

Association Constants of the Complexes between 8-Hydroxyquinolines with Ammonia and Methylamine in 90% Methanol + Water Mixtures

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8-Hydroxyquinoline (HQ), 5-chloro-7-iodo-8-hydroxyquinoline (ICHQ) and 5,7-diiodo-8-hydroxyquinoline (I₂HQ) form stable yellow complexes with NH₃ and CH₃NH₂ at room temperature but decompose above 323 K. The association constants of the complexes at 298 K calculated spectrophotometrically in 90% methanol solution have been found to be fairly high. The stability of the complexes with NH₃ or CH₃NH₂ are usually in the order, ICHQ > I₂HQ > HQ.

8-Hydroxyquinoline (HQ) is a good fungicidal and analytical reagent¹ whereas 5-chloro-8-hydroxy-7-iodoquinoline (ICHQ) and 5,7-diiodo-8-hydroxyquinoline (I₂HQ)² have fungicidal and amebicidal properties. In spite of their side-effects on mylooptic nerves, they are highly effective against intestinal amebiosis and used extensively in India.

The compounds, however, are almost insoluble in water but sparingly soluble in aqueous ethanol and aqueous methanol. Instant yellow colouration was observed on addition of NH₃ to the alcoholic solutions of these reagents indicating the complex formation. The colour remained unchanged in excess of NH₃ at room temperature on prolonged standing (even for 3 months) indicating the stability of the complexes in solution though the colour disappeared, i.e. the complexes decomposed above 323 K. The colour of the complex was less intense with HQ. Similar complex formation was observed with CH₃NH₂. The intensity of HQ + CH₃NH₂ complex was less. But the colour of the complexes changed from yellow to dark brown with time.

It was thus desirable to study the stability of the complexes in solution. However, in view of low solubility of the hydroxyquinolines even in 50% aqueous methanolic solution the complex formation was studied in 90% MeOH.

Results and Discussion

The spectra of the compounds show two distinct bands, one at 260 nm (presumably due to ¹L_b band arising from benzene ring structure) and the other at ~320 nm due to $n \rightarrow \pi$ transition associated with intra-molecular hydrogen bonding.

The complex formation between HQ, ICHQ and I₂HQ with NH₃ or CH₃NH₂ is apparent from the colour change and the large shift in the absorption maxima of the mixtures towards the long wavelength region. The wavelength of the maximum absorption of the parent component (HQ) is modified by the substituents but those of the complexes remain almost unchanged though a slight red-shift is observed when CH₃NH₂ is used in place of NH₃. 90% MeOH

solution appeared to be best for the study as all the compounds are fairly soluble in this medium. The absorption maxima of the compounds and their complexes (the bands around 260 nm are not shown) are recorded in Table 1.

TABLE 1—ABSORPTION MAXIMA OF THE COMPOUNDS AND THEIR COMPLEXES

Compd	λ_{\max} nm	λ_{\max} (nm) of complexes with	
		NH ₃	CH ₃ NH ₂
HQ	310-315 (flat)	~350, ~380 (flat)	~350, ~380 (flat)
ICHQ	325	350, 380	351, 383
I ₂ HQ	340	350, 380	351, 383-84

The complexes formed between the components have been assumed to be 1 : 1 and the equilibrium constant *K* for the complexes



can be written as

$$K = \frac{a_{DA}}{a_D a_A} = \frac{C_{DA}}{C_D C_A} \cdot \frac{\gamma_{DA}}{\gamma_D \gamma_A} \approx \frac{C_{DA}}{C_D C_A} \quad (2)$$

where, D = NH₃ or CH₃NH₂; A = H₂Q, ICHQ or I₂HQ. Since D, A and DA are uncharged and the concentrations of A, D and DA are low, $\gamma_{DA} / \gamma_D \gamma_A$ can be regarded to be unity.

Since NH₃ or CH₃NH₂ does not absorb in the uv or in the visible region but the hydroxyquinolines and their complexes with NH₃ or CH₃NH₂ show significant absorption in the uv region, Benesi-Hildebrand or Scott equation^{3,4} could not be utilised. The following procedure was adopted to calculate *K*.

We have,

$$K = \frac{x}{(C_1-x)(C_2-x)} \approx \frac{x}{(C_1-x)C_2} \quad (3)$$

when $C_2 \gg x$

$$\text{or } \frac{C_1}{x} = 1 + \frac{1}{KC_2} \quad (4)$$

where, C_1 and C_2 are the initial concentrations of A and D, and x is the concentration of complex formed.

Since,

$$d_1 = \epsilon_1 C_1 \quad (5)$$

$$d = \epsilon x + \epsilon_1 (C_1 - x) \quad (6)$$

($l = 1 \text{ cm}$)

$$\text{Thus, } x = \frac{d - d_1}{\epsilon - \epsilon_1} \quad (7)$$

where d_1 and d are the absorptivities of HQ and mixture of HQ and complex and ϵ_1 and ϵ are the molar absorptivities of A and the complex respectively. Putting equation (7) in (4) and rearranging

$$\frac{\epsilon - \epsilon_1}{\left(\frac{d}{C_1} - \frac{d_1}{C_1}\right)} = 1 + \frac{1}{KC_2} \quad (8)$$

$$\text{or, } \frac{1}{(\epsilon^a - \epsilon_1)} = \frac{1}{(\epsilon - \epsilon_1)} + \frac{1}{KC_2} \cdot \frac{1}{(\epsilon - \epsilon_1)} \quad (9)$$

where, ϵ^a is the arbitrary molar absorptivity of the complex assuming total conversion of C_1 to complex. The equation is exactly the same as the equation developed by Ketelaar *et al.*^{4,5}. The plot of $1/(\epsilon^a - \epsilon_1)$ against C_2 gives $1/K(\epsilon - \epsilon_1)$ as slope and $1/(\epsilon - \epsilon_1)$ as intercept from which K can be calculated. The K values and ϵ of the complexes are recorded in Table 2. The band at 380 nm has been utilised to calculate the association constant of the complexes as the differences in absorptivity values are maximum in this region.

