

## Determination of Ionization Constants of Overlapping Dibasic Acids in Acetonitrile-H<sub>2</sub>O Mixtures

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**Summary:** Dissociation constants of few overlapping dibasic acids in acetonitrile at 25°C have been studied by potentiometric method. Data were analyzed by computer program written in GW-BASIC for calculation of pK<sub>a</sub> values of overlapping dibasic acids. Because of ion pair formation the incomplete dissociation of the compound has been taken into account in the calculation of pK<sub>a</sub> values. The resolution of acid strength in acetonitrile relative to that in water has been determined for each compound by plotting the pK<sub>a</sub> values vs. percent composition of solvent. Gibb's free energy ( $\Delta G^{\circ}$ ) is also studied. The results show greater resolution in acetonitrile than in water.

### Introduction

Acid-base equilibria is disturbed by addition or removal of species foreign to the equilibria. The nature of solvents effects on equilibrium constant.

Many chemists require to know the dissociation constants of organic acids and bases in non-aqueous media. Therefore in recent years much attention has been paid to a quantitative explanation of the medium effect on pK<sub>a</sub> values [1-8].

Acetonitrile is one of the most important dipolar aprotic solvent. It is used extensively as a reaction medium in synthesis and for mechanistic studies, as well as in electro-chemistry, spectrophotometry and liquid chromatography. It owes its manifold application in such diverse fields to combination of physical properties [9] particularly its high polarity ( $\pi = 0.75$ ) [10] accompanied by only modest "Chemical" solvating power towards many polar and ionic solutes. In common with all other dipolar aprotic solvents [11] acetonitrile typically behaves as a very weak electrophile. It is a much weaker hydrogen bond donor than water ( $\alpha = 0.19$ ) [10] but unlike photophilic dipolar aprotic solvent [11], it is also weak hydrogen bond acceptor ( $\beta = 0.31$ ) [10].

The acid-base equilibria of a series of benzodiazepines in acetonitrile have previously been studied [12]. Jose Barbosa and other studied dissociation constants of protonated bases in

another series of cardiovascular compound, the  $\beta$ -blocker in acetonitrile [13].

This paper discusses equilibrium constant of few overlapping dibasic acids (adipic acid, succinic acid, glutaric acid, tartaric acid and fumaric acid) in acetonitrile-water mixture.

There are different methods [14-17] by which equilibrium constant of weak acids and bases can be determined. The potentiometric methods are widely used to study ionic equilibria in aqueous and non-aqueous solvents, than the other methods such as spectrophotometric and conductometric [18-21]. Potentiometric method was used for the determination of equilibrium constant of compounds under investigation, where the data were analyzed by a computer program. The program has been written to work on IBM-PC or compatible computers.

### Results and Discussion

Table-1 shows pK<sub>a</sub> values of studied systems in aqueous and mixed (acetonitrile-H<sub>2</sub>O) media.

The equation which used to calculate K<sub>1</sub><sup>T</sup> and K<sub>2</sub><sup>T</sup> (by method of least squares) is

$$\frac{1}{K_1^T} = \frac{X}{10^{(2.046, \text{FS})}} - K_2^T = \frac{Y}{10^{(1.535, \text{FS})}} \quad (1)$$

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Table-1: Thermodynamic  $pK_a$  values of Dibasic acids in aqueous and acetonitrile-water mixture at 25°C.

Acid		$pK_a$				
		%Acetonitrile-Water				
		0	10	20	30	40
Adipic	$pK_1$	4.405	4.581	4.752	4.962	5.199
	$pK_2$	5.465	5.546	5.893	6.051	6.420
Succinic	$pK_1$	4.203	4.686	4.730	4.812	4.931
	$pK_2$	5.723	5.440	5.491	5.483	5.602
Glutaric	$pK_1$	4.508	4.593	4.672	4.791	4.982
	$pK_2$	5.494	5.601	5.663	5.772	5.996
Fumaric	$pK_1$	3.061	3.087	3.142	3.204	3.252
	$pK_2$	4.461	4.483	4.565	4.638	4.694
Tartaric	$pK_1$	3.006	3.316	3.452	3.553	3.752
	$pK_2$	4.484	4.561	4.703	4.807	4.891

The activity coefficients can be expressed in exponential form by defining a function "FS", of the ionic strength.  $K_1^T$  and  $K_2^T$  are thermodynamic constants.

