

## Determination of Dissociation and Thermodynamic Constants of 8-Methylquinoline by Potentiometry in Aqueous and Mixed Organic-Water Solvent Systems

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The dissociation constant ( $pK_a$ ) and thermodynamic parameters ( $\Delta G$ ) of 8-methylquinoline are determined in aqueous and in mixed organic-water (Dioxane, EtOH and MeOH) solvent systems. It is observed that dissociation constant of 8-methylquinoline in aqueous system decreases with the increase of temperature. The curve shows some what linear decrease from 10% to 50% composition of solvent. It is to be noted that  $pK_a$  values of this compound are lower than quinoline and some of its methyl derivatives. For mixed organic-water solvent systems concentration ionization constant  $pK_a^M$  and thermodynamic ionization constant  $pK_a^T$  values versus percent composition decrease slowly with increase in percent of EtOH, MeOH and Dioxane. The curve of the  $pK_a$  versus percent composition shows some what linear decrease in this range.

The data have been obtained potentiometrically by titrating aqueous 8-methylquinoline solutions with hydrochloric acid. The values of dissociation constant were obtained from these data by a computer program written in GW-BASIC. From  $pK_a$  values Gibb's free energies  $\Delta G$  for the respective  $pK_a$  values have also been calculated.

### Introduction

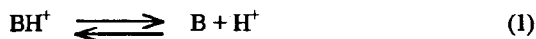
The ionization constant is an important parameter in determining the behaviour of compounds in various applications. It is used to measure the strength of acids and bases. The dissociation constants  $pK_a$  of weak acids and bases are widely used in pharmaceutical industries, in spectroscopy, in biological sciences, in preparative chemistry and in structure elucidation of newly isolated species. The  $pK_a$ 's are useful criteria of identifying particularly the substances, which do not melt [1-3]. Information about the ionization constant is useful in many ways e.g., different ionic species have different ultra-violet spectra and significant spectrophotometry can be done only at a chosen pH at which ionic species are present. The ionic species of a given substance may differ in their physical, chemical and biological properties [2].

The aim of the present study is three fold, first to find out the  $pK_a$  value of 8-methylquinoline at high temperatures up to 50°C in aqueous solutions and see the effect of temperature on  $pK_a$  values. Secondly to calculate the  $pK_a$  values in non-aqueous media and analyze the effect of hydro-organic water solvent mixtures of an acid base equilibria of these compounds at 25°C. Thirdly to determine the thermodynamic parameters. Quinoline derivatives are

extensively used in oils, polymer, and pharmaceutical industries and as chelating agent for various ions in analytical chemistry. There are different methods [3-7], which are being used for the determination of dissociation constants of weak bases and acids. These methods have certain limitations, such as solubility, range of  $pK_a$  and time requirements etc. [5-8]. The quick method for this purpose is potentiometry [3-10] while spectrophotometry is very accurate but it is time consuming [5-8]. The potentiometric titration has been improved by elimination of carbon dioxide using dried and purified nitrogen gas [2]. The temperature is controlled to an accuracy of  $\pm 0.1^\circ\text{C}$ .  $pK_a$  values were obtained by analyzing the experimental data with a computer program written in GW-BASIC to work on IBM PC [11].

### Theory

Any monoacidic base  $BH^+$  dissociates as follows.



$$K_a^M = \frac{[B][H^+]}{[BH^+]} \quad (2)$$

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$$pK_a^M = pH + \log \frac{[BH^+]}{[B]} \quad (3)$$

where the terms square brackets [ ] represent molar concentration,  $pK_a^M$  is concentration ionization constant. The thermodynamic ionization constant  $pK_a^T$  for a base is:

$$pK_a^T = \frac{\{H^+\}\{B\}}{\{BH^+\}} \quad (4)$$

$$\{B\} = [B]Y_B \quad (5)$$

$$\{BH^+\} = [BH^+]Y_{BH^+} \quad (6)$$

$$-\log Y_i = \frac{Az^2\sqrt{I}}{1 + B_i\sqrt{I}} \quad (7)$$

In which the term  $Y_B$  and  $Y_{BH^+}$  are the respective activity coefficients calculated by means of eq. (7) and the term in {} are activities of respective ions. A and B are the constants, z is valency of ion and I is ionic strength [11] given by:

$$I = 0.5 \sum C_i z^2 \quad (8)$$

where  $C_i$  is molar concentration of ion i, z is its valency and  $\sum$  is summation. Activity coefficients are calculated by eq. (7). These approximate activity coefficient are then used to calculate the hydrogen ion or hydroxyl ion concentration i.e. ( $[H^+] = \{H^+\}/Y_i$  or  $[OH^-] = \{OH^-\}/Y_i$ ) by eq. (7) and also ratios of activities of the non-protonated to protonated species for bases is [3]:

$$\frac{\{B\}}{\{BH^+\}} = \frac{(C - C_A - [OH^-] + [H^+])}{(C_A + [OH^-] - [H^+])Y_{BH^+}} \quad (9)$$

