



## Pelagia Research Library

Der Chemica Sinica, 2015, 6(7):93-99



### Ultrasonic studies of molecular interaction of gallic acid with ethanol

G. M. Jamankar and M. S. Deshpande

Anand Niketan College, Anandwan, Warora, Dist. Chandrapur, M.S.(India)

---

#### ABSTRACT

*The ultrasonic study of Gallic acid and Ethanol mixtures has been employed in understanding the nature of the molecular interactions in pure components and their mixtures. The measurement of speed of sound gives valuable information about the physical properties and strength of molecular interactions in the mixtures. The present study reports measurements of densities, viscosity and speed of sound for gallic acid and ethanol at various temperature range 298K, 303K, 308K, 313K. Most of the work on binary mixtures is channelized towards the estimation of thermodynamic parameters like adiabatic compressibility ( $\beta$ ), free length ( $L_f$ ), isothermal compressibility ( $\beta_i$ ), Gibbs free energy ( $\Delta g$ ), internal pressure ( $\pi_i$ ), free volume ( $V_f$ ). This parameter has been used to understand different kinds of association in pure components as well as in the binary mixture. Results are used to explain the nature of molecular interactions between mixing compounds.*

**Key words:** Gallic acid, adiabatic compressibility, Gibbs free energy, internal pressure

---

#### INTRODUCTION

Development in the ultrasound technology and its potential benefits has triggered interest on the application of ultrasound on a wider range of chemistry and processing [1]. The use of ultrasonic waves to understand the intermolecular interactions in tannins and their mixtures with ethanol may be of immense help.

Tannins [2] are polyphenols [3], although originally the name tannin was given to the plant extracts exhibiting astringency, without knowing their chemical structures. The characteristics distinguishing tannins from plant polyphenols of other types are basically the properties of the former: binding to proteins, basic compounds, pigments, large-molecular compounds and metallic ions, and also anti-oxidant activities, *etc.* These features of tannins lead to qualitative and quantitative analytical differences between tannins and other polyphenols. On the other hand, in the past there was a vague concept that tannins are intractable mixtures of phenolics of rather large molecules, which is inconsistent with the findings exemplified above. Polyphenols classified in to two types: type A, with constant structures, and type B of variable composition. The molecule of tannic acid may contain gallic acid up to pentagalloyl glucose. Gallic acid (3, 4,5-trihydroxybenzoic acid), found in a variety of plants, is extensively used in tanning, ink dyes, as well as in the manufacturing of paper [4]. In addition, the gallate moiety is a key component of many foods and drinks, e.g. there are two gallate moieties in the important polyphenol, (-)-*epi*-gallocatechin-3-gallate (EGCG); this and related polyphenols are responsible for the antioxidant, anticarcinogenic, and antiviral properties of some of the most widely consumed beverages in the world, such as green tea. The three aromatic phenoxyl groups of gallic acid are prone to oxidation with the formation of hydrogen peroxide, quinones, and semiquinones.

Here our attempts are to investigate nature of ultrasonic study of Gallic acid and Ethanol mixtures to understand nature of molecular interactions in pure components and their mixtures. Measurement of speed of sound gives valuable information about the physical properties and strength of molecular interactions in the mixtures [5-8]. Various physicochemical study of product formation in many industrial processes needs knowledge of thermodynamic and physical properties of systems [9]. Ultrasonic velocity of liquids provides an insight into the investigation of the intermolecular arrangement of liquids and help to understand the thermodynamic and acoustic properties of the liquid mixtures [10].

In the present study measurements of densities, viscosity and speed of sound for gallic acid and ethanol at various temperature[11] range 298k, 303k, 308k, 313k is carried out. Based on these values and employing various formulae, thermo-acoustical parameters [12] are estimated. These parameters have been used to understand different kinds of association in pure components, as well as, in the binary mixture. Results are used to explain the nature of molecular interactions between mixing compounds [13-14].

### MATERIALS AND METHODS

The liquid mixture of various concentrations in mole fraction was prepared by taking AR grade chemicals. The study was carried out for the temperatures 298K, 303K, 308K and 313K at fixed frequency 2MHz