SPECTROPHOTOMETRIC DETERMINATION OF ACIDITY CONSTANTS OF SOME ANTHRAQUINONE DERIVATIVES IN METHANOL-WATER MIXTURES

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ABSTRACT: *A spectrophotometric method is used to determine the acidity cons-tants of some derivatives of 9,10-anthraquinone in binary methanol-water mix-tures at 25°C. There is a linear inverse relationship between pK_a of all acids and the mole fraction of methanol in the mixed solvent. The influence of substituents in the molecular structure on the ionization constants is discussed.*

KEY WORDS: *Spectrophotometry, Acidity constants, Anthraquinone derivatives*

INTRODUCTION

Acidity is of great value in many fundamental problems such as, extraction, ion transport, complex formation and mechanism of drug action [1].

9,10-Anthraquinones are the largest group of natural quinones and industrially the most important ones [2-4]. Synthetic derivatives of anthraquinone and their naturally occurring derivatives have been used for medical purposes [5,6].

The acidity constants of some anthraquinones are measured in various methanol-water mixtures at 25°C by spectrophotometric method. The acidity constants of some other anthraquinone derivatives have already been reported in the literature [8,9].

MATERIALS AND METHODS
Reagents

Ammonia and oxalic acid were purchased from BDH; HPLC grade methanol, reagent grade per-

chloric acid, reagent grade succinic acid, lithium hydroxide, and sodium pechlorate were purchased from Merck, and used without further purification. Triply distilled deionised water was used throughout.

1-Hydroxy- 8 -(allyloxy)- 9,10- anthraquinone (A_1), 1- hydroxy- 4 -(allyloxy)- 9,10- anthraquinone (A_2), 1- hydroxy- 4 -(methoxy)- 9,10- anthraquinone (A_3); 1,8- dihydroxy- 9,10- anthraquinone (A_4), 1,4- dihydroxy- 9,10- anthraquinone(A_5), 1- hydroxy-2-[1-(3- hydroxy- propyl) oxy methyl]-9,10- anthraquinone (A_6), 1,8- di- hydroxy- 2 -(allyl)- 9,10- anthraquinone (A_7), 1,8- di- hydroxy- 2,7- bis(allyl)- 9,10- anthraquinone (A_8) were synthesized [7] and used after recrystallization from pure benzene. Fig. 1 shows the structure of the used acids.

Apparatus
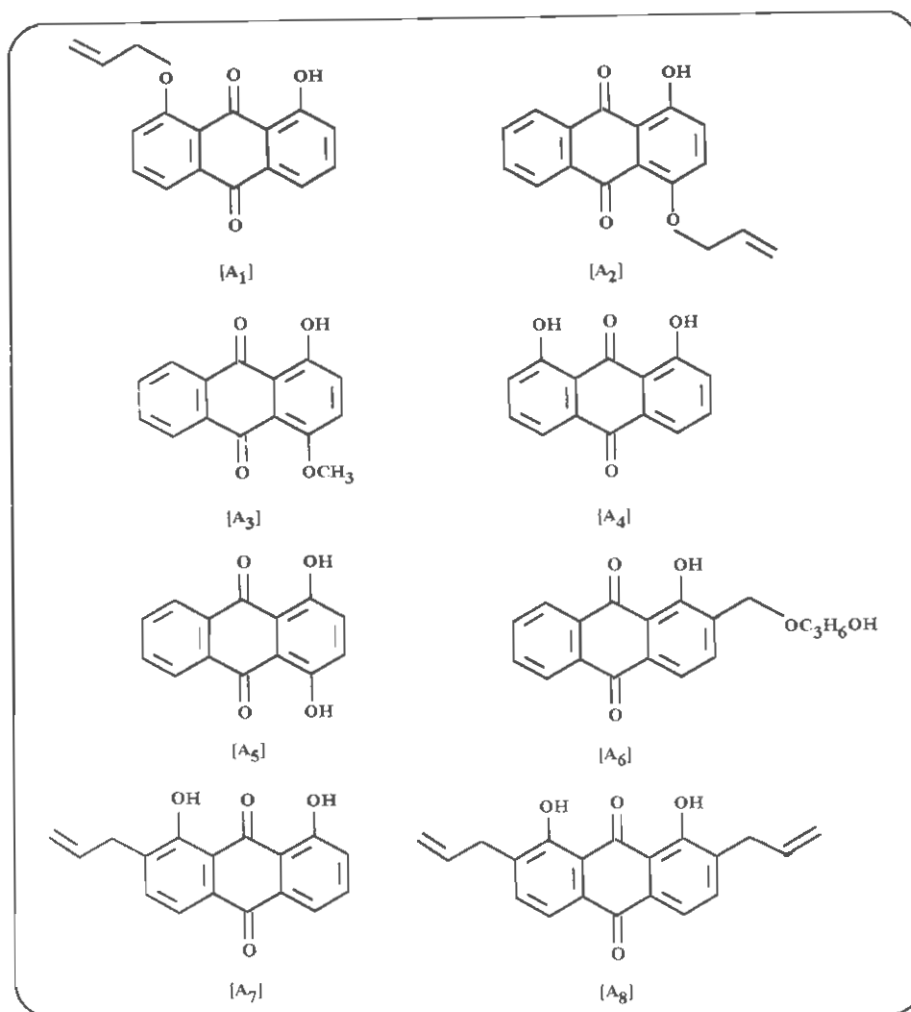
The spectra were recorded on a GBC 911 spectro-

