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MOLECULAR INTERACTIONS IN SOLUTIONS OF SODIUM SALT OF 4-AMINO-2-HYDROXY BENZOIC ACID: AN ULTRASONIC STUDY

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ABSTRACT

Ultrasonic velocity, density, viscosity have been measured experimentally in the ternary mixtures of sodium salt of 4-Amino 2-Hydroxy Benzoic acid, water and Ethanol with various concentration at 298K,303K and 308K keeping constant frequency at 4MHz. As the acoustical parameters like adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, Rao's and Wada's constant, relative association and free volume would be more useful to predict and confirm the molecular interaction, these have been determined by using ultrasonic velocity, density and viscosity of the prepared solution. The variation of these parameters will reveal the solvent (water+ethanol) attracting nature of the salt. So an attempt is made to determine and study the variation of the above mentioned parameters in case of solutions of sodium-4-amino-2-hydroxy benzoic acid in 50% alcohol at various concentrations in the temperature range from 298K,303K and 308K keeping constant frequency at 4MHz. It has been identified that there is a strong solute–solvent interaction occurring in ternary solutions. This may be due to the greater possibility of hydrogen bonding between 4-amino-2-hydroxy benzoic acid, water and ethanol molecules.

KEYWORDS:- Ultrasonic velocity, adiabatic compressibility, relaxation time, acoustic impedance, Rao's and Wada's constant.

INTRODUCTION

The study of intermolecular interactions has inspired many researchers and extensive investigations have been carried out in aqueous solutions. Ultrasonic velocity in liquids and

liquid mixtures provide valuable information about their physic-chemical properties and the nature of molecular interactions in them.[1-3] Different ultrasonic parameters have been calculated with a view to investigate the exact nature of the molecular interactions.[4-5] The ultrasonic studies of liquid mixtures have of greater significance in under-standing intermolecular interactions between the component molecules as they can locate numerous applications in industrial and technological processes.[6]

Aminosalicylic acid was introduced to clinical use in 1944. It was the second antibiotic found to be effective in the treatment of tuberculosis, after streptomycin. PAS formed part of the standard treatment for tuberculosis prior to the introduction of rifampicin and pyrazinamide. Sodium salt of 4-amino salicylic acid is soluble in water. In the present study, various acoustical parameters of solutions of sodium-4-amino-2-hydroxy benzoic acid in 50% alcohol at various concentrations have been evaluated at different temperatures ranging from 298K,303K and 308K. Several authors.[7-13] have concentrated on the binary and ternary system of variety of organic compounds but only a few have concentrated on the concentration effect. In other words, the studies made in the direction of the molecular interactions based on the variation of the binary mixtures of one component in the mixed co-solvent of other two liquids at one or two components, that too ultrasonic studies are not made in this direction. The present work aims at an understanding of the molecular interactions of sodium 4-amino-2-hydroxy benzoic acid in the co-solvent(ethanol+water) at three concentrations at 4 MHz frequency. From an experimental measurement of velocity, density and viscosity at 298K,303K and 308K. In these three concentrations, the excess parameters/deviations have been computed and results are analysed to estimate the molecular interactions. Mostly strong interactions between the co-solvent and the solute at three concentrations of the co-solvent are indicated in these mixtures.

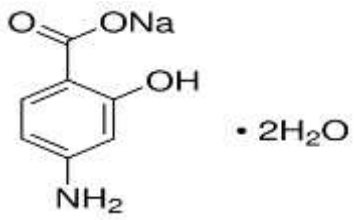
EXPERIMENTAL SECTION

MATERIALS

Sodium salt of 4-amino 2-hydroxy benzoic acid used in the present work was of analytical reagent (AR) grade. The solution was prepared by using 50% mixture of double distilled water and 99.99% pure ethanol as a solvent. Weights have been taken on digital electronic balance. (Model-CB/CA/AT-Series).

METHODS

The ultrasonic velocities have been measured by using ultrasonic Interferometer (Model-M-83, Mittal Enterprises, New Delhi) operating at 4MHz frequency with an accuracy of ±2m/s. The viscosities (η) of solution and solvent were determined using Ostwald's viscometer by calibrating with double distilled water. The densities (ρ) of the solution were measured accurately using digital densitometer (Model - DMA-35, Anton Paar). The ultrasonic velocity was measured at 4MHz frequency at 298K, 303 K. and 308K. The temperature of cell was maintained with continuous circulation of water by using thermostat.



RESULTS AND DISCUSSSION

The acoustical parameters were calculated from v, η andd_S values using standard formulae.

