

SPECTROPHOTOMETRIC INVESTIGATION OF THE ACID-BASE PROPERTIES OF SOME 8-HYDROXYQUINOLINE-5-SULPHONIC ACID DERIVATIVES

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Abstract. The absorption spectra of some 8-hydroxyquinoline-5-sulphonic acids are investigated in buffer solutions of varying pH values. The spectral shifts are explained on the basis of the existence of two acid-base equilibria involving the protonation of the quinoline nitrogen and the dissociation of a proton from the phenolic group. The pK_a values are determined from the spectral changes with pH and commented upon in terms of molecular structure.

Introduction

8-Hydroxyquinoline and its derivatives are of special interest as chelating agents. Recently, metal chelates with some derivatives of 8-hydroxyquinoline-5-sulphonic acid were investigated in our laboratories.¹ The structure of these metal chelates was established by investigating their ir spectra in comparison with those of the ligands. Also, the stability constants of these chelates were determined by applying absorption spectrophotometry in the visible and uv regions.² Since chelate formation involves a portion displacement from the 8-OH group, the stability of the metal chelate would depend upon the acid dissociation constant of the ligand used.

In the present paper, the acid-base properties of some 8-hydroxyquinoline-5-sulphonic acid derivatives are investigated using absorption spectrophotometry in the uv and visible regions. The effects of substitution on pK_a and λ_{max} are also considered.

Experimental

The 8-hydroxyquinoline-5-sulphonic acid used was a BDH product; the other derivatives were obtained by iodination, nitration and nitrosation¹ of the present compound. The products were recrystallized from boiling water.

10^{-3} M solutions of the compound were obtained by dissolving an accurately weighed amount of the solid in the requisite volume of redistilled water. The solutions of lower concentrations used for spectrophotometric measurement were obtained by accurate dilution.

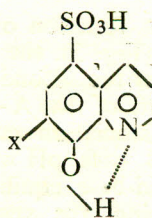
The buffer solutions used for pH control were the components of the modified universal series of Britton and Robinson.¹³

The absorption spectra were recorded using a Unicam SP 800 quartz spectrophotometer within

the 200-500 nm range using 1.0 cm matched silica cells. The pH of the buffer solution was checked by the aid of a Radiometer model 28A. The ir spectra were recorded using a Unicam SP 200G infrared spectrophotometer using the KBr wafer technique.

Results and Discussion

The compounds included in the present investigation have the general formula :



in which X = H (a), I (b), NO (c) and NO₂ (d)

(I)

The absorption spectra of the compounds in ethanol display two or three bands below 300 nm and one band above 300 nm. In analogy to the case of quinoline and its derivatives,⁴ the bands below 300 nm can be assigned to $\pi-\pi^*$ transitions within the aromatic nucleus while the broad band at the longer wavelength corresponds to an intramolecular charge transfer interaction. The $\pi-\pi^*$ bands below 300 nm display slight shifts in their position and extinction; however, the C. T. band is distinctly influenced by the nature of the substituent. The band generally shifts to red in the order (H \rightarrow I \rightarrow NO \rightarrow NO₂), i.e. as the acceptor character of the substituent increases.

The spectra of the compounds under investigation changes with changed pH of the medium (Fig. 1). In solutions of pH 2.5 the spectra display two peaks in the C. T. band region; with rise in pH the extinction of the longer wavelength band decreases whereas that of the shorter wavelength increases till only one band is observed at pH 5.5-6.5. At higher pH the absorbance of the band decreases again while a new band at longer wavelength is

developed. The spectra display generally two well defined isosbestic points, the first within the pH range 2–6 and the second for the pH range 6–12 (Fig. 1). The existence of these isosbestic points denotes the existence of two equilibria, probably of the acid-base type within the whole pH range.

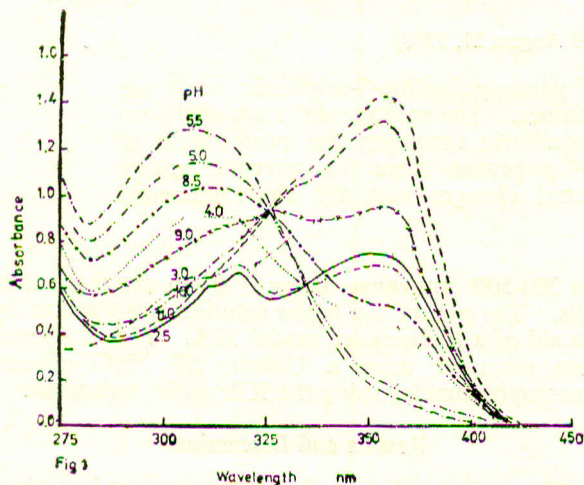
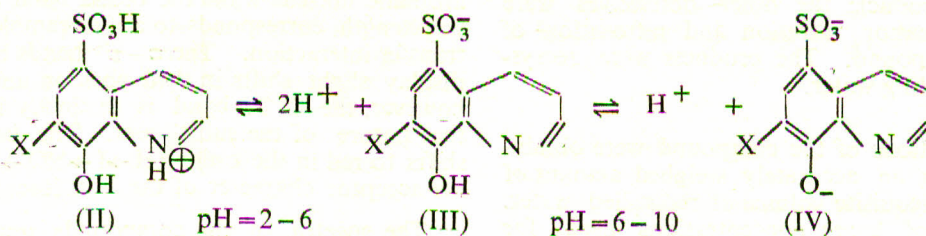