As shown in Table-1,  $pK_a$  values of acids in mixed media are much higher than in water. Further, as the proportion of solvent increases from 10 to 40%,  $pK_a$  values increase linearly. The increase in  $pK_1$  and  $pK_2$  values is mainly due to the effect of solvent.

In Table-2 Gibb's free energy,  $\Delta G^\circ$ , of different compound has been calculated in aqueous and mixed media. It is noted from Table-2 that  $\Delta G^\circ$  values in (acetonitrile-water) are higher than in aqueous medium.  $\Delta G^\circ$  values increase linearly in acetonitrile-water solvent system as the proportion of acetonitrile increases from 10 to 40% (w/w).

Table-2:  $\Delta G^\circ$  values of Dibasic acids in aqueous and acetonitrile-water mixture at 25°C.

Acid		$\Delta G^\circ$ (kJ/mol)				
		%Acetonitrile-Water				
		0	10	20	30	40
Adipic	$\Delta G_1^\circ$	25.601	26.150	27.125	28.321	29.677
	$\Delta G_2^\circ$	31.204	31.656	33.639	34.538	36.647
Succinic	$\Delta G_1^\circ$	23.991	26.748	26.999	27.467	28.145
	$\Delta G_2^\circ$	32.668	31.053	31.342	31.296	31.978
Glutaric	$\Delta G_1^\circ$	25.731	26.216	26.668	27.346	28.439
	$\Delta G_2^\circ$	31.359	31.970	32.325	32.949	34.225
Fumaric	$\Delta G_1^\circ$	17.472	17.619	17.933	18.288	18.560
	$\Delta G_2^\circ$	25.464	25.590	26.058	26.472	26.794
Tartaric	$\Delta G_1^\circ$	17.158	18.928	19.702	20.280	21.418
	$\Delta G_2^\circ$	25.593	26.032	26.844	27.439	27.920

Fig. 1 shows the effect of aqueous and mixed media on  $pK_1$  values of dibasic acids, while

Fig. 2 shows the effect on  $pK_2$  values. As solvent concentration increases from 10 to 40 percent, a notable change is observed in  $pK_a$  values.

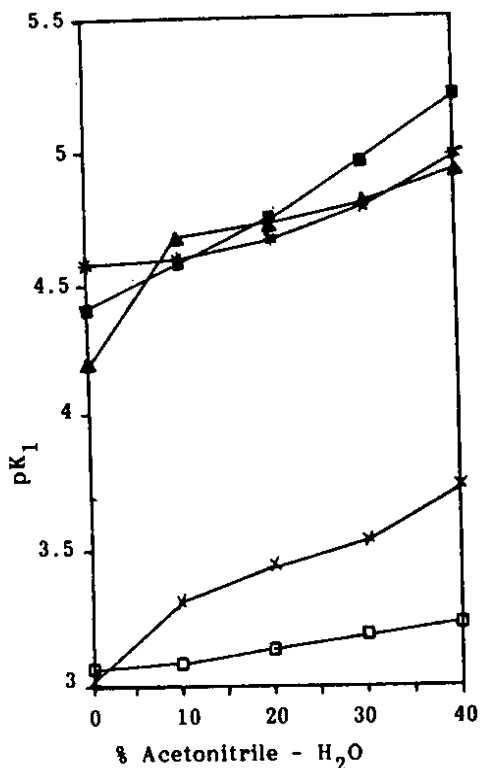


Fig. 1: The effect of the solvent composition on  $pK_1$  of dibasic acids. (■) Adipic (□) Fumaric (X) Tartaric (\*) Glutaric (Δ) Succinic

Practically acetonitrile has no hydrogen donor capacity, where as water has a high hydrogen bonding donor capacity with a solvatochromic parameter of 1.17 [10]. Thus, acids such as carbon acids, the anions of which are not hydrogen bonded in hydrogen bond donating solvents, do not exhibit resolution of acid strength between amphoteric and aprotic solvents [11] and no difference was found in resolution of acid strength between non hydrogen bond donor solvents such as acetonitrile, N,N-dimethylformamide and dimethylsulphoxide [22].

