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Research Article

PHYSICOCHEMICAL STUDY OF P-AMINO BENZOIC ACID

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ABSTRACT
Some physicochemical properties such as dissociation constant, acoustical parameters and thermal studies of p-amino benzoic acid are studied in methanol and ethyl acetate at 298.15 K. The dissociation constant of para amino benzoic acid is studied in higher in methanol + water system. The acoustical properties have been evaluated from experimental data of density, viscosity and ultrasonic velocity. It is observed that in both exist strong solute-solvent interactions in the studied solutions. Thermal degradation of PABA is found to be a single step process.

Keywords: *p-amino Benzoic Acid, Dissociation Constant, Acoustical Parameters, Thermal Analysis*

INTRODUCTION
Para amino benzoic acid (PABA) is an essential nutrient for some bacteria and is largely non toxic. The deficiency of P-amino benzoic acid causes fatigue, irritability, nervousness, headache, graying hair and digestive problems, such as constipation and depression might manifest itself as well as constipation. Weeping eczema has also been noted in people with its deficiency as well as patchy areas on the skin.
In the present work, some physicochemical properties of PABA such as kinetics of decomposition, dissociation constants and acoustical properties in some solvents are studied.

MATERIALS AND METHODS
Para amino benzoic acid was recrystallized from methanol before use. The solvents; methanol and ethyl acetate used in the present study were of B.D.H Analar grade and were purified by standard procedure (Ridlick *et al.,* 1986).
Dissociation: The dissociation constant of PABA are studied in mixed solvents; methanol + water and ethyl acetate+ water systems at 298.15 K by Calvin Bjerrum pH titration technique.
For this, two set of solutions are prepared. Milli-Q water (Millipore Pvt. Lt. Bangalore-India) was used for dissociation studies. An electrical balance (Mettler Toledo AB204-S) with an accuracy of ± 0.1mg was used for solution preparation.
(i) 2 ml HNO_3 (1.0M) + 4 ml water + 30 ml methanol/ethyl acetate + 4.0 ml $NaNO_3$ (1.0 M).
(ii) 2 ml HNO_3 (1.0M) + 4 ml water + 28 ml methanol/ethyl acetate + 2.0 ml PABA solution (0.1M) + 4.0 ml $NaNO_3$ (1.0 M).
These solutions were titrated against 0.5 M-sodium hydroxide and the corresponding pH was measured using Systronic pH meter (Model No. EQ 664). The glass electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively. Before operation, the glass electrode was immersed in 0.1 M HCl for twenty minutes. Then, it was washed thoroughly with Milli-Q-water. The pH meter was calibrated with buffer solution of known pH.
Acoustical Properties: The solutions of PABA were prepared in methanol and ethyl acetate over a wide range of concentrations. The density (ρ), ultrasonic velocity (U) and viscosity (η) of pure solvents and their solutions were measured by a single capillary pycnometer, single crystal variable path ultrasonic interferometer (operating at 2 MHz) and Ubbelohde viscometer respectively. The accuracy of density, velocity and viscosity are ± 0.0001 g/cm^3, ± 0.1% cm/sec and 0.05%. All the measurements were carried out at 298.15 K. The uncertainty of temperature is ± 0.1 K and that of concentration is 0.0001 moles /dm^3.
Thermal Analysis: Thermal analysis was by Differential Scanning Calorimetry (DSC) and Thermo gravimetric analysis (TGA) techniques. These measurements were made on the instrument "Pyris-1, Perkin Elmer Thermal Analysis" at the heating rate of 10^0 C /min in nitrogen atmosphere.

RESULTS AND DISCUSSION

Dissociation: From these titration curves, the average number of protons ($\overline{n_H}$) associated with the PABA can be calculated by the equation given by Irving and Rossotti (Irving and Rossoti, 1954).

$$\overline{n_H} = Y - \left\{(V''-V')\left(N^0+E^0\right)\right\} \Big/ \left\{\left(V^0+V'\right)T_L^0\right\}$$

where Y is the number of displaceable protons. For PABA, Y is taken as one. $V^{/}$ and $V^{//}$are the volume of alkali required at the same pH for both HNO_3 and PABA titration curves respectively. V^0 is the initial volume of the test solution. N^0, E^0 and T^0_L are the initial concentration of the alkali, nitric acid and PABA respectively.

It is observed that the value of $\overline{n_H}$ are found to be between zero to one suggesting there by that PABA has one replaceable protons.

The dissociation constants in both the solvent systems are evaluated by half integral and average methods.