1) Adiabatic Compressibility $\beta = 1/v^2 \rho_S$ …(1)

2) Free Length $L_f = K\sqrt{\beta_S}$ …(2)

3) Specific acoustic impedance $Z = Vs \cdot \rho_S$ …(3)

4) Rao's Constant $R = (M_{eff}/\rho_S) \times V^{1/3}$ …(4)

5) Wada's Constant $W = (M_{eff}/\rho_S) \times \beta^{-1/7}$ …(5)

6) Apparent Molar Compressibility -

$$\Phi_K = [1000 (\beta_S\rho_0 - \beta_O\rho_S) / m \rho_S\rho_0] + (\beta_S M / \rho_S) \quad \text{…(6)}$$

7) Relative Association - $R_A = \rho_S / \rho_0[Vo / Vs]^{1/3}$ …(7)

8) Relaxation time – $\tau = 4/3 \beta \times \eta$ …(8)

9) Free Volume $V_f = M_{eff} \times v_s / k \times \eta$ ….(9)

Where k = 4.28×10^9, Temperature Independent Constant for all liquids.

10) Equivalent Conductance $-\mu = Kc[1000/N]$ ….(10)

The symbols have their usual meaning.

The experimental data relating to viscosity, density and ultrasonic velocity at 298K,303K and 308K for frequency 4MHz for the mixture are given in Table no. 1.

Table 1: Density, Velocity and Viscosity at 298, 303, 308 K (At Frequency-4MHz)

Sr.No.	Temperature (^{0}K.)	Concentration (M)	Density(ρ_S) (Kg/m^3)	Velocity (v_s) (m/s)	Viscosity(η) (Pa.S.) or Kg m^{-1} s^{-1}
1	298	0.1	910.93	9876.42	2.43E-03
2		0.01	927.9	7800.15	2.32E-03
3		0.001	916.84	7812.23	2.43E-03
4	303	0.1	909.5	13339.3	2.15E-03
5		0.01	925.32	6372.28	2.05E-03
6		0.001	916.36	8104.68	2.11E-03
7	308	0.1	908	8347.68	1.92E-03
8		0.01	923.05	7986.66	1.83E-03
9		0.001	915.6	7425.2	1.85E-03

Table 2:- Adiabatic Compressibility, Acoustic impedance and Free length at 298K, 303K, 308 K.

Sr.No.	Temperature (^{0}K.)	Concentration (M)	Adiabatic Compressibility (β_S)N^{-1}m^2	Acoustic Impedance Z (Kgm^{-2}S^{-1})	Free length L_f(m)
1	298	0.1	1.1E-11	9179145	6.53E-12
2		0.01	1.8E-11	7270518	8.26E-12
3		0.001	1.76E-11	7279431	8.25E-12
4	303	0.1	6.1E-12	12354880	4.88E-12
5		0.01	2.6E-11	5927496	1.02E-11
6		0.0 1	1.6E-11	7529248	8.02E-12
7	308	0.1	1.6E-11	7704909	7.89E-12
8		0.01	1.7E-11	7397244	8.23E-12
9		0.001	2E-11	6869051	8.86E-12

Table 3: Relative association, Apparent molar compressibility and relaxation time at 298K, 303K, 308 K. at 4MHz Frequency.

Sr.No.	Temperature (^{0}K.)	Concentration (M)	Relative Association(R_A)	Relaxation Time(τ) S	Apparent molar comp.(ϕk)
1	298	0.1	7.51E-01	3.57E-14	-5.39E-10
2		0.01	8.15E-01	5.46E-14	-4.71E-09
3		0.001	8.14E-01	5.71E-14	-4.72E-08
4	303	0.1	6.69E-01	1.74E-14	-6.6E-10
5		0.01	8.60E-01	7.25E-14	-4.42E-09
6		0.001	7.93E-01	4.62E-14	-5.5E-08
7	308	0.1	7.72E-01	3.98E-14	-6.33E-10