The difference in hydrogen bond accepting capacity between acetonitrile ( $\beta = 0.031$ ) [10] and water ( $\beta = 0.047$ ) [23] is much smaller, however

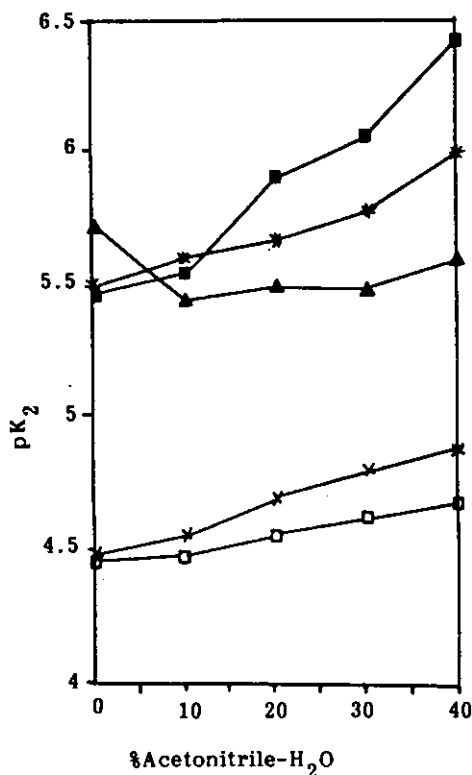


Fig. 2: The effect of the solvent composition on  $pK_2$  of dibasic (■) and Adpict (□) Fumeric (X) Tartaric (\*) Glutaric (Δ) Succinic

the difference in their hydrogen bond donor capacities and acetonitrile solvates  $HB^+$  cation much better than  $A^-$  anions. This explains why the resolution of acid strength of cation acids  $HB^+$  is very much smaller than for uncharged acids  $HA$ .

Traditional  $pK$  measurements reflect the degree of dissociation of species in a given solvent but do not provide a valid measure of the relative proton activity [24]. One of the main purpose of the studies dealing with the influence of solvents on acid-base equilibria is to obtain a solvent independent acidity or basicity scale.

#### Experimental

All the reagents were of analytical grade and were used without further purification. Fresh purified and distilled acetonitrile was used. All the solution were prepared in doubly distilled and

carbon dioxide free conductivity water. Solutions of adipic, succinic, tartaric, fumaric and glutaric acid were of 0.01, 0.009, 0.01, 0.008 and 0.01M respectively. Sodium hydroxide solution of 0.1 M in water and in 10, 20, 30 and 40 percent v/v acetonitrile-water were also prepared and standardized against potassium hydrogen phthalate (dried at 120°C) by potentiometric method. The potentiometric titration were performed in thermostated jacket cell containing Ingold combined glass and Ag/AgCl reference electrode saturated with potassium chloride. The temperature of the cell kept constant by circulating water from JULABO HC thermostated bath accurate to  $\pm 0.01^\circ\text{C}$ . Prior to experiment, the glass electrode was calibrated with  $\pm 0.05\text{M}$  potassium hydrogen phthalate ( $\text{pH} = 4.01$  at  $25^\circ\text{C}$ ) and 0.1M sodium tetraborate ( $\text{pH} = 9.18$  at  $25^\circ\text{C}$ ).

The pH of titrand in the cell was measured with PHILIPS PW 9420 digital pH meter. The titrant was delivered by Mettler DV-10 dispenser readable to 0.01ml. The potentiometric titrations were performed on 50 ml of acid solution as titrand and sodium hydroxide as titrant. The solution was made carbonic acid free by bubbling a purified nitrogen gas. The  $pK_a$  values of each acid were calculated from the mean of three experimental data analysed by computer program in GW-BASIC language.

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