TABLE 2—EQUILIBRIUM CONSTANT (K) AND EXTINCTION COEFFICIENT (ϵ) OF DIFFERENT COMPOUNDS

Compd.	K	$\times 10^3 \epsilon$
HQ + NH ₃	25.2	0.3028
ICHQ + NH ₃	188.56	3.581
I ₂ HQ + NH ₃	130.80	3.565
HQ + CH ₃ NH ₂	27.5	0.933
ICHQ + CH ₃ NH ₂	261.156	3.87
I ₂ HQ + CH ₃ NH ₂	197.65	4.462

The complexes have been found to be fairly stable and the association constants of the complexes with NH₃ or CH₃NH₂ are in the order: $K_{\text{ICHQ}} > K_{\text{I}_2\text{HQ}} > K_{\text{HQ}}$, i.e. substitution of I or Cl in HQ have pronounced effect on the stability of the complexes. The replacement of H by CH₃ of the donor NH₃ increases the stability of the complexes as the electron donating capability of donor is increased.

It is known that the K values are dependent on the donor and acceptor moieties. For complexes between σ -acceptors such as I₂ and n -donors like NH₃ or CH₃NH₂⁶, the intermolecular overlap may be regarded to be considerable rendering K values fairly high as evident from the K values of complexes between I₂ and NH₃ or alkylamines in CCl₄. However, it is difficult to suggest the possible overlap between HQ and NH₃ but the substitution like I and Cl in HQ definitely increases the stability of the complexes. It is in-

teresting to note that the increase in stability between I₂HQ + NH₃ and ICHQ + NH₃ follows the similar pattern as observed in case of complexes between pyridine with I₂ and ICl in CCl₄ at 298 K though the magnitudes are considerably different.

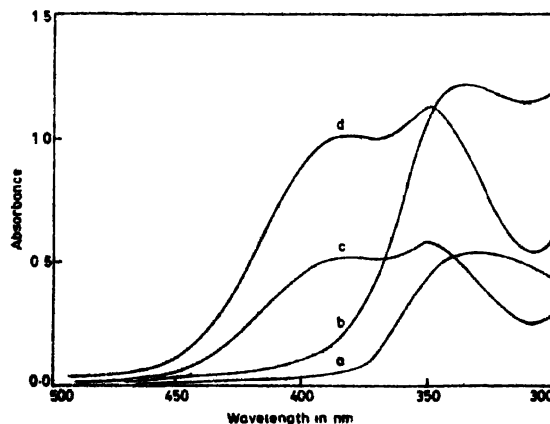


Fig. 1. Variation of absorbance with wavelength of I₂HQ + NH₃ in 90% MeOH: (a) $0.15 \times 10^{-3} M$ I₂HQ, (b) $0.30 \times 10^{-3} M$ I₂HQ, (c) $0.15 \times 10^{-3} M$ I₂HQ + 0.1 M NH₃ and (d) $0.30 \times 10^{-3} M$ I₂HQ + 0.1 M NH₃.

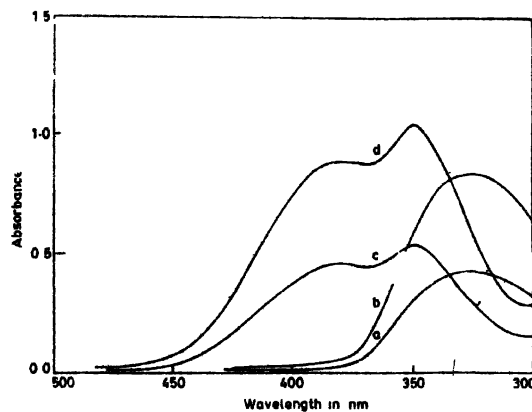


Fig. 2. Variation of absorbance with wavelength (in nm) of ICHQ + NH₃ in 90% MeOH: (a) $0.12 \times 10^{-3} M$ ICHQ, (b) $0.24 \times 10^{-3} M$ ICHQ, (c) $0.12 \times 10^{-3} M$ ICHQ + 0.1 M NH₃ and (d) $0.24 \times 10^{-3} M$ ICHQ + 0.1 M NH₃.

Experimental

8-Hydroxyquinoline (E. Merck) was crystallised twice from anhydrous alcohol and dried. The purity was confirmed by m.p. determination (349 K). ICHQ (East India Pharmaceutical Ltd., Calcutta) was crystallised twice from glacial acetic acid and then with anhydrous ethanol. The dried purified compound decomposed at 445 K. I₂HQ was first crystallised from xylene (twice) and then from pure absolute alcohol (twice). The dried sample melted at about 483 K with extensive decomposition. NH₃ and CH₃NH₂ (G.P., E. Merck) were standardised with standard HCl

(B.D.H.). Standard solution of potassium biphthalate (G.R., E. Merck) was used for standardising NaOH (E. Merck) solution. Methanol (G.R., E. Merck) was distilled before use.

Addition of NH_3 to methanolic (90%) HQ, ICHQ and I_2HQ gave intense yellow coloured complexes (Figs.1 and 2) and the stability of the complexes were studied spectrophotometrically within 24 h though the complexes were stable for several months.

A Hitachi 200-20 spectrophotometer was used.

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