In half integral method, pK_1^H value was evaluated at $\overline{n_H}$ =0.5 whereas in average method, for all the points below $\overline{n_H}$ =1, the following equation was used to determined pK_1^H

$$log\ pK_1^H = pH + log\,\bar{n}_H \big/ \left(\bar{n}_H - 1\right)$$

From these evaluated various values of log pK_1^H, average values of pK_1^H were calculated.

The dissociation constants of PABA by both average and half integral methods are given in Table 1 in methanol + water and and ethyl acetate + water systems. It is observed that pK_1^H value is maximum in methanol and minimum in ethyl acetate. The higher pK_1^H suggests that dissociation decreases in methanol. Further, comparison of pK_1^H values in the two solvent systems suggests that CDCA is more acidic in ethyl acetate + water system.

Table 1: The pK^H values for PABA evaluated by Average and half-integral methods in methanol and ethyl acetate.

Solvent	Half-integral method	Average method
Methanol	9.91	9.91
Ethyl acetate	8.27	8.30

Acoustical Properties: The experimental data of density (ρ), viscosity (η), and sound velocity (U) for pure solvents and solutions of PABA are reported in Table 2. It is observed that all these experimental values increase with concentration in both the solvents.

Table 2: Experimental values of density (ρ), viscosity (η), ultrasonic velocity (U) of PABA in methanol and ethyl acetate at 298.15 K

	Methanol			Ethyl acetate		
Conc. (mol/lt)	ρ (g/cm^3)	U (cm/s)	η (poise)	ρ (g/cm^3)	U (cm/s)	η (poise)
0.00	0.7858	1.1100	5.4485	0.896	1.1488	4.6604
0.01	0.792	1.1110	5.6252	0.8975	1.1504	4.7626
0.02	0.7925	1.1117	5.6926	0.8985	1.1515	4.8865
0.04	0.7931	1.1124	5.8095	0.8995	1.1523	5.0468
0.06	0.7939	1.1129	5.9432	0.9003	1.1533	5.1379
0.08	0.7945	1.1138	5.9762	0.9014	1.1544	5.3538
0.10	0.7949	1.1152	6.177-4	0.9023	1.1559	5.4096

From these experimental data, various acoustical parameters like specific acoustical impedance (Z), Adiabatic compressibility (κ_s), intermolecular free length (L_f), Vander waal's constant (b), relaxation strength (r), internal pressure (π), solvation number (S_n), etc. were evaluated using the equations reported earlier [Bhesaniya and Baluja (2014)]. Some of these values are given in Table 3.

Table 3: Some evaluated acoustical parameters for solution of PABA in methanol and ethyl acetate at 298.15 K

Conc. (mol/lt)	Z ($gm^{-2}.s^{-1}$)	r	π *10^{-8}	b $cm^3.mol^{-1}$
Methanol				
0.00	0.8722	0.5187	1072.3979	40.7464
0.01	0.8799	0.5178	1087.6659	40.6573
0.02	0.8810	0.5172	1087.1017	40.8610
0.04	0.8822	0.5166	1084.2278	41.2881
0.06	0.8835	0.5162	1083.1357	41.7030
0.08	0.8849	0.5154	1072.5146	42.1273
0.10	0.8865	0.5142	1076.5099	42.5614
Ethyl acetate				
0.00	1.0293	0.4845	326.6605	98.3344
0.01	1.0324	0.4831	330.0379	98.2536
0.02	1.0346	0.4821	334.0577	98.2274
0.04	1.0365	0.4813	338.9534	98.2842
0.06	1.0383	0.4804	341.3867	98.3625
0.08	1.0406	0.4794	347.9145	98.4074
0.10	1.0430	0.4781	349.0499	98.4737

Table 2 shows the experimental data of density, viscosity and ultrasonic velocity. It is observed that all these values increase with concentration in both the solvents. The variation of ultrasonic velocity with concentration is also shown in Figure 1.

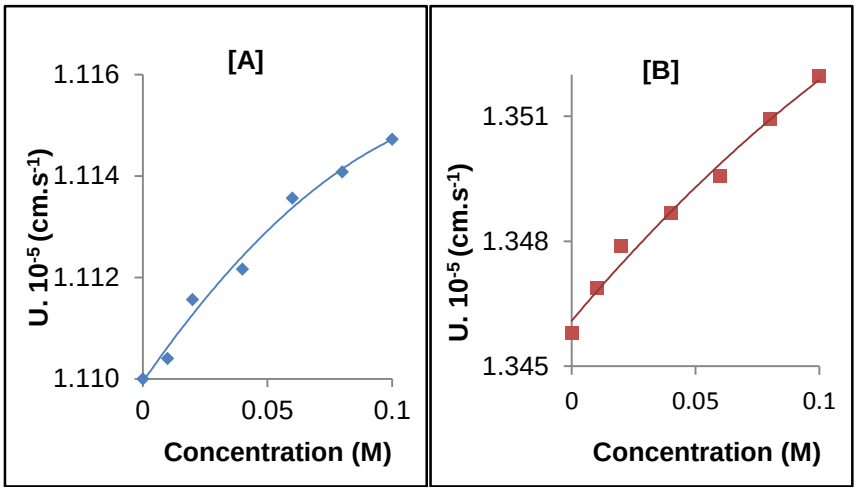

Figure 1: The variation of ultrasonic velocity with concentration in [A] methanol and [B] ethyl acetate