Fig. 1

The plot of absorbance as a function of pH yields curves with two inflections (Fig. 2), the first one within the pH range 3–5 and the second one within the range 8–10. Both parts of the A–pH curves resemble association and dissociation curves revealing that the spectral changes with pH would be due to shifts in the two acid-base equilibria. The acid-base equilibria influencing the spectral changes, similar to the case of 8-hydroxyquinoline^{5,6} would be the protonation of the heterocyclic nitrogen and the dissociation of the OH group. Thus, the equilibria exhibited in solution over the whole pH range can be formulated as follows :



The ionization of the sulphonic group does not affect the absorption spectra⁷ and accordingly the pK values to be determined are those due to the dissociation of the phenolic OH-group (pK_a) and protonation of the heterocyclic nitrogen (pK_p). The pK values are determined from the variation of absorbance with pH using the methods described before.⁷⁻¹⁰

1. *The half-height method.* For this method,

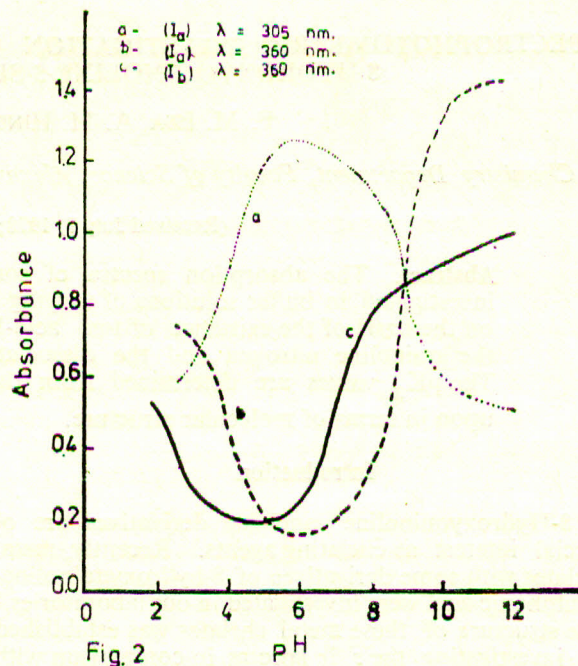


Fig. 2

the pH at half height of the A–pH curve ($A_{\frac{1}{2}}$) is equal to $\text{pK}' (\text{pK} + \log \gamma')$. The values of $A_{\frac{1}{2}}$ are determined from the relation :

$$A_{\frac{1}{2}} = \frac{(A_1 + A_{\min})}{2}$$

In these relations A_1 is the limiting absorbance, A_{\min} is the minimum absorbance value on the A–pH curve and γ' is the activity coefficient term.

2. *The modified limiting absorbance method.*¹⁰ The equation applied in this method is

$$\text{pH} = \text{pK} + \log \gamma' + \log \frac{(A - A_{\min})}{A_1 - A}$$

where A is the absorbance at the corresponding pH. The plot of $\log (A - A_{\min}) / (A_1 - A)$ as a function of pH is a linear relation from which pK can be evaluated.

3. *The modified isosbestic point method.*¹⁰ For this method, the relation given is

$$\text{pH} = \text{pK} + \log \gamma' + \log \frac{\epsilon_{\lambda_1}}{\epsilon_{\lambda_2}} + \log \left\{ \frac{(A - A_{\min})\lambda_2}{(A - A_{\min})\lambda_1} \right\}$$

where λ_1 and λ_2 are the wavelengths corresponding to the maximum absorption of the two equilibrium forms (II and III) or (III and IV).

4. The Colleter⁹ method as modified for acid-base equilibria.¹² The relation applied in this method is :

$$K = \frac{C_{\text{H}_2^+} - M C_{\text{H}_3^+}}{M - 1},$$

$$\text{where } M = \frac{(A_3 - A_1)}{A_2 - A_1} \cdot \frac{(C_{\text{H}_1^+} - C_{\text{H}_2^+})}{C_{\text{H}_1^+} - C_{\text{H}_3^+},$$

in which A_1 , A_2 and A_3 are absorbance values at three different H^+ ion concentrations, $C_{\text{H}_1^+}$, $C_{\text{H}_2^+}$ and $C_{\text{H}_3^+}$.

