PROTON-LIGAND STABILITY CONSTANTS OF SOME QUINOLINOL DERIVATIVES IN DIOXANE-WATER MEDIA

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The practical proton–ligand stability constants p_KH of 7–(∝ Aryl aminobenzyl) – 8 – quinolinol have been determined potentiometrically in 70% dioxane (v/v). The values are discussed with their structures and substituents present in the structure.

The acid-base equilibria of 7 (∝ Aryl amino-benzyl) derivatives of 8-quinolinols have not been studied at all. Only the compounds have been prepared by Phillips et al.[1,2] It is therefore of interest to determine the proton–ligand stability constants of some derivatives viz. 7-(∝ Aminobenzyl) Quinolinol (ABQ). 7- (∝-m-nitroanilinobenzyl) - quinolinol (m NO_2. ABQ) and 7- (∝-p-tolyl) quinolinol (p CH_3. ABQ.)

The compounds were prepared by the method of Phillips et al[1,2]. The p_KH values were determined by direct pH titration method as described by Irving and Rossotti[3].

Most of the chemicals were of AnalaR (BDH) quality, Dioxane was purified by the method of Vogel[4]. Carbonate-free NaOH was prepared according to Albert and Sargent[5]. The pH measurements were made on phillips pH meter using glass–calomel electrode assembly.

The values of p_KH were obtained by plotting the formation curves of $\bar{n}_A$ vs B (pH meter readings).

The values of p_KH were also obtained by plotting a graph of $\frac{\bar{n}_A}{1-\bar{n}_A}$ vs B to obtain a straight line. The values were calculated by pointwise calculation method and by half integral method. They are given in table 1. A comparison of p_KH in 70% dioxane due to phenolic OH group shows that the order is

$$m\text{-}NO_2\text{. ABQ} < 8\text{-quinolinol} < ABQ < p.\ CH_3\text{. ABQ}$$

These observations are mainly interpreted in terms of inductive, resonance and steric effects.

The dissociation constants of 7- (∝ Arylamino benzyl) 8-quinolinols are weaker than 8 quinolinol probably due to strong electron donating characteristics of the attached group in 7th position. Thus aryl amino benzyl is strong electron donating group.

p.CH_3.ABQ is less acidic than ABQ, perhaps due to electron donating inductive effect of-CH_3 group para position. The -NO_2 group is electron with drawing group. The compound m-NO_2. ABQ is more acidic with smaller p_KH, due to replacement hydrogen by strongly electron-withdrawing group.

A large steric effect on acidity is associated with the decrease in acidity. The higher proton–ligand stability constants of 7- (∝ Arylaminobenzyl) – quinolinols than 8-quinolinol may be due to the steric effect as large bulky group is attached at seventh position, making the anion less stable, ionisation less, and acid weak.

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TABLE 1 Proton-Ligand Formation Constants
Temp = 25 ± 1°C.

No.	0.1 M KNO_3 compounds	70% dioxane : wat
1	8 quinolinol	10 80
2	ABQ	12.25
3	p. CH_3. ABQ	12.65
4	m NO_2 ABQ	9.90

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