The ultrasonic velocity is found to increase non-linearly with concentration. The velocity depends on intermolecular free path length (L_f). Larger the intermolecular free path length, smaller will be the velocity and vice versa. It is evident from Figure 2 that intermolecular free path length decreases non-

linearly with concentration. The increase of velocity and decrease of intermolecular free path length suggests close association between PABA and solvent molecules.

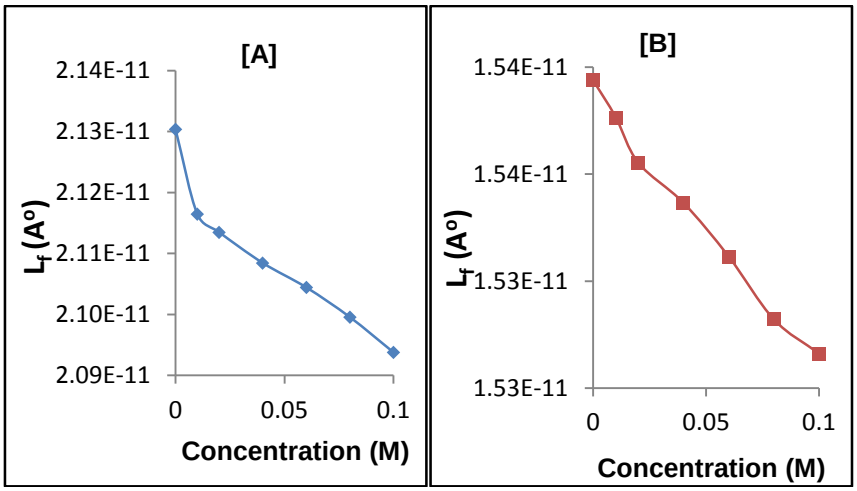

Figure 2: The variation of intermolecular free path length with concentration in [A] methanol and [B] ethyl acetate

Table 3 shows that relaxation strength (r) decreases whereas Z increases with concentration. This again suggests that PABA molecules interact strongly with concentration.
The variation of adiabatic compressibility with concentration is shown in Figure 3. It is observed that adiabatic compressibility (κ_s) decreases with concentration for both the solvents. The increase of U and Z and decrease of L_f and κ_s suggests the existence of solute-solvent interaction in the studied systems.

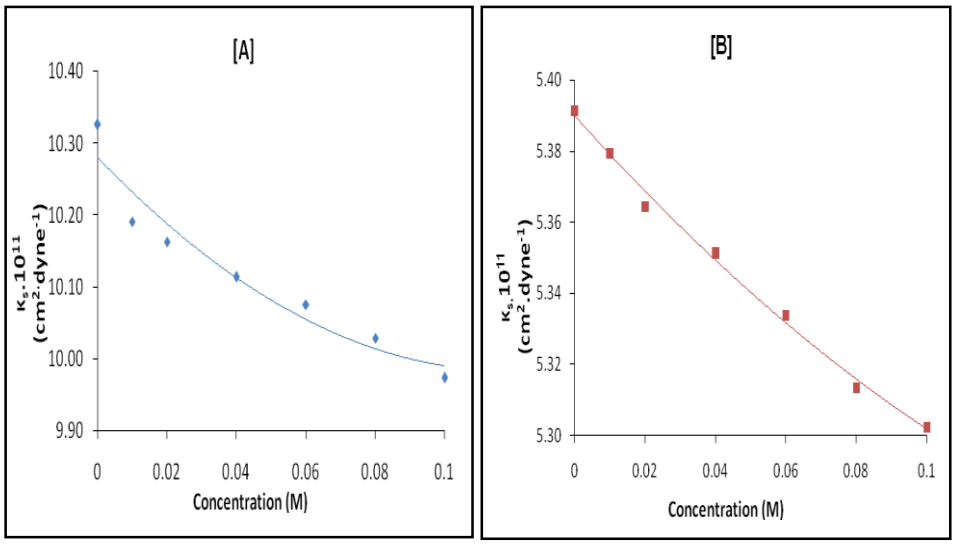

Figure 3: The variation of adiabatic compressibility (κ_s) with concentration in [A] methanol and [B]ethyl acetate.

