Dissociation Constant Studies of Acridine and *p*-Nitroanaline Spectrophotometrically at Various Temperatures

[1]SAEEDUDDIN, [2]M. ANWAR*, [2]S.T. HUSSAIN AND [3]M.SHARIF
[1]*SAL Government College Mirpur Khas (Sindh) Pakistan*
[2]*Department of Chemistry University of Balochistan, Quetta Pakistan*
National Centre of Excellence I n Analytical Chemistry
[3]*Allama I.I. Kazi Campus University of Sindh Jamshoro, Pakistan*

(Received 15th January, 2002, revised 19th June, 2002)

Summary: The dissociation constant of Acridine and p-nitroanaline from 20°C to 50°C at 5°C interval in aqueous media have been determined spectrophotometrically at ionic strength of 0.01 M $KN0_3$. A computer program, which calculate dissociation constants of mono acidic bases by treating spectrophotometric data have been developed and written in GW-BASIC. The results have been obtained for Acridine and p-nitroanaline at various temperatures. The pK_a values of Acridine at 25°C and 50°C by using 354 nm analytical wavelength, are 5.744 ± 0.008 and 5.013 ± 0.0010 while for p-nitroanaline at 25°C and 50°C are 0.999 ± 0.006 and 0.577 ± 0.01 respectively. Thermodynamic parameters i.e Gibb's free energy ΔG, enthalpy ΔH and entropy ΔS are also calculated at different temperatures.

Introduction

The characterization and determination of the species involved in chemical equilibria are the aim of many studies in several branches of science and many authors [1-6] have extensively reviewed the experimental methods and numerical approaches used to obtain ionic equilibria. Spectrophotometry has definite advantages over other techniques for such purpose including simplicity of operation, high degree of precision and direct applicability to a wide range of system [2,7-9]. The strengths of acids and Bases are described by its dissociation in a given solution [9]. It is the proportion of different ionic species of substances present in solution at a particular pH. The survey of literature shows that the surface ionization and complexion constants. pK_{a1}, pK_{a2}, pK_{an}, pK_{cat} were found to be temperature constant and back round electrolyte dependent. Some of these values from the literature are given in Table-1.

Table-1: Surface ionization constant for magnetite in KNO_3 solution at various temperature

T (K)	PK_a1	pK_a2	pK_{an}	pK_{cat}	Ref.
303	404	9.00	9.33	7.07	8
323	4,15	8.70	5.84	7.02	
313	3.70	8.20	5.20	6.71	

The dissociation constants of Acridine and p-nitroanaline have been studied previously [9] at 25 °C- From Table 1, it is also obvious that the pK values were observed to be temperature dependent and decreased with increase in temperature. Similar results are also observed by other authors i.e, Zno[10] and αAl_2O_3 [10-12].

The literature survey further shows that the ionization constant data in aqueous and non aqueous solvents at different temperatures are not frequently available [13,14] The pKa values are very important both in chemical and pharmaceutical industries.

Both methods, spectrophotometric and potentiometric have been used widely for determination of dissociation constants of acids and bases [9,13,15-181. The potentiometric method is quick but it fails when compound is insoluble in aqueous solution. The spectrophotometric method is accurate and can be used to determine dissociation constant of compounds which are slightly soluble in water but is time consuming. To get better results with out approximations, the experimental data was analyzed by computer program written in GW-BASIC language to calculate pK values of mono acidic bases. This paper deals with the study of ionic equilibria of Acridine and p-nitroanaline at different temperature from 25°C to 50°C at 5°C interval.

Results and Discussion

The dissociation constants of Acridine and p-nitroanaline are determined spectrophotometricalty in aqueous media (1% ethanol) at low ionic strength and low concentration in order to obtain experimental pka values.

