



RESEARCH ARTICLE

STUDIES IN THE ACOUSTICAL PARAMETERS OF SALICYLIC ACID SOLUTION AT DIFFERENT FREQUENCIES

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ABSTRACT

The molecular interactions in the liquids provide valuable information about the liquids and solutions. The nature of interactions between molecules in liquids and solutions can be elucidated by using the thermodynamic and acoustical parameters. The study of propagation of ultrasonic waves in liquid systems is established as a simple and significant tool in determining the nature of interactions between molecules in solution. The ultrasonic velocity, viscosity and density of salicylic acid solution in ethanol were measured at 303.15 K at different frequencies. Using the above data, acoustic parameters such as adiabatic compressibility, Rao's Constant, Wada's Constant, Specific acoustic impedance and intermolecular free length are evaluated and variations of these parameters are analyzed. Apparent molar compressibility and Relaxation time was determined by using above data. The results are interpreted in terms of solute solvent interactions occurring in the solution.

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INTRODUCTION

The propagation of ultrasonic waves in a liquid gives valuable information which is used by many researchers (Paneerselvan and Geetha) to study the properties of liquids. The Physical and Chemical behavior of solutions and their molecular interactions can be studied by measuring the density, viscosity and ultrasonic velocity (Ali *et al.*, 2004; Ramnathan *et al.*, 2004; Mehra 2005, Kopinstka *et al.*, 2005). Measurements of these parameters with respect to different frequencies at 303.15 K will help to determine the acoustic parameters such as adiabatic compressibility, intermolecular free length, specific acoustic impedance, Rao's Constant, Wada's Constant. Literature survey shows that ultrasonic study of liquid mixtures is highly useful in understanding the nature of molecular interaction (Aswale *et al.*, 2005; Aswale *et al.*, 2007; Aswale *et al.*, 2008; Aswale *et al.*, 2008). Salicylic acid and its derivatives are widely used in the medicinal field. In the present work, the ultrasonic velocity, density and viscosity of pure solvent ethanol and salicylic acid solution were measured at 1 to 6 MHz. For this investigation, 0.01 M solution of Salicylic acid in ethanol was used and all the readings were taken at 303.15 K. The experimental data is used for the calculation of various thermodynamic and acoustic parameters (Mmerki 2010) by which molecular interaction in solution can be interpreted.

Experimental work

The 0.01M solution of salicylic acid (Molecular weight 138.12) was prepared by using AR grade salicylic acid and pure ethanol. The density measurements were carried out by using specific gravity bottle and single pan sensitive digital balance (Model – CB/CA/CT-Series Contech) having an accuracy of ± 0.0001 g. The density of 0.01M salicylic acid solution was found to be 817.4Kg/m³. The

ultrasonic velocity was measured by using multifrequency ultrasonic interferometer (Model M-83, Mittal Enterprises) having an accuracy ± 2 m/s, at 1 to 6 MHz frequency. All the readings were taken at 303.15 K. The viscosity of the solution was measured by Ostwald's viscometer and was found to be 1.0850×10^{-3} Kg m⁻¹ s⁻² at 303.15 K.

Computation

By using the ultrasonic velocity, viscosity and density, following acoustic parameters were calculated.

$$1) \text{ Adiabatic Compressibility } \quad \beta = 1/v^2 d_s \quad \dots(1)$$

$$2) \text{ Intermolecular free length } \quad L_f = K \sqrt{\beta_s} \quad \dots(2)$$

$$3) \text{ Specific acoustic impedance } \quad Z = V_s \cdot d_s \quad \dots(3)$$

$$4) \text{ Rao's Constant } \quad R = (M_{\text{eff}}/d_s) \times v^{1/3} \quad \dots(4)$$

$$5) \text{ Wada's Constant } \quad W = (M_{\text{eff}}/d_s) \times \beta^{-1/7} \quad \dots(5)$$

$$6) \text{ Apparent Molar Compressibility } -\Phi_K = [1000 (\beta_s d_o - \beta_o d_s) / (m d_s d_o) + (\beta_s M / d_s)] \quad \dots(6)$$

$$7) \text{ Relative Association } - R_A = d_s / d_o [V_o / V_s]^{1/3} \quad \dots(7)$$

$$8) \text{ Relaxation time } - \quad \tau = 4/3 \beta \times \eta \quad \dots(8)$$

The symbols have their usual meaning.