The type of interactions in a solution can also be confirmed by the solvation number, which is a measure of structure forming or structure breaking tendency of a solute in a solution. Figure 4 shows that solvation number (S_n) increases with concentration and are positive in both the solvents. The positive S_n values suggest structure forming tendency of PABA in solution. This further confirms that there exist strong solute-solvent interactions in the studied solutions.

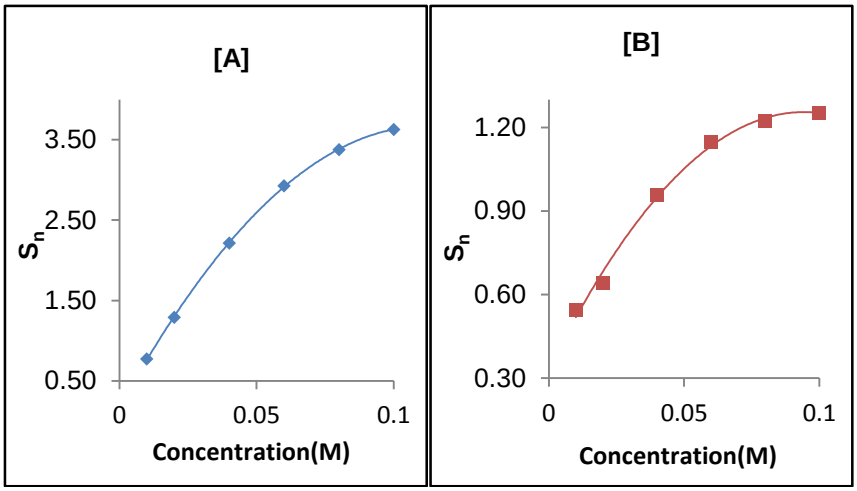

Figure 4: The variation of solvation number (S_n) with concentration in [A] methanol and [B] ethyl acetate

Thus, it is concluded that in both the solvents, solute-solvent interactions exists for p-amino benzoic acid.
***Thermal studies*:** The TGA thermo gram of p-amino benzoic acid is given in Figure 5.

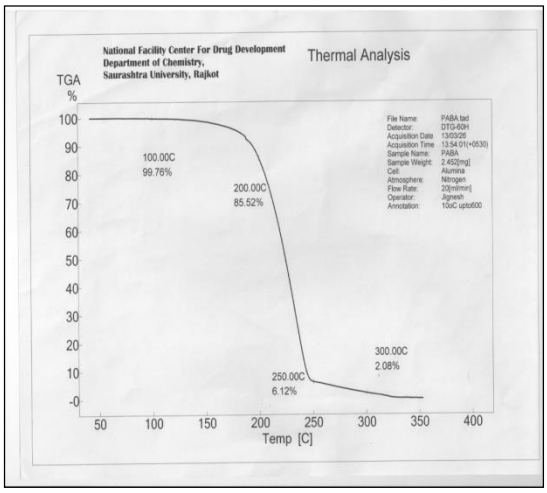

Figure 5: The Thermogram of p-amino benzoic acid

The degradation is single step process. The decomposition temperature range is found to be approximately from 200-245 ^{0}C and the maximum degradation temperature is 231.9 ^{0}C.
Further, various kinetic parameters, such as order of the degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have also been calculated from the thermogram using Freeman-Anderson equation (Anderson and Freeman, 1961):

$$\Delta \ ln \ dW/dt = n^{/} \Delta \ lnW - (E/R) \Delta \ (1/T)$$

where W is residual mass evaluated from thermogram, $n^{/}$ is order of reaction, E^* is energy of activation, T is temperature and R is gas constant.
From the slope of Freeman-Anderson plot, energy of activation (E) was evaluated whereas intercept gives the order of reaction ($n^{/}$).
The frequency factor $A^{/}$ is calculated by the following equation:

$$A^{/} = (E\beta/RT^2)\ e^{E/RT}$$

where β is heating rate. The entropy change (ΔS^*) is also evaluated using equation:

$$\Delta S^* = R \ ln \ (A^{/}h/kT)$$

where *h* is Planck's constant and *k* is Boltzmann constant.
All these evaluated kinetic parameters are reported in Table 4.

Table 4: The kinetic parameters of p-amino benzoic acid

n	E kJ.mol^{-1}	A Sec^{-1}	ΔS^o J.mol^{-1}.K^{-1}
0.479	91.454	1.356X10^{19}	123.446

The order of reaction is less than one and entropy is positive. The positive entropy indicates that the transition state is less ordered than the original compound (Mishra *et al.*, 2002).

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