Potentiometric and Spectrophotometric Studies on 8-Quinolinol and Its Derivatives. V. Ionization of 8-Quinolinol-5-Sulfonic Acid and 7-Iodo-8-Quinolinol-5-Sulfonic Acid in Aqueous Solution

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For the investigation of the metal compounds of 8-quinolinol-5-sulfonic and 7-iodo-8-quinolinol-5-sulfonic acids the ionization constants of the acids were required. The earlier determinations are, however, few and ionic strength and temperature are not specified. Therefore a reinvestigation was necessary.

These acids are dibasic and their ionization can thus be represented formally by

$$H_2A \rightleftharpoons HA^- + H^+$$

(1)

$$HA^- \rightleftharpoons A^- + H^+$$

(2)

The law of mass action gives

$$\frac{[H^+][HA^-]}{[H_2A]} = K_1$$

(3)

and

$$\frac{[H^+][A^-]}{[HA^-]} = K_2$$

(4)

where \((H^+)\) is the activity of the hydrogen ion and the symbols in brackets are concentrations. For the determination of \(K_1\) and \(K_2\) the familiar method was used in which sodium hydroxide was added in such an amount that the quotients \([HA^-]/[H_2A]\) or \([A^-]/[HA^-]\) were nearly unity. The pH measured is then approximately the pK required. In this case we can write with sufficient accuracy

$$\frac{[HA^-]}{[H_2A]} = \frac{c_B + [H^+]}{(c - c_B - [H^+])}$$

(5)

and

$$\frac{[A^-]}{[HA^-]} = \frac{(c_B - c)}{(2c - c_B)}$$

(6)
where \( c \) and \( c_B \) are the stoichiometric concentrations of the acid and sodium hydroxide added. The more exact equations can easily be derived \(^1\) but are here unnecessary.

The experimental procedure was the same as previously in this series \(^2\). All reagents used were the best obtainable.

**RESULTS**

Table 1 includes the results on the first ionization of the acids investigated. Each value for the ionization constant is a mean value of four measurements. The deviation of two identical measurements was never greater than 0.01 for \( pK' \). The relatively poor solubility in water does not admit the use of higher concentrations than about 0.003 moles per litre for 8-quinolinol-5-sulfonic acid and 0.005 moles per litre for 7-iodo-8-quinolinol-5-sulfonic acid. The ionic strength is calculated according to the equation \( I = \frac{1}{2} \sum z_i^2 c_i \), where \( c_i \) are molarities. In equation (5) the hydrogen ion concentration is of considerable significance, particularly in the case of the iodine derivative. The hydrogen ion concentration was obtained from the pH value measured using the activity coefficient values of the hydrogen ion according to Näsänen, Lumme and Mukula \(^2\).

<table>
<thead>
<tr>
<th>8-quinolinol-5-sulfonic acid</th>
<th>7-iodo-8-quinolinol-5-sulfonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sqrt{I} )</td>
<td>( \sqrt{I} )</td>
</tr>
<tr>
<td>pH</td>
<td>( p_{H^+} )</td>
</tr>
<tr>
<td>0.040</td>
<td>4.131</td>
</tr>
<tr>
<td>0.307</td>
<td>4.050</td>
</tr>
<tr>
<td>0.748</td>
<td>4.085</td>
</tr>
<tr>
<td>1.050</td>
<td>4.160</td>
</tr>
<tr>
<td>1.460</td>
<td>4.317</td>
</tr>
</tbody>
</table>

\( c = 3.00 \cdot 10^{-3}; \quad c_B = 1.50 \cdot 10^{-3}. \quad c = 5.00 \cdot 10^{-3}; \quad c_B = 2.50 \cdot 10^{-3} \)

For the 8-quinolinol-5-sulfonic acid the method of least squares gave

\[ pK'_{1,0} = 4.092. \quad a = 1.44. \quad B = 0.207. \quad (25^\circ C). \]

The values for 7-iodo-8-quinolinol-5-sulfonic acid, because of its considerable strength, are not sufficiently accurate for the calculation of the parameters in equation (7) according to the method of least squares. Therefore the thermo-
dynamic constant was calculated by means of equation (7) using the values of \( \alpha \) and \( B \) obtained for 8-quinolinol-5-sulfonic acid. For this constant the mean value

\[
pK_{1,0} = 2.514 \pm 0.009 \quad (25^\circ \text{C})
\]

was obtained. The manner of calculation seems to be justified, for in Fig. 1, where the first ionization constants are represented as functions of ionic strength, we see that the effect of ionic strength is in both cases almost equal within the experimental error.

