Spectrophotometric Determination of Ionization Constants of Some 8-Hydroxyquinoline Azo Dyes

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SUMMARY

The ionization constants of p-N(CH₃)₂ N, p-COCH₃ N, o-AsO(OH)₂ N (phenylazo)-8-hydroxyquinoline were determined spectrophotometrically. The absorption spectra were recorded in buffer solutions covering the pH range 0.5 – 12. The variation of absorbance with change of pH value is used to calculate the different ionization steps. The absorption bands are assigned to certain electronic transitions and the change in band position is attributed to the change of the existing species.

INTRODUCTION

8-hydroxyquinolineazo dyes were used as chromophoric reagents for several metal ions(1). They are of great pharmaceutical importance as they have a diabetogenic and bacteriostatic properties(2). They were used successively as mordant dyes applicable to cotton, artificial textiles and polypropylene fibers(3).

The analytical properties of a number of 5- (substituted phenylazo)-8-hydroxyquinoline were investigated(4), they were found to be useful as pH indicators.

The present investigation deals with the spectrophotometric determination of ionization constants of some 8-hydroxyquinolineazo dyes.

\[
\text{where } X = p-N(CH₃)₂ \text{ (I), p-COCH₃ (II) and o-AsO(OH)₂ (III).}
\]
EXPERIMENTAL

The azo compounds under investigation were prepared by coupling the diazotized amines with 8-hydroxyquinoline in alkaline medium\(^5\).

The 0.001 M solutions of the 5-(arylazo)-8-hydroxyquinoline were prepared by dissolving the accurate amount of the acid form in the proper volume of ethanol.

A series of universal buffer solutions covering the range of pH values 2 to 12 was prepared as recommended by Britton and Rhoibinson\(^6\). The Walpole acetate buffer solutions\(^6\) (pH values 0.6 – 5.0) were also prepared.

The absorption spectra of the azo-dyes under investigation were scanned in acetate and Britton and Rhoibinson buffer solutions of different pH values at 27 °C using a PYE UNICAM SP 1750 recording spectrophotometer.

The methods applied for the calculation of pK values of the different azo dyes are the half height, and limiting absorbance methods\(^7\).

RESULTS AND DISCUSSION

The absorption spectra of 4 x 10\(^{-5}\) M o-arsonophenylazo-8-hydroxyquinoline (III) in buffer solutions of varying pH values are represented graphically in Fig. (1) as example. In acid solution of pH \(\approx 1\), the spectra of I and II are characterized by two absorption bands absorbing maximally at 388 and 496 nm for I and 390 and 498 nm for II, while III exhibits only one band with \(\lambda_{\text{max}}\) at 400 nm. These bands are due to absorption of the protonated form liable to exist in acid solutions, dipositively charged ion in case of I and monopositively charged ions in case II or III. By increasing the pH of the solution, the absorbance of the shorter wavelength band decreases where it disappears completely in solutions of pH more than 7.5. In alkaline solution an intense broad band with its maximum absorbance at 508, 524 and 492 nm exists for I, II and III respectively. This band is assigned to \(\pi - \pi^*\) electronic transition influenced by intramolecular charge transfer from or to the phenyl ring according to the substituent present. The absorbance of this band inc-
increases with increasing pH value of the solution attaining a limiting value at pH 11.0, 9.0 and 11.0 respectively. This indicates the complete transformation of the dye molecule to the corresponding anion liable to predominate in alkaline solution as a result of the ionization of the quinolinic OH group. However, for the α-AsO(OH)₂-derivative III a second decrease in absorbance was observed after pH 9 where it becomes constant at pH 12.

The spectra are characterized by the presence of the common isobestic points in conformity with the presence of equilibria in solutions, namely the acid-base one under these conditions. The spectra of I show this point at 438 nm within the pH range 9.0–11.0. The spectra of III exhibit three isobestic points at 418, 426 and 464 nm for the pH range 1.0–4.5, 6.5–8.0 and 9.0–12.0 respectively. Also the spectra of II exhibit two isobestic points. The first in acidic solution at 418 nm within the pH range 0.66–3.0 and the second in alkaline solution at 466 nm within the pH range 8.0–11.0. These results are in agreement with the existence of more than one equilibrium in such solutions.
The absorbance-pH curves given in Fig. (2) indicate clearly the existence of more than one ionization step, either by exhibiting several steps (ascending or decending) or by exhibiting two steps, resembling the titration curve of weak dibasic acid. The number of steps in the curve may be taken as the number of ionizations of the active groups existing in the molecule. The variations of absorbance with pH are used for the calculation of the dissociation constants applying the previously recommended methods\(^7\). The results are treated statistically and the values depicted in Table (1).
Fig. 2: Absorbance - pH curves of I, II and III. I at 530 nm (c), II at 510 nm (b) and III at 490 nm (a).

Table 1. Results of determination of the dissociation constants of I, II and III

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>( pK_p^* )</th>
<th>( pK_p )</th>
<th>( pK_a )</th>
<th>( pK_a^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.39 ± 0.033</td>
<td>3.43 ± 0.035</td>
<td>9.21 ± 0.043</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>—</td>
<td>3.12 ± 0.026</td>
<td>7.67 ± 0.038</td>
<td>—</td>
</tr>
<tr>
<td>III</td>
<td>—</td>
<td>3.96 ± 0.086</td>
<td>7.30 ± 0.041</td>
<td>9.77 ± 0.042</td>
</tr>
</tbody>
</table>

\( pK_p^* \): Deprotonation constant of the N\((CH_3)_2\) group.
\( pK_p \): Deprotonation constant of the quinolinic OH group.
\( pK_a \): Ionization constant of the quinolinic OH group.
\( pK_a^* \): Ionization constant of the arsionic group.

For the p-N-dimethyl derivative I the \( pK \) value of 2.39 is due to deprotonation of the aliphatic nitrogen atom \( (N(CH_3)_2) \) while the value of 3.43 is due to the quinolinic nitrogen atom which is less basic than the aliphatic one. The ionization of the quinolinic OH group corresponds to \( pK_a = 9.21 \). This high value may be due to the presence of the electron
donating \((N(\text{CH}_3)_{2})\) group \((\sigma = -0.83)\). The presence of the electron withdrawing p-COCH\(_3\) groups in II manifests its effect by lowering the \(pK_p\) and \(pK_a\) values down to 3.12 and 7.67 respectively.

For the o-arsonophenylazo-8-hydroxyquinoline, the spectrophotometric studies detect the existence of three ionization steps, namely the deprotonation of the quinolinic nitrogen, ionization of the quinolinic OH-group and the arsomic OH-group. The respective values are 3.96, 7.30 and 9.77. The ionization of the first proton from the AsO(OH)\(_2\) group is overlapping with the deprotonation step and hence the compound shows only three ionization steps in the spectrophotometric investigation.

REFERENCES