There is an empirically derived approximation, suitable for results obtained with a set calibrated in 0.02 pH unit, e.g. for bases:

$$pK_a^T = pH + \log \frac{[BH^+]Y_i - \{H^+\}}{[B] + \{H^+\}} \quad (10)$$

where  $Y_i$  can be obtained from eq. (7).

## Results and Discussions

The protonation constants of 8-methylquinoline are determined in water at 20, 25, 30, 35, 40, 45 and 50°C and in percent composition from 10, 15, 20, 25, 30, 35, 40, 45 and 50 percent in organic-water solvent mixtures at 25°C. The protonation constant of this compound obtained by refining the experimental data with the aid of computer program PKAS [12] written in GW-BASIC language. In methyl derivatives the  $pK_a^M$  value of 2, 6-methylquinoline are higher than those of quinoline [15]. It means that these derivatives dissociates slower than quinoline. However in 8-methylquinoline, the values of  $pK_a^M$  are lower than those of quinoline. The insertion of methyl group usually gives rise the base strengthening effect. The ionization constant varies with the temperature. The correlation curve is usually a parabola with a flat maximum. Increase in temperature causes decrease in  $pK_a$  values, at 20°C  $pK_a^M$  is  $4.715 \pm 0.004$  and at 50°C it is  $4.529 \pm 0.002$ . The  $pK_a$  values calculated are given in Table 1 together with reported values. The total decrease is 0.186 units for  $pK_a^M$ . The ionization constant and Gibb's free energy data in Table 1 clarify the effect of temperature versus  $pK_a$  values and effect of temperature on Gibb's free energy  $\Delta G$  values.

Many chemists are interested in calculating the concentration ionization constant  $pK_a^M$  and thermodynamic ionization constant  $pK_a^T$  values of organic acids and bases in non-aqueous media. The effect of solvent on acid base equilibria of the compound is studied in different organic water mixtures at 25°C. The solvent systems chosen are: Dioxane-water, EtOH-water and MeOH-water. The percentage composition of organic components varies from 10% to 50% in the step of 5% each. The ionization constant  $pK_a^M$  and  $pK_a^T$  of 8-methylquinoline decreases with the increase of percent composition in all the three solvent systems. The data of each solvent Dioxane-water, EtOH-water and MeOH-water are shown in Table 2 to 4. These tables show that  $pK_a$  value in 50% dioxane-water is  $3.742 \pm 0.006$ , in 50% EtOH, it is  $4.449 \pm 0.006$  and in 50% MeOH-water system it is  $4.343 \pm 0.006$ . The graph if drawn between  $pK_a$  versus percent composition is a form of parabola with a flat maximum around 20°C in case of aqueous solution. A similar trend is observed for  $\Delta G$  versus temperature in case of aqueous solution. Solvent

Table 1: Effect of Temperature on  $pK_a^M$ ,  $pK_a^T$  and Thermodynamic Parameters of 8-Methylquinoline in Aqueous Solution

S. No.	Temp. In °C	$pK_a^M$	$pK_a^T$	$\Delta G$ of $pK_a^M$	$\Delta G$ of $pK_a^T$
1	20	4.715 ± 0.004	4.687 ± 0.008	-6.325 ± 0.005	-6.287 ± 0.011
2	25	4.705 ± 0.004	4.676 ± 0.008	-6.418 ± 0.005	-6.379 ± 0.011
3	30	4.660 ± 0.002	4.631 ± 0.006	-6.463 ± 0.003	-6.423 ± 0.008
4	35	4.606 ± 0.005	4.577 ± 0.009	-6.494 ± 0.008	-6.453 ± 0.012
5	40	4.572 ± 0.004	4.543 ± 0.007	-6.551 ± 0.006	-6.509 ± 0.010
6	45	4.551 ± 0.002	4.552 ± 0.007	-6.625 ± 0.003	-6.572 ± 0.010
7	50	4.529 ± 0.002	4.499 ± 0.007	-6.696 ± 0.002	-6.652 ± 0.010

