as functions of ionic

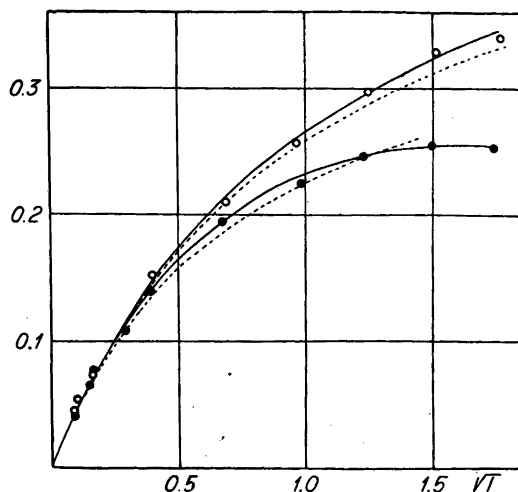


Fig. 2. Effect of ionic strength on ionization of 8-quinolinol. Upper curves, $p(f_{H_2Ox} + / f_{HOx})$; lower curves $p(f_{Ox-} - / f_{HOx})$. Solid lines, potentiometric results; dotted lines, spectrophotometric results; ●, ○, experimental (potentiometric).

strength. The agreement between potentiometric and spectrophotometric measurements is seen to be very satisfactory. The values obtained for $p f_{H+}$ and $p f_{OH-}$ are in satisfactory agreement with the earlier determinations⁶.

The former is obtained from equation (22) and for the latter we obtain from (20) and (23)

$$p f_{OH-} = \frac{0.509\sqrt{I}}{1 + 1.018\sqrt{I}} - 0.083 I \quad (26)$$

The values obtained for the activity coefficients are naturally based on the pH scale described above.

SUMMARY

The ionization of 8-quinolinol in aqueous solutions of potassium chloride are investigated by three independent methods. The values obtained for the thermodynamic ionization constants with these three different methods are in very satisfactory agreement. The results concerning the effect of potassium chloride with a potentiometric and spectrophotometric method also agree very well. The activity coefficients of hydronium and hydroxyl ions were determined. These results are in good agreement with the earlier measurements. The ultra-violet absorption spectra of 8-quinolinol were determined at several pH values.

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