The values evaluated experimentally are listed below.

RESULTS AND DISCUSSION

The measured values of ultrasonic velocity along with adiabatic compressibility (β_s) acoustic impedance (Z) and intermolecular free

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length (L_f) are calculated for the binary system and shown in the Table 1. Since, the adiabatic compressibility is inversely proportional to velocity, the trend in the adiabatic compressibility with concentration is the reverse of the trend in ultrasonic velocity with concentration in the binary system. The plot of the adiabatic compressibility versus frequency (Figure 1) shows that sudden decrease from 1 MHz to 2MHz frequency and it is almost linear from 2MHz to 6MHz suggests that this system is closed to ideal ones. In this case, interactions are weak. The decrease of adiabatic compressibility values with increase in frequency indicates the closed packing of molecules and also suggests that there is a solute-solvent interaction.

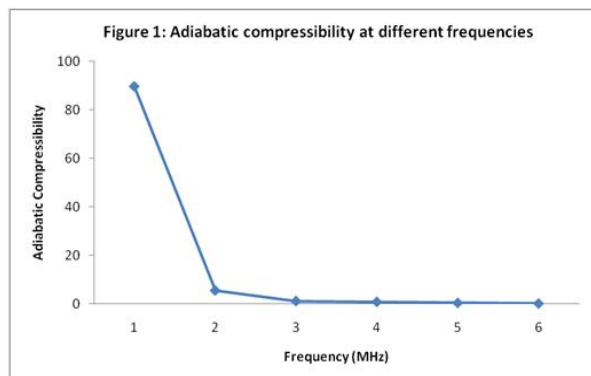


Fig 1. Adiabatic compressibility at different frequencies

Free length is the distance between the surfaces of the neighboring molecules. The intermolecular free length in binary liquid mixtures can be used to assess the attraction between the component molecules. In this case, from 1MHz to 6MHz frequency, free length decreases regularly and thus indicates that there is enhanced molecular association and from the graph (Figure 2), with increase of frequency and decrease of free length, molecules gets closely packed.

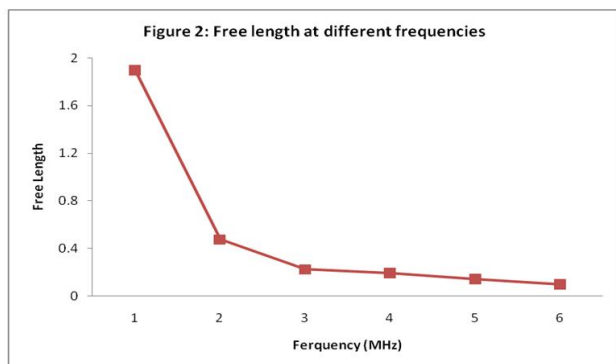


Fig.2. Free length at different frequencies

Acoustic impedance increases with frequency. It shows the trend of linear increase of specific acoustic impedance with frequency at a given temperature. As the strength of intermolecular attraction increases, the ultrasonic velocity also increases; consequently specific acoustic impedance values also increase (Figure 3). Acoustic relaxation time is found to decrease with increase in frequency at constant temperature. It is directly proportional to adiabatic compressibility. The variation indicates the adiabatic compressibility play a dominant role in the system. Rao's Constant is called as molar velocity of sound. The values of Rao's Constant and Wada's Constant increases with the frequency (Figure 5), these values are in good agreement with the relation of frequency and velocity. It shows the presence of solute-solvent interaction. The variation in the values of Relative association, Acoustic impedance, Free length, Adiabatic compressibility, Rao's Constant and Wada's Constant shows that there is interaction between the two functional groups that is between the Carboxyl (-COOH) group and hydroxyl group (-OH).