*To whom all correspondence should be addressed

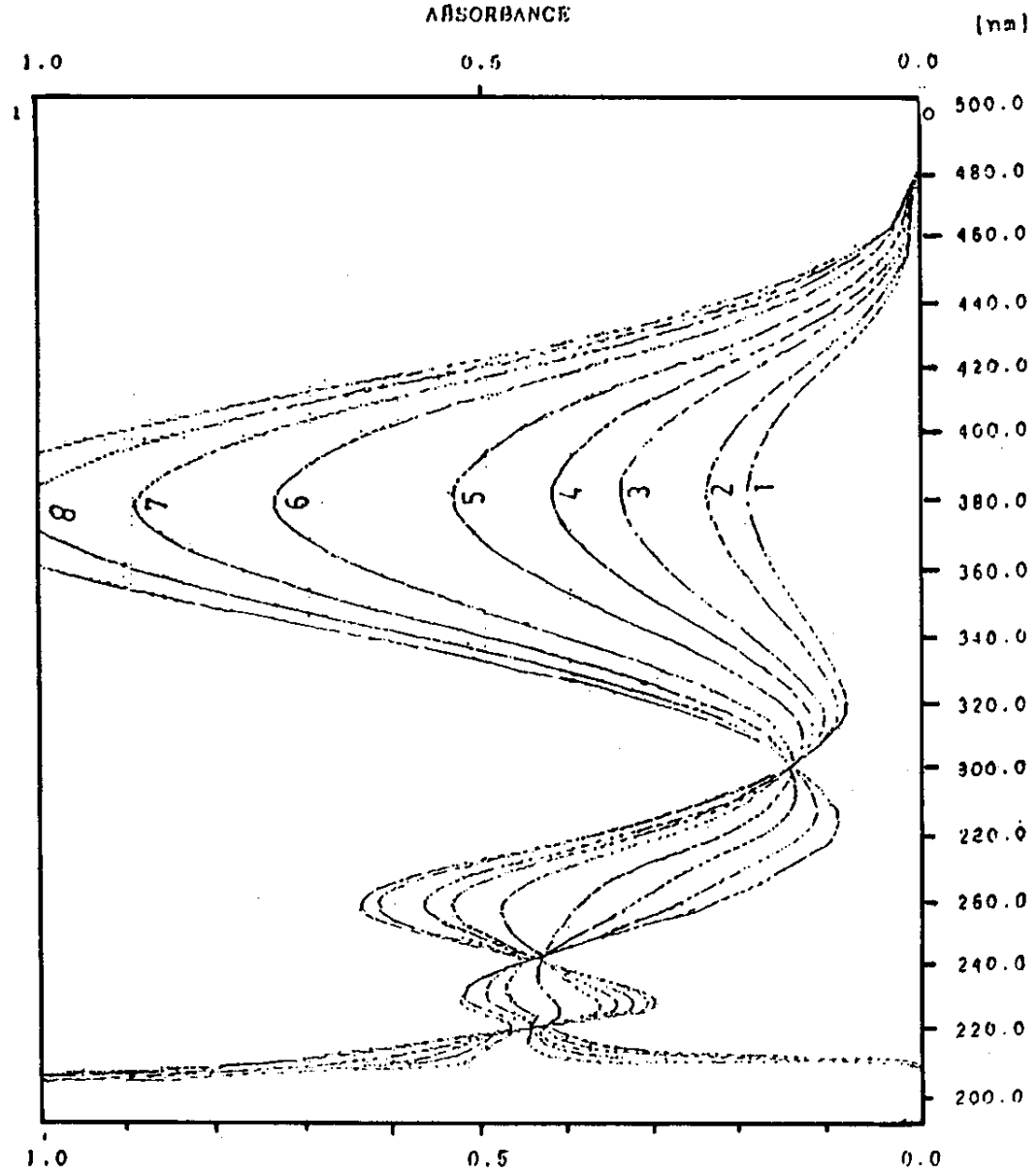

Fig. 1: Graph showing the spectral scan of *p*-nitroanaline hi different pH solutions.

Fig. 1 and Fig. 2 are the spectral scan for analytical wave length used for the determination of pka values of p-nitroanaline and Acridine respectively. A change in temperature causes a shift in equilibrium point which is of both practical and theoretical interest. The survey of literature shows that the ionization constant values for both investigated compounds are reported at only 25 °C [1] so, efforts have been made to extend the temperature range upto 50 °C to furnish more data and to get further the effect of temperature on dissociation constant.