Fig. 1 : Anthraquinone derivatives

photometer and the absorbance measurements at fixed wavelengths were made with a Metrohm a 622 probe type photometer. The pH values were determined with a Metrohm 362 pH meter using a combined glass electrode.

Procedure

For calibration of the pH meter in various binary methanol-water mixtures, the 0.01 M solution of oxalate and succinate buffers were employed. The reference values of pH of these buffer solutions in different methanol-water mixtures have been reported previously [10]. The procedure introduced by *Asuero* et al. [11,12] was employed to determine the acidity constants. In this procedure, the absorbance of 1.0×10^{-4} M acids was first measured in highly

acidic and basic media. Then the absorbance measure- ments were taken at two pH values close to pK_a in different methanol-water mixtures. The acidity cons- tants were computed from the system of two simulta- neous equations which resulted from substituting the $[H^+]$ and absorbance values in the mass balances [11].

$$(A_0 - A) K_a - [H^+] A_1 = [H^+] A \qquad (1)$$

where A_0 , A_1 and A are the absorbances of totally deprotonated acid R, totally protonated acid HR, and the mixture of two forms at the working pH and at the wavelength measured, respectively. The two unknowns in this method are A_1 and K_a . Except with the highly acidic and basic solutions, the ion strength of all other solutions was kept constant at

0.01 M using sodium perchlorate. For a diprotic acid with the ionization equilibria $H_2R \rightleftarrows H^+ + HR^-$ and $HR^- \rightleftarrows H^+ + R^{2-}$, the mixed acidity constants are given by:

$$(A- A_0)K_{a2} - A_1[H^+] = (A- A_2)[H^+]^2/K_{a1} = -A[H^+] \quad (2)$$

where A_0 , A_1 and A_2 are the absorbances of pure R^{2-}, HR^- and H_2R, respectively. The required unknowns K_{a1} , K_{a2} and A_1 were obtained by solving the simultaneous equations obtained for the three solutions.

RESULTS AND DISCUSSION

The visible spectrum of anthraquinone derivatives $A_1 - A_8$ in different methanol-water mixtures at various pH values were recorded. Fig. 2 shows a sample spectrum. The presence of clear isosbestic points in the resulting spectra indicated that only two species (i.e. R^- and HR) are in equilibrium under the experimental conditions used. The pK_a values of these molecules were evaluated in different methanol-water mixtures at 25°C spectrophotometrically. Sample absorbance-pH plots for molecules A_8 in different methanol-water mixtures is shown in Fig. 3. In all cases, the procedure was repeated at least three times and resulting average values and corresponding standard deviations for each acid in different solvent mixtures are summarized in Table 1.

The nature of solvent plays an important role in the acid-base equilibria as can be seen from Table 1. In all cases the acidity decreases drastically by an increase in the mole fraction of methanol in the
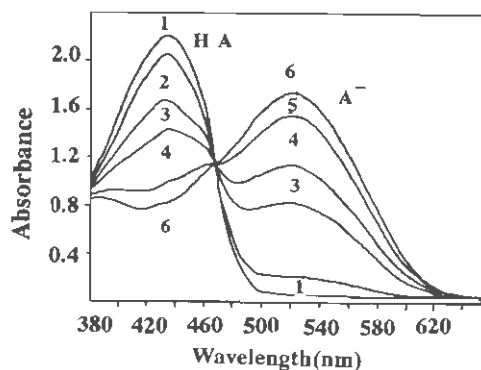
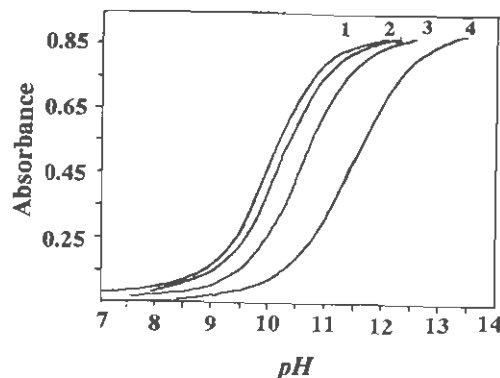*Fig. 2 : Visible spectra of A_3 at various pH in methanol solution*

Fig. 3 : Absorbance-pH plots for A_8 in different methanol-water mixtures; $\lambda_{max} = 525nm$; wt% methanol: 1,70; 2,80; 3,90; 4,100.

solvent mixtures.