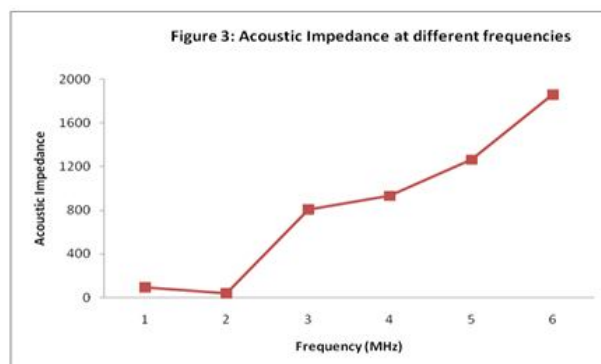


Fig. 3. Acoustic Impedance at different frequencies

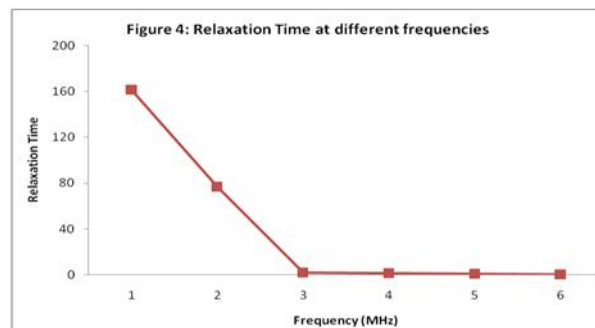


Fig.4. Relaxation Time at different frequencies

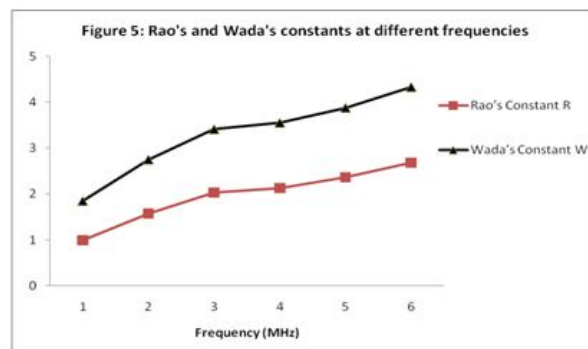


Fig.5. Rao's and Wada's constants at different frequencies

Table 1. Ultrasonic velocity, Adiabatic Compressibility, Acoustic impedance and Free length of 0.01 M salicylic acid solution at 303.15 K

Frequency MHz	Velocity m/s	Adiabatic Compressibility ($\beta_s \times 10^{11} \text{Pa}^{-1}$)	Acoustic Impedance $Z \times 10^4 (\text{Kg m}^{-2} \text{S}^{-1})$	Free length $L_f \times 10^{-2} \text{m}$
1	1169.31	89.476	95.5540	1.8994
2	4671.81	5.6053	38.1873	0.4754
3	9896.28	1.2492	808.9219	0.2244
4	11407.60	0.9401	932.4572	0.1947
5	15501.00	0.5091	1267.1008	0.1432
6	22802.40	0.2352	1863.8682	0.0974

Table 2. Relative association, apparent molar compressibility and relaxation time of 0.01 M salicylic acid solution at 303.15 K.

Frequency MHz	Relative Association (R_A)	Apparent Molar Compressibility $\Phi k \times 10^{-12}$	Relaxation Time $t \times 10^{-14}$
1	1.0688	- 6901.83	161.6756
2	1.0446	- 1503.75	76.9369
3	0.8660	- 4191.93	2.2571
4	1.0271	- 382.16	1.6986
5	1.0304	- 128.36	0.9199
6	1.0037	- 154.79	0.4251

Table 3. Rao's Constant and Wada's Constant of 0.01 M salicylic acid solution at 303.15 K

Frequency (MHz)	Rao's Constant (R)	Wada's Constant (W)
1	0.9956	1.8549
2	1.5807	2.7554
3	2.0301	3.4145
4	2.1286	3.5560
5	2.3577	3.8817
6	2.6814	4.3344

Conclusion

From the structure of the solute and the solvent, the interaction is mainly between the Carboxyl group (-COOH) of solute and hydroxyl group (-OH) of solvent. Hence the solution has more hydrogen bonds which not only strengthen the intermolecular forces resulting in decrease of Adiabatic Compressibility but also increases the velocity in that formulation. The increase in the value of acoustic impedance is an indication of strong interaction between the solute and solvent. From the above findings, it is observed that the molecular association between the solute-solvent molecules arising from intermolecular

hydrogen bonding and the variation of acoustic parameters with frequency at 303.15 K strongly supports the molecular association occurring in these systems.

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