8		0.01	7.86E-01	4.14E-14	-6.22E-09
9		0.001	8.04E-01	4.85E-14	-5.93E-08

Table.4 Rao's Constant, Wada's Constant, Free volume and Equivalent conductance

Sr.No.	Temperature(0 K).	Concentration(M)	Rao's Constant (R)	Wada's Constant (W)	Free Volume (V_f) m^3mol^{-1}	λ=Kc*(1000/N) mhos eq.
1	298	0.1	2.16E-03	3.71E-03	8.407E-07	18470
2		0.01	2.00E-03	3.47E-03	6.351E-07	35600
3		0.001	1.98E-03	3.43E-03	5.825E-07	134000
4	303	0.1	2.39E-03	4.04E-03	0.158E-07	22100
5		0.01	1.87E-03	3.27E-03	5.602E-07	47000
6		0.001	2.00E-03	3.46E-03	7.558E-07	130000
7	308	0.1	2.08E-03	3.59E-03	9.445E-07	26000
8		0.01	1.99E-03	3.45E-03	9.101E-07	59000
9		0.001	1.94E-03	3.37E-03	8.015E-07	160000

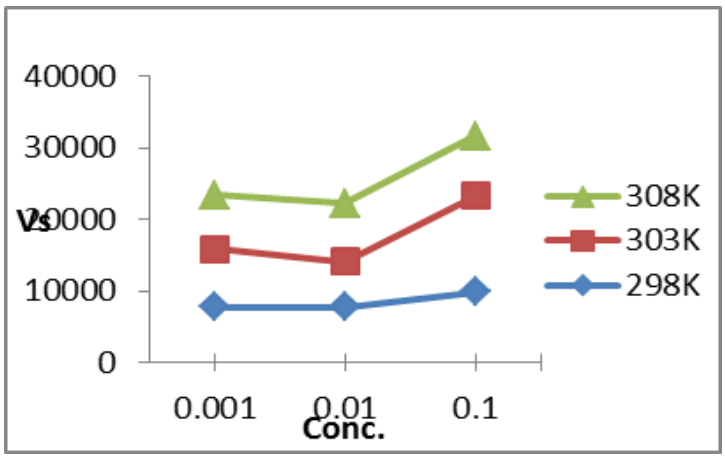


Fig.1

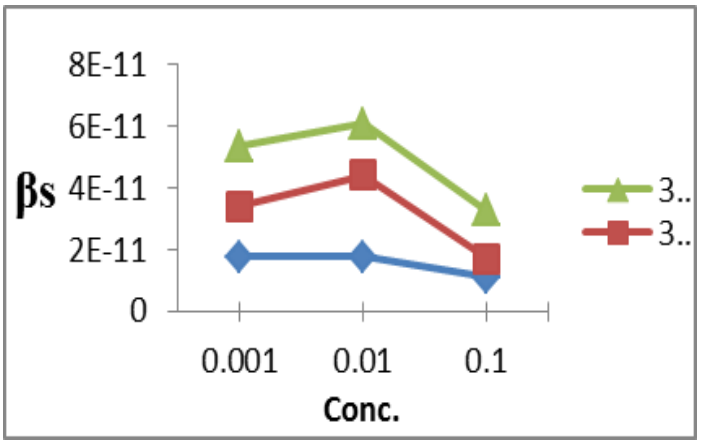
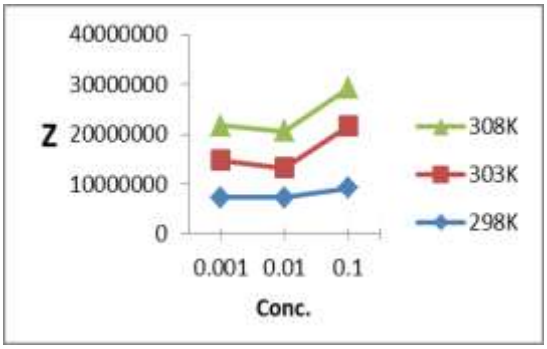


Fig.2



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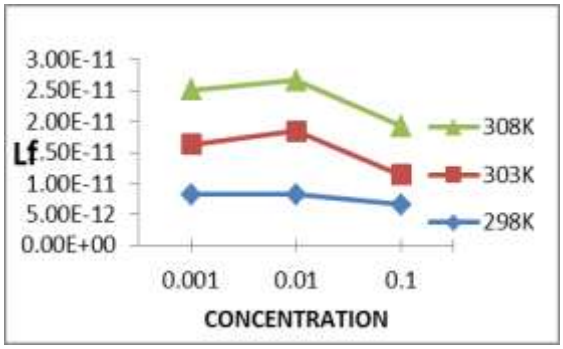