The results concerning the second ionization are summarized in Table 2. In this case the Debye-Hückel equation

\[
pK'_2 = pK'_{2,0} - \frac{1.527 \sqrt{I}}{1 + \alpha \sqrt{I}} + BI
\]

was used. The method of least squares gave the values of Table 3.

**Table 2.** Determination of the second ionization constants of 8-quinolinol-5-sulfonic acid and 7-ido-8-quinolinol-5-sulfonic acid in potassium chloride solution at 25\(^\circ\)C.

<table>
<thead>
<tr>
<th>8-quinolinol-5-sulfonic acid</th>
<th>7-ido-8-quinolinol-5-sulfonic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sqrt{I} ) ( pK'_2 )</td>
<td>( \sqrt{I} ) ( pK'_2 )</td>
</tr>
<tr>
<td>0.0662</td>
<td>0.0963</td>
</tr>
<tr>
<td>0.312</td>
<td>0.148</td>
</tr>
<tr>
<td>0.744</td>
<td>0.216</td>
</tr>
<tr>
<td>1.042</td>
<td>0.331</td>
</tr>
<tr>
<td>1.447</td>
<td>0.523</td>
</tr>
</tbody>
</table>

\[ c = 3.00 \cdot 10^{-3} \]

\[ c_B = 4.50 \cdot 10^{-3} \]

\[ c = 5.00 \cdot 10^{-3} \]

\[ c_B = 7.50 \cdot 10^{-3} \]
Fig. 2. Molar extinction coefficients of the neutral constituents of 8-quinolinol-5-sulfonic acid (middle curve) and 7-iodo-8-quinolinol-5-sulfonic acid (upper curve) compared with that of H₂Ox⁺ (lower curve).

<table>
<thead>
<tr>
<th>pK₂,0</th>
<th>α</th>
<th>B</th>
<th>pK₁,0</th>
<th>α</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.776</td>
<td>1.62</td>
<td>0.088</td>
<td>7.417</td>
<td>1.71</td>
<td>0.0386</td>
</tr>
</tbody>
</table>

Table 3.

In Fig. 1 the second ionization constants are represented as functions of ionic strength. The effect of temperature on pK₂' was preliminary investigated over the range 15°—45° C. For both acids the decrease of pK₂' was, on average, 0.095 for one degree rise in temperature.

DISCUSSION

van Urk has investigated the indicator properties of 7-iodo-8-quinolinol-5-sulfonic acid. Feldman and Powell have determined colorimetrically the ionization constants of this acid; the ionic strength and temperature are not given. From their values we obtain pK₁' = 2.44 and pK₂' = 7.15. These values are in good agreement with our values at ionic strength 0.05 (25° C), for which we obtained pK₁' = 2.44 and pK₂' = 7.17.

Phillips and Merritt have determined spectrophotometrically the ionization constants of 8-quinolinol-5-sulfonic acid and have obtained pK₁' = 4.004 and pK₂' = 8.86 of which the first constant is in relatively good agreement with our value but the second constant differs somewhat more. Temperature and ionic strength are not stated. No other determinations seem to have been made.
Fig. 3. Molar extinction coefficient of the HA⁻ ions of 8-quinolinol-5-sulfonic acid (upper full line) and 7-ido-8-quinolinol-5-sulfonic acid (dotted line) compared with that of HOx (lower full line).