It has been shown that the energy required for the separation of charges in acid dissociation, which is inversely proportional to the solvent dielectric constant, is compensated by the solvation energy of the resulting ions [10]. Since both the dielectric constant, ε, and solvating ability (as expressed by the Gutmann donor number, DN) [13] of methanol ($\varepsilon = 32.6$ and DN= 19) are much lower than those of water ($\varepsilon = 87.3$ and DN= 33) [14], the observed decreases in the extent of dissociation of acid molecules by increase in mole fraction of methanol in the binary methanol-water mixtures is not surprising.

The relationship between the first acidity constant of acids and mole fraction of methanol in the binary mixtures are illustrated in Fig. 4. There is a good linear relationship between pK_{a1} and X_{MeOH} in all cases studied. The same kind of relationship is also reported [8,9] and data obtained from the study of complexation of a number of ligand-metal ion systems in methanol-water [15], acetonitrile-water [16, 17] and ethanol-water [18,19] (mixed solvents) give similar relationship. It is reasonable to assume that the preferential hydration of the conjugated bases is mainly responsible for such a monotonic dependence of ionization constant upon the solvent composition.

The order of acidity of anthraquinone derivatives is shown as A5>A3>A7>A2>A1>A4≈A8>A6 .

The difference between acidity of these compounds may be due to different effects like inductive, field, and resonance effects and hydrogen bonding.

Table 1: Acidity constants of some anthraquinone derivatives in different methanol water mixtures

Acid	λ_{max} in basic solution, nm		Solvent composition (wt. %methanol in water)			
			70	80	90	100
A_1	495	pK_{a1}	9.68±0.01	9.97±0.2	10.87±0.01	12.47±0.00
A_3	525	pK_{a1}	9.22±0.02	9.69±0.02	10.40±0.03	12.40±0.02
A_4	510	pK_{a1}	9.81±0.05	10.34±0.05	10.57±0.04	11.71±0.02
		pK_{a2}	11.31±0.02	11.55±0.02	12.13±0.02	12.13±0.02
A_5	545	pK_{a1}	8.90±0.01	8.57±0.03	9.46±0.02	10.34±0.01
		pK_{a2}	10.33±0.02	10.84±0.03	11.92±0.01	12.53±0.03
A_6	497	pK_{a1}	9.97±0.10	10.42±0.02	11.14±0.02	12.13±0.07
		pK_{a2}	10.94±0.02	11.78±0.08	12.56±0.03	13.76±0.01
A_7	510	pK_{a1}	9.28±0.02	9.72±0.03	10.27±0.02	11.11±0.06
		pK_{a2}	11.46±0.05	11.54±0.02	12.31±0.04	13.40±0.05
A_8	525	pK_{a1}	9.82±0.01	10.12±0.01	10.53±0.04	11.31±0.04
		pK_{a2}	11.32±0.08	11.54±0.09	12.65±0.07	12.77±0.04
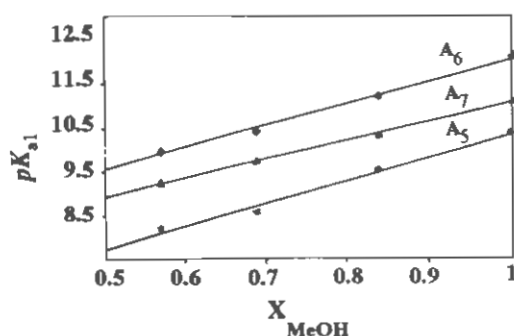
Fig. 4 : pK_{a1} values vs. X_{MeOH} for different acids

Moreover, solvation of the acids and their conjugate bases is also of importance, this can exert considerable influence on the acid strength. If a conjugate base is more solvated than its acid, its stability is increased. In fact, the solvent molecules interact more orderly with the $-O^-$ group by hydrogen bonding than the -OH group. This represents a considerable loss of freedom and decrease in the entropy. The molecule A_1 is weaker acid than A_2 . The conjugate base of A_1 is not stable because there is a repulsive force between the conjugate form of carbonyl group and allyloxy group. Also, solvation of the conjugate base of A_1 is weaker than that of the conjugate base of A_2 . The molecule A_6 is the weakest acid in this series. Probably the repulsive force between the con-

jugate base of acid and oxygen of ether in the side arm and weakest solvation are responsible for this order. The molecule A_5 is the strongest acid since the canjugate base is stabilized by resonance and hydrogen bonding.

ACKNOWLEDGMENTS

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