Results summarize in Table 2 and 3 shows the effect of temperature on pka values of p-nitroanaline and Acridine respectively. Fig, 3 shows that as temperature increases from 20 to 50°C then pka values of Acridine decrease from 5.589 to 5.013 and total decrease is 0.882 unit while Fig. 4 shows the effects of temperature on pka values of p-

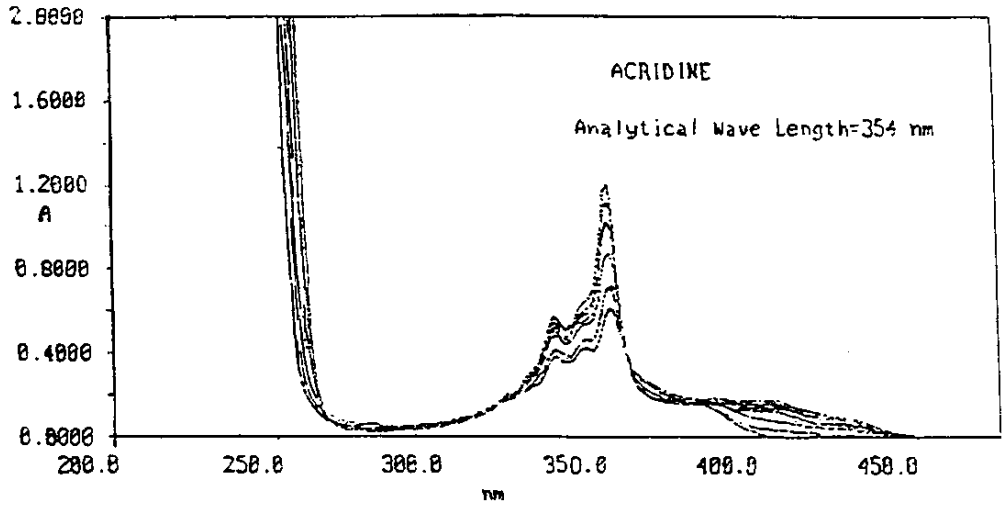

Fig. 2: Graph showing the spectral scan of Acridine in different pH solutions.

Table-2: pka values at different temperature and thermodynamic constant.

Temp.	Pka Evaluated	Pka Reported	ΔG kca/mole	ΔH kcal/mole	ΔS cal/mole/k
25	0.999 ±0.006	1.101±0.02	1.363	7.221	19.650
30	0.947 ±0.009		1.314	7.270	
35	0.856 ±0.008		1.207	7.262	
40	0.810 ±0.009		1.161	7.31	
45	0.702 ±0.01		1.022	7.273	
50	0.577 ±0.01		0.853	7.203	

Table 3: Pk_a values of Acridine at different temperature and thermodynamic constant.

Temp. °C	Pk_aT Evaluted	Pk_a Reported	G cal/mole	ΔH Kcal/mole	ΔS cal/mole/k
20	5.895 ± 0.001	5.62 ± 0.02	.907	12.767	16.582
25	5.774 ±0.008		.836	12.779	
30	5.593 ± 0.006		.758	12.784	
35	5.446± 0.009		.679	12.788	
40	5.292 ±0.007		.583	12.775	
45	5.154 ±0.001		.503	12.778	
50	5.013 ±0.001		.412	12.770	

nitroanaline. As temperature increases from 25 to 50 °C then pka values decrease from 0.999 to 0.577 unit. Decrease in pka values for each 5°C rise in temperature is same except between 35 to 40°C where it is minimum.