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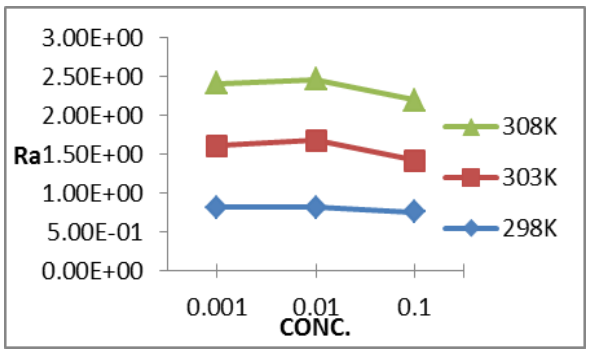

Fig.5

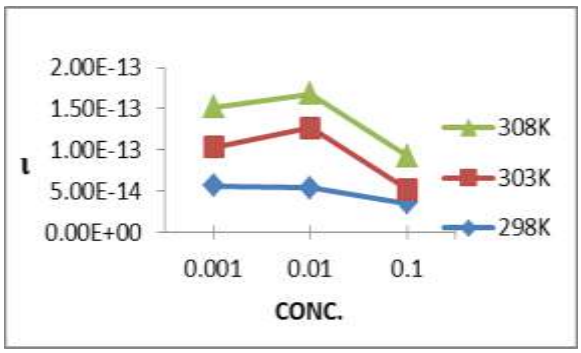

Fig.6

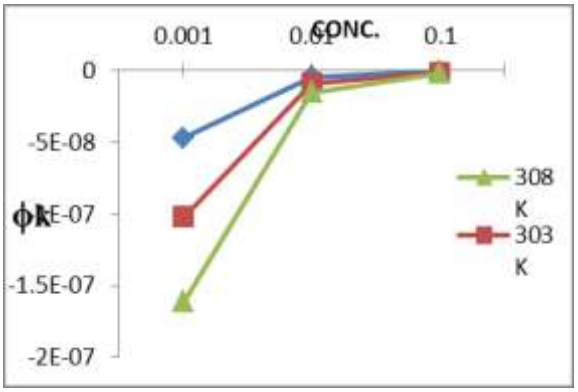

Fig.7

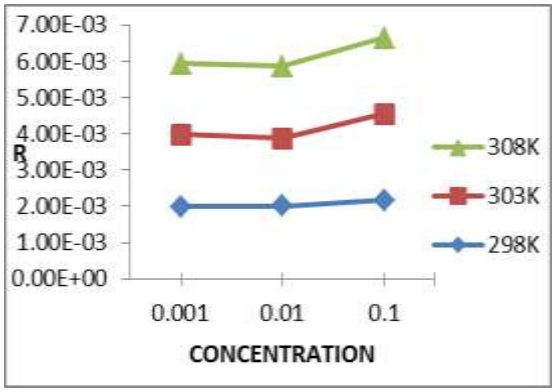

Fig.8

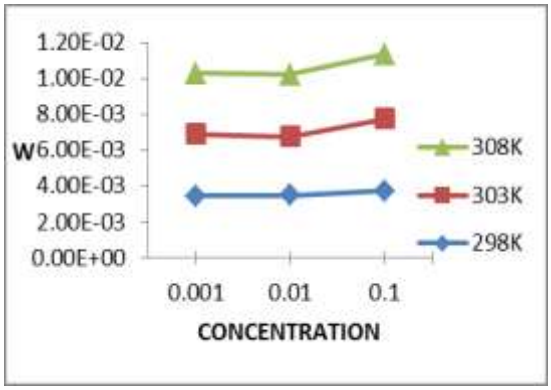

Fig.9

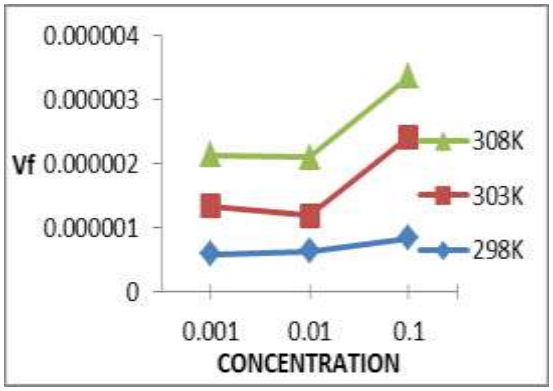

Fig.10

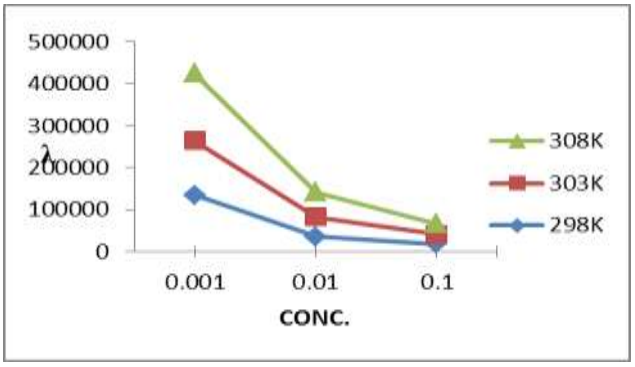

Fig.11

Acoustical parameters such as adiabaticcompressibility, acoustic impedance, intermolecular free length, acoustical relaxation time, Rao'sconstant, Wada'sconstant are represented in **Table 2-3** and represented graphically in **fig.2-11.**

A variation of ultrasonic velocity with concentration signifies interaction between solute and solvent molecules (**Table-1**). Interaction is weakest at minimum velocity. The present study indicates that ultrasonic velocity varies with molarity and shows a general increase with concentration but this increase is not regular as shown in **table 1 and fig.1.**

The adiabatic compressibility values decrease with increase in molarity of 4-amino-2-hydroxy benzoic acid in 50% alcohol(**Table-2 and Fig.2).** The decrease in adiabatic compressibility values with increase in concentration may be attributed to increase in number of compressible molecules. **Table 2** and **fig. 3**represents plots between acoustical impedance and molarity of solutions. It shows the trend of general increase of specific acoustic impedance with concentration at a given temperature. As the strength of intermolecular attraction increases the ultrasonic velocity also increases, consequently the acoustical impedance value also increases.

Free length is the distance between the surfaces of the neighboring molecules. Variation in free length with concentration and temperature is shown in **Table -2** and **fig.4**. As regard to changes in concentrations, the variation is similar to that of adiabatic compressibility. Acoustic relaxation time is found to decrease with increase in concentration. It is directly proportional to adiabatic compressibility and viscosity (**Table 3** and **fig. 6**). The variation indicates that the adiabatic compressibility plays a dominant role in the system. Variation in viscosity with concentration and temperature are also found to affect the relaxation process.

The variation of molar sound velocity or Rao'sconstant and molar compressibility or Wada's constant are found to increase linearly with concentration as shown in **Table 4** and **Fig. 8-9**. It shows the presence of solute-solvent interactions.[14-15] The calculated value of apparent molar compressibility is shown in **table 3** and represented graphically in **fig.7**. The apparent molar compressibility values are negative at all temperatures and concentration. The $\phi_k$values decrease from higher negative value to lower negative values with effect from concentration.