The earlier authors describe these compounds as typical ampholytes. Thus in acidic solution the reagents should exist as positive ions. The titration curve shows, however, that in moderately acidic solutions the reagents exist as neutral molecules. Because of the great acidic strength of the sulfonic group it is very probable that the reagents exist in acidic solutions as zwitterions like

\[
\begin{array}{c}
\text{SO}_3^- \\
\text{OH} \\
\text{N} \\
\text{H}^+ \\
\end{array}
\]

For the same reason the importance of ions like H₃A⁺ seems to be slight. The effect of ionic strength on ionization also shows that the compounds in question are dibasic acids. The limiting theoretical slope of the Debye-Hückel equation is namely for pK₁⁺ = 0.509 and for pK₂⁺ = 1.527 in the case of the sulfonic acid derivatives but −0.509 and +0.509 respectively for 8-quinolinol².

In figures 2—4 the ultraviolet spectra of the three constituents H₂A, HA⁻, A⁻ of the acids investigated are compared with the spectra of the corresponding constituents of the parent compound 8-quinolinol: H₂O⁺, HOx, Ox⁻.
Fig. 4. Molar extinction coefficients of the $A^-$ ions of 8-quinolinol-5-sulfonic acid (upper full line) and 7-ido-8-quinolinol-5-sulfonic acid (dotted line) compared with that of $Ox^-$ (lower full line).

These spectra can be obtained directly. The spectrum of $H_2A$ was obtained using a solution with a slight excess of a strong acid and the spectrum of $A^-$ using an excess of strong hydroxide. The spectrum of $HA^-$ was obtained using a buffer solution with a pH corresponding to the first equivalent point. At this pH the constituents $H_2A$ and $A^-$ have negligible effect on the spectra. In Fig. 2 the spectra of $H_2A$ and $H_2Ox^+$ are represented. About the same maxima appear in all cases. The effect of the substituents is, however, distinct. The maximum at 355—360 m$\mu$ (which can be related to the polar structure II of 8-quinolinol)

I

II

III

has been strengthened in the sulfonic acid derivatives. Also the double maximum of the sulfonic acid derivatives at 305—315 m$\mu$ is stronger than in the spectrum of $H_2Ox^+$, especially that of the 7-ido-8-quinolinol-5-sulfonic acid.
In the latter case a shift to the longer wavelength appears. This maximum at 325 m$\mu$ also occurs as a little shoulder in the spectrum of the constituent \( \text{HA}^- \) of 7-iodo-8-quinolinol-5-sulfonic acid, as we see in Fig. 3, where the spectra of \( \text{HA}^- \) and HOx are represented, but is hardly noticeable in the spectrum of \( \text{A}^- \) represented in Fig. 4. We further see from Fig. 3 that the constituent \( \text{HA}^- \) of the iodine derivative has a maximum at 435 m$\mu$. This maximum does not appear in the spectra of the two other constituents of this derivative, probably because of the greater importance of the polar structures in these cases. From Fig. 4 we see that the constituent \( \text{A}^- \) of 8-quinolinol-5-sulfonic acid has a very strong maximum at 355 m$\mu$ which corresponds to the structure II, but that the maximum at 335 m$\mu$ has degenerated to a shoulder. The constituent \( \text{A}^- \) of the iodine derivative still has a relatively strong maximum also at 335 m$\mu$. The spectra of \( \text{A}^- \), like OX$^- \), display shoulders at 305—315 m$\mu$. The spectra thus show that the substituent SO$_3^-$ increases the importance of the quinoid structure II and the substituent I the importance of the polar structure III as expected. Both substituents raise the acid strength considerably as expected.

**SUMMARY**

The ionization of 8-quinolinol-5-sulfonic acid and 7-iodo-8-quinolinol-5-sulfonic acid has been investigated. The first and second ionization constants of these dibasic acids, previously treated as typical ampholytes, have been determined. The effect of ionic strength on the ionization has been investigated in potassium chloride solution. The ultraviolet spectra of the three constituents of these acids in aqueous solution have been measured and compared with those of 8-quinolinol. The structures and the effect of substitution on the ionization have been discussed.

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**REFERENCES**


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