The change in thermodynamic properties that are Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS associated with an acid-base reaction can be found from the variation of its equilibrium constant with temperature. These properties affords interesting insights into acid-base behavior, particularly with regards to solvation effects. Change in thermodynamic function ΔG, ΔH and ΔS at 25 °C have been calculated by using the following equation [19].

$$pKa = \frac{\Delta H}{RT} - \frac{cp\,LnT}{R} - \frac{\Delta S}{R} + \frac{Acp}{R} \qquad (7)$$

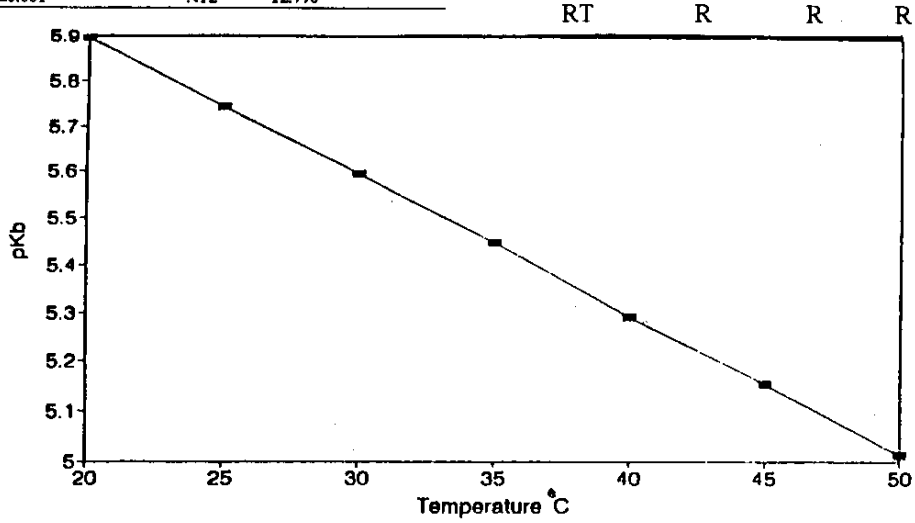

Fig. 3: Graph showing the effect of temperature on pka of Acridine.

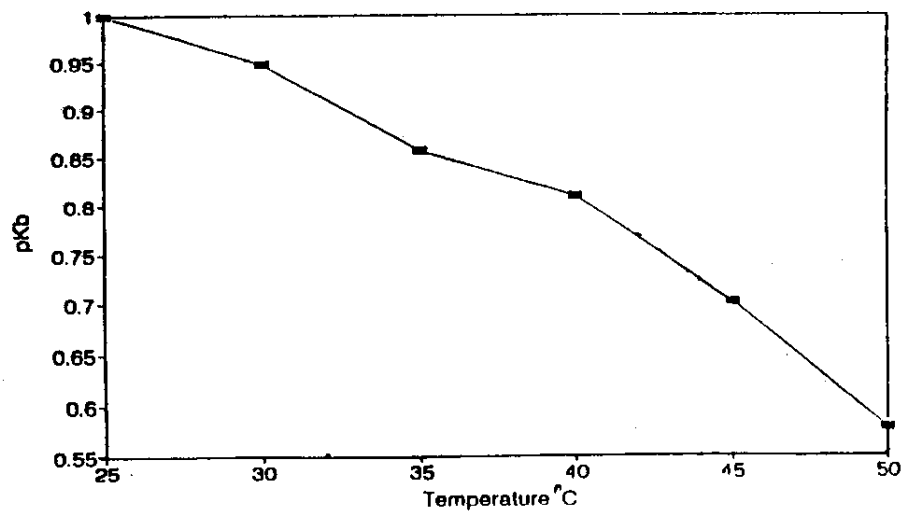

Fig. 4: Graph showing the effect of temperature on pka of *p*-nitroanaline.