Alcohols are polar molecules and water is polar in nature, if polar solute is added in polar solvent, there may be dipole-dipole interaction in between solute and solvent molecules, due to polar nature of alcohol and water, they get associated through hydrogen bonding, also there is considerable evidence showing that alcohols exist as closed ring structures as dimers andtrimers. As the concentration of the solution increases, relative association value decreases as shown in **Table 3** and represented graphically in **fig. 5**. The relative association is influenced by two factors 1) the breaking up of the solvent molecules on addition of electrolyte to it and 2) the salvation of ions that are simultaneous present, Relative association is the measure of extent of association of components in the medium. It is a property of understanding the molecular interaction in liquid mixtures and solutions. As discussed relative association depends on either of breaking up of the solvent molecules on addition of solute to it or the salvation of ions that are present.[16] the result shows that as concentration increases, relative association decreases.

The values of free volume are presented for different values of temperature and concentration as shown in **Table 4** and **Fig. 10.** The increase in the values of free volume with concentration may be due to weakening of ion-solvent interactiona at higher concentration suggesting the loosening of solvent structure.[17] Also specific conductance increases with increase in concentration and equivalent conductance decreases with increase in concentration showing that there is loosening of solvent molecules due to entry of solute molecules. These results indicate that the sodium-4-amino-2-hydroxy benzoic acid has been solvated by dipole-dipole interactions with the dimer or trimer of alcohol molecule or water molecule.

CONCLUSION

In this work, the acoustic properties of sodium-4-amino-2-hydroxy benzoic acid in 50% alcohol are reported for different concentration and different temperature. The orientation in the solvent molecules around the ions is attributed to the influence of electrostatic field of

ions there by lowering the compressibility of the solutions. The increase in the ultrasonic velocity with increase in concentration may be due to the polar nature of the solute and solvent molecules which leads to the dipole attractive forces. Various acoustical parameters suggested the existence of molecular interactions in the solutions. Also it shows that there are both solute-solute and solute-solvent interactions in the system.

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