The data reported for this method are the mean of 6-8 values obtained from these calculations.

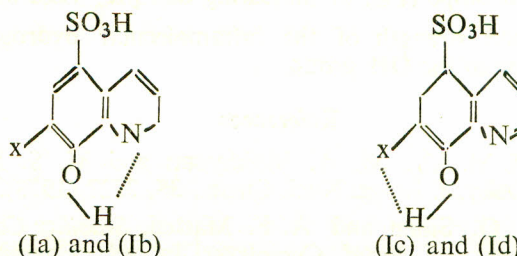
The pK_p and pK_a value determined for the compounds under investigation are collected in Table I.

TABLE I. THE DISSOCIATION CONSTANTS OF SOME DERIVATIVES OF 8-HYDROXYQUINOLINE-5-SULPHONIC ACID

Compound No.	Method				Mean
	(1)	(2)	(3)	(4)	
Results of pK_p					
(Ia)	4.10	4.05	4.00	4.05	4.05
(Ib)	2.85	—	2.85	2.98	2.89
(Ic)	4.80	—	4.70	4.37	4.62
(Id)	5.48	5.35	5.35	5.38	5.39
Results of pK_a					
(Ia)	8.85	8.65	8.65	8.70	8.71
(Ib)	7.40	—	7.50	7.47	7.46
(Ic)	9.40	—	9.50	9.69	9.53
(Id)	9.60	9.50	9.65	9.60	9.58

The results indicate that the dissociation constants depend upon the nature of the substituent. The pK value of (Ib) are lower than those of (Ia) which are in accordance with the acceptor character of iodine. Contrary to this behaviour the pK values of (Ic) and (Id) are higher than for (Ia) which does not agree with expectations in the light of the acceptor character of the NO and NO_2 groups. The lower acid character of (Ic) and (Id) compared to (Ia) can be explained by the existence of intramolecular

hydrogen bonding between the OH group and the substituent (NO or NO_2) and not with the heterocyclic nitrogen as in the case of (Ia) and (Ib).



Support for this opinion is gained by investigating the ir spectra of the compounds. For (Id) the NO_2 bands are found at 1540 (sh) and 1330 cm^{-1} which are lower than nitrobenzene but not much different from those of *o*-nitrophenol.¹¹ With (Ic) the NO band is found at 1540 cm^{-1} , which is quite comparable to those of the NO group involved in intramolecular hydrogen bonding with phenolic groups.¹² Also the ν_{OH} bands of (Ic) and (Id) (3460 and 3450 cm^{-1}) are at a lower wave number than that of (Ia) (3500 cm^{-1}) whereas (Ib) has a higher value (3530 cm^{-1}). This indicates a weaker intramolecular hydrogen bonding in (Ib) compared to (Ia) but a stronger hydrogen bonding with (Ic) and (Id), which would not be the case if the intramolecular hydrogen bonding involved the heterocyclic nitrogen.

The destruction of the intramolecular hydrogen bonding with the heterocyclic nitrogen increases the availability of its lone pair for protonation; hence the higher pK_p values in the case of (Ic) and (Id): the strong intramolecular hydrogen bonding of the OH-group with the substituent lowers its acidic character;

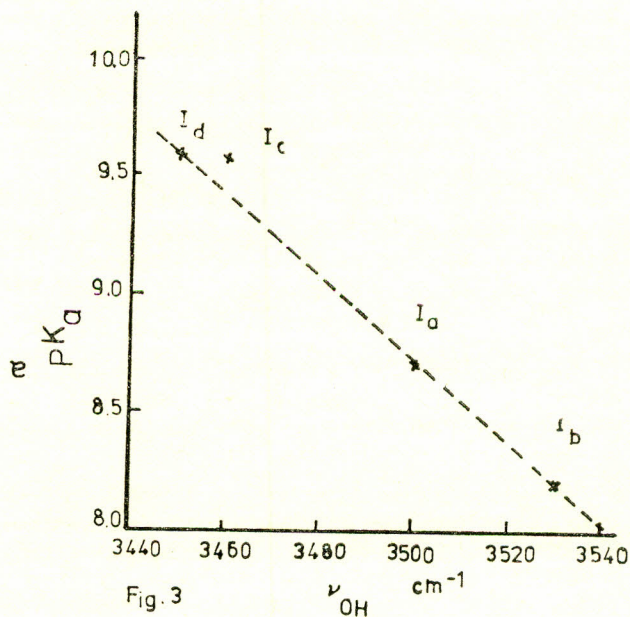


Fig. 3

Fig. 3

hence the rise of pK_a . The plot of pK_a as a function of the ν_{OH} is a more or less linear relation with negative slope (Fig. 3) indicating that pK_a rises with increased strength of the intramolecular hydrogen bonding of the OH group.

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