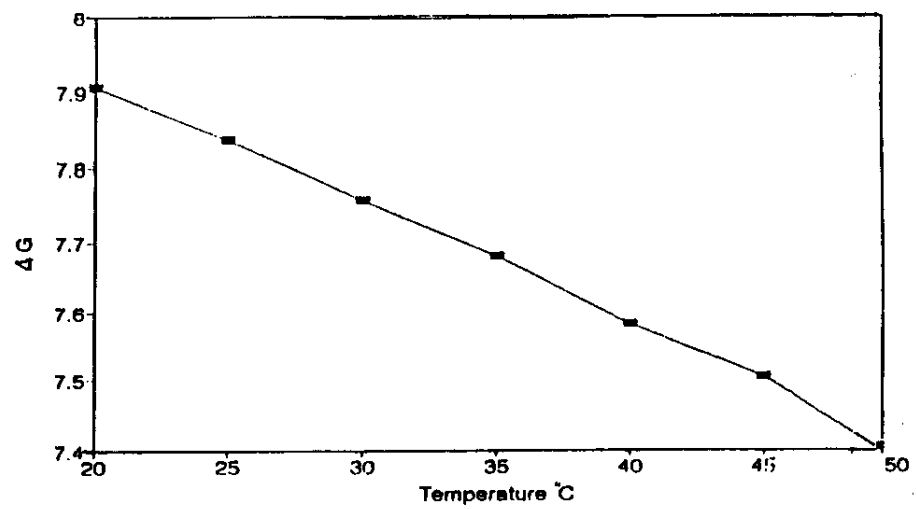

Fig. 5: Graph showing the effect of temperature on ΔG of Acridine.

If cp is zero over the temperature range investigated, Eq (7) reduces to

$$pKa = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Where $\Delta G = \Delta H - T\,\Delta S$

It is noted from Table 3 and Fig. 5 that as temperature increase, ΔG value for Acridine decreases and this decrease is linear.

From Table 3 and Fig. 6 it is observed that ΔG value for p-nitroanaline is also effected with change in temperature, as temperature increases from 25 to 50 °C, ΔG values decrease linearly.

It is concluded that pka values and thermodyonamic parameters, ΔG, ΔH are temperature dependent.

Experimental

A Perkin Elmer Lambda-2 UV-VIS spectrophotometer (1cm cell) was used for spectrophoto-

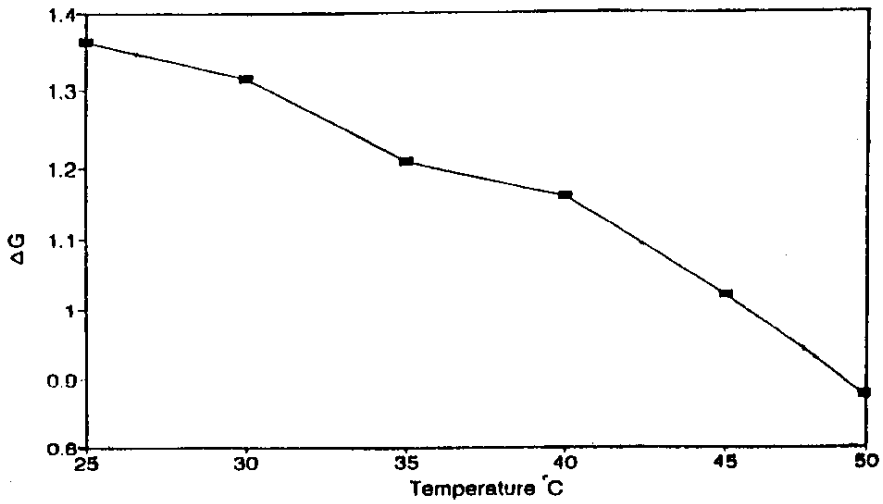

Fig. 6: Graph showing the effect of temperature on ΔG of *p*-nitroanaline.

meteric measurements. The temperature of the cell holder containing sample solution was controlled by circulating water from GFL thermed 5001 electronic thermostat bath accurate to ± 0.01 °C. A Philips PW 9420 digital pH meter coupled with glass and reference Ag/AgCl electrode was used. Prior to experiment the pH meter was calibrated with known buffers of 0.05 M potassium hydrogen pthalate (pH 25 °C 4.008) and 0.01 M potassium dihydrogen phosphate (pH 25°C = 6.89) [20,21] JULABO HC thermostat bath was used to control a temperature by circulating water through double wall glass cell.

Solution

All the reagents were of Analytical grade (Merck) and were used without further purification. All the solutions were prepared from double distilled and degased water. Buffer solution of 0.01 M ionic strength were prepared from potassium nitrate which was recrystallized twice in water. For spectroscopy 0.002 M Acridine and 8.7 x 10^{-5}M p-nitroanaline at various pH in citric acid Sodium acetate buffer, adjusted by pH meter, were prepared. The ionic strength of solutions were kept at 0.01 M with KNO_3 (Merck A.R). The carbonate free stock solutions of 0.01 M NaOH, 0-1 M HCl were prepared and standardized against potassium hydrogen pthalate and Borax respectively by potentiometric method [19]. The Acridine was dissolved in refluxed and distilled ethanol (Merck).