Note: The reported  $pK_a$  value of 8-methylquinoline at 20°C is 4.63 [14]

Table 2: Effect of Percent Composition on  $pK_a^M$ ,  $pK_a^T$  and Thermodynamic Parameters of 8-Methylquinoline in Dioxane-Water Solvent System

S. No.	% Comp:	$pK_a^M$	$pK_a^T$	$\Delta G$ of $pK_a^M$	$\Delta G$ of $pK_a^T$
1	10	4.307 ± 0.005	4.278 ± 0.006	-5.875 ± 0.006	-5.836 ± 0.008
2	15	4.186 ± 0.005	4.158 ± 0.007	-5.710 ± 0.006	-5.672 ± 0.009
3	20	4.123 ± 0.005	4.095 ± 0.007	-5.624 ± 0.006	-5.586 ± 0.010
4	25	4.054 ± 0.004	4.025 ± 0.008	-5.530 ± 0.006	-5.491 ± 0.011
5	30	3.981 ± 0.005	3.952 ± 0.010	-5.430 ± 0.007	-5.392 ± 0.012
6	35	3.852 ± 0.005	3.823 ± 0.008	-5.254 ± 0.007	-5.215 ± 0.011
7	40	3.918 ± 0.005	3.890 ± 0.008	-5.344 ± 0.007	-5.306 ± 0.011
8	45	3.802 ± 0.005	3.774 ± 0.010	-5.187 ± 0.008	-5.148 ± 0.014
9	50	3.742 ± 0.006	3.715 ± 0.010	-5.106 ± 0.006	-5.068 ± 0.013

Table 3: Effect of Percent Composition on  $pK_a^M$ ,  $pK_a^T$  and Thermodynamic Parameters of 8-Methylquinoline in EtOH-Water Solvent System

S. No.	% Comp:	$pK_a^M$	$pK_a^T$	$\Delta G$ of $pK_a^M$	$\Delta G$ of $pK_a^T$
1	10	4.804 ± 0.003	4.775 ± 0.006	-6.553 ± 0.003	-6.514 ± 0.008
2	15	4.762 ± 0.002	4.734 ± 0.006	-6.496 ± 0.003	-6.457 ± 0.008
3	20	4.709 ± 0.004	4.681 ± 0.007	-6.424 ± 0.005	-6.385 ± 0.010
4	25	4.657 ± 0.003	4.628 ± 0.007	-6.352 ± 0.004	-6.313 ± 0.009
5	30	4.607 ± 0.005	4.579 ± 0.008	-6.284 ± 0.007	-6.264 ± 0.011
6	35	4.546 ± 0.004	4.518 ± 0.007	-6.202 ± 0.005	-6.163 ± 0.009
7	40	4.505 ± 0.005	4.476 ± 0.008	-6.145 ± 0.007	-6.106 ± 0.010
8	45	4.472 ± 0.002	4.444 ± 0.008	-6.100 ± 0.006	-6.062 ± 0.010
9	50	4.449 ± 0.006	4.241 ± 0.008	-6.069 ± 0.009	-6.031 ± 0.012

trend is some what not so predominant. In some case decrease is some what linear, but it appears that graphs are parts of parabolas with maximum at 10% composition in case of  $pK_a$  and maxima around 50% composition in case of  $\Delta G$ 's. The  $\Delta G$  values of 8-methylquinoline increase with the increase of percent composition (less negative as we go to high percentages). The value for  $\Delta G$  is obtained from the following equation:

$$\Delta G = -RT \ln K_a = -RT \ln(10) \log K_a = RT \ln(10) pK_a \quad (11)$$

We have calculated Gibb's free energies  $\Delta G$  from the value of  $pK_a^M$  and  $pK_a^T$  in aqueous and in 10 to 50 percent solvent systems. It is observed that there is a regular increase in Gibb's free energy ( $\Delta G$ )

with increase of temperature and percent composition of mixed organic-water solvents for Dioxane-water, EtOH-water and MeOH-water. Same pattern is observed for  $\Delta G$  values of  $pK_a^T$ . The overall change in  $pK_a^M$  and  $pK_a^T$ ,  $\Delta G$  of  $pK_a^M$  and  $\Delta G$  of  $pK_a^T$  of the compound is given in Tables 1 to 4.

The degree of dissociation of the compound varies with percent composition of solvent-water system and temperature. Solvents are distinguished from their dielectric constants and hydrogen bonding capabilities. Water, EtOH, and MeOH have greater hydrogen bonding capacity and dielectric constant of 78.5, 32.6 and 24.3 respectively. In pure water  $pK_a$  values are highest and MeOH-water has lowest values. Dioxane has lowest dielectric constant of 2.21

Table 4: Effect of Percent Composition on  $pK_a^M$ ,  $pK_a^T$  and Thermodynamic Parameters of 8-Methylquinoline in MeOH-Water Solvent System

S. No.	% Comp:	$pK_a^M$	$pK_a^T$	$\Delta G$ of $pK_a^M$	$\Delta G$ of $pK_a^T$
1	10	4.630±0.003	4.602±0.005	-6.316±0.004	-6.278±0.007
2	15	4.581±0.002	4.552±0.006	-6.248±0.003	-6.210±0.007
3	20	4.550±0.003	4.521±0.006	-6.206±0.004	-6.167±0.009
4	25	4.512±0.005	4.483±0.008	-6.154±0.007	-6.116±0.010
5	30	4.481±0.005	4.453±0.008	-6.113±0.006	-6.074±0.010
6	35	4.442±0.005	4.413±0.008	-6.059±0.007	-6.020±0.001
7	40	4.412±0.003	4.384±0.008	-6.081±0.004	-5.980±0.010
8	45	4.381±0.004	4.352±0.009	-5.976±0.006	-5.937±0.012
9	50	4.343±0.003	4.314±0.007	-5.924±0.004	-5.885±0.009

and no ability to form H-bond. The  $pK_a$  values in dioxane system are therefore lowest.

### Experimental

In solution preparation chemicals used were of analytical grade and doubly degassed distilled water was used throughout. An approximate 0.1 M solution of HCl was prepared which is diluted by successive dilution method up to 0.01 M standardized with primary standard solution of sodium carbonate.

The solution of 8-methylquinoline was prepared by weighing the compound with accurate digital balance (SARTORIUS BA110S). The potentiometric titrations were performed in a thermostated double walled glass cell containing 20 ml of sample solution with HCl. The pH was determined with Philips PW 9420 digital pH meter which is coupled with Ingold combined glass and Ag/AgCl reference electrode filled with 3 M (KCl) potassium chloride. The temperature was controlled by circulating water through the jacketed measuring cell. JULABO HC thermostated bath accurate to  $\pm 0.1^\circ\text{C}$  was used for controlling the temperature. Prior to experiment, the glass electrode was calibrated with buffers of pH of 4.05 at  $25^\circ\text{C}$  and 6.98 at  $25^\circ\text{C}$  [2]. The sample solution was kept mixed by stirring with magnetic stirrer and inert by nitrogen gas. For dispensing titrant, Mettler burette DV-10 accurate to 0.01ml was used. The data obtained at different temperatures were analyzed by a computer program written in GW-BASIC for calculation of dissociation constants of 8-methylquinoline.

### Conclusion

Ionization constant of 8-methylquinoline in aqueous solutions agrees to the values reported in literature. Real problem in non-aqueous solvents lies

in the fact that a very few data are available in the literature at 18 or  $20^\circ\text{C}$ . The present work gives  $pK_a$  values at high temperatures (up to  $50^\circ\text{C}$ ) in aqueous and in dioxane, EtOH and MeOH-water mixed solvent systems at  $25^\circ\text{C}$ . The  $pK_a$  values of solvents other than water are very different from those which are in aqueous solutions e.g.  $pK_a$  of 8-methylquinoline in water is  $4.715 \pm 0.004$ , in 50% dioxane is  $3.742 \pm 0.006$ , in 50% EtOH is  $4.449 \pm 0.006$  and in 50% MeOH is  $4.343 \pm 0.003$ . It is observed that concentration ionization constant  $pK_a^M$  and thermodynamic ionization constant  $pK_a^T$  values in aqueous solutions decrease with rise of temperature. The curve of  $pK_a$  verses temperature appears to be a form of parabola. In case of dioxane-water, EtOH-water and MeOH-water solvent systems.  $pK_a^M$  and  $pK_a^T$  verses percent composition decrease slowly by increasing the addition of the solvents. The curve of the  $pK_a^M$  and  $pK_a^T$  verses percent composition is a distorted parabola. These findings leads to conclude that the solvents which establish hydrogen bonding (Water, EtOH and MeOH) decrease in  $pK_a$  are minimum but dioxane which does not show hydrogen bonding effect,  $pK_a$  value decrease is maximum.

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