Procedure

All the solutions of the Acridine 10^{-4} M and p-nitroanaline 10^{-5} in aqueous (I= 0.01) media at various pH at 25°C were scanned on spectrophotometer for obtaining analytical wavelength. The absorbance at 354 nm of different pH solutions of Acridine and 380 nm for p-nitroananline aqueous media was observed. The pKa values of both compounds were calculated from the pH and the relationship between the absorbance of solution of molecular and ionized form [22,9] The spectrophotometric data were treated on SPEMON computer program for pKa values. Before and during titration pure nitrogen was bubbled through the solution to remove dissolved oxygen and efficient stirring was achieved with magnetic stirrer the temperature of the solution was maintained constant by circulating water through double jacket measuring cell from thermostat bath.

Theory

Observed absorbance A at the analytical wavelength is the sum of absorbance of the ionised species Ai and the molecular species A_m

$$A=A_I + A_m \quad \ldots\ldots(1)$$

The absorbance of either component is related to its molar concentration C by a general expression.

$$A= \epsilon LC$$

Where ε is molar absorption coefficient of the particular species and L is the optical wavelength of Cell.

The concentration of ionized species in the mixture is FC where F is the fraction ionized, this for acid

$$F_1 = \frac{[A]}{[A] + [HA]} \quad (2)$$

$$A_1 = F_1 C$$

Here the contribution of F_1 to the observed absorbance of mixture is $\epsilon_1 F_1 C_1$ similarly, the contribution of the molecular species to the observed absorbance of the mixture is $M F_M C_1$ molecular form.

Where ϵ_1 and ϵ_M are the molecular absorption coefficient of ionized and molecular species

The fraction of ionized and molecular species are given by expression obtained by replacing

$$[HA] \text{by} \quad \frac{[H^+][A^-]}{Ka}$$

$$F_1 = \frac{[A^-]}{([A^-]+[HA])} \quad \text{Where } [HA] = \frac{[H^+][A^-]}{K_a}$$

$$F_1 = \frac{[A^-]}{[A^-] + \frac{[H^+][HA]}{Ka}}$$

$$F_1 = \frac{[A^-] K_a}{(K_a[A^-] + [H^+][A^-])} = \frac{[A] K_a}{[A](K_a + [H^+])}$$

If the same cell optical length is used through out, then

$$A = (\epsilon_1 F_1 + \epsilon_M F_M) C \quad (3)$$

Because $\epsilon = A/C$ So,

$$E = \frac{(\epsilon_1 F_1 + \epsilon_M F_M)}{C} = (\epsilon_1 F_1 + \epsilon_M F_M)$$

Putting the value of F_1 from equation (1)

$$\epsilon = \frac{\epsilon_1 K_a}{K_a + [H^+]} + \frac{\epsilon_M [H^+]}{[H^+] + K_a} \quad (4)$$

Or replacing ϵ by A

$$A = \frac{A_1 K_a}{[H^+] + K_a} + \frac{A_{1M} [H^+]}{[H^+] + K_a} \quad (5)$$

$$A([H^+] + K_a) = A_1 K_a + A_{1M} [H^+]$$

$$A [H^+] + A K_a = A_1 K_a + A_{1M} [H^+]$$

$$Ka = \frac{[H^+](A - A_{1M})}{A_1 - A}$$

$$Pka = -\log [H^+] - \log \frac{(A - A_M)}{A_1 - A} \quad (6)$$

$$Pka = pH + \log \frac{(A_1 - A)}{(A - A_M)} \quad (7)$$

Conclusions

1. The pKa values of Acridine and p-nitroanahne were observed to decrease with the increase in temperature.
2. The values of Gibbs free energy ΔG for Acridine were also observed to decrease linearly with the increase in temperature.
3. The values of enthalpy ΔH were observed to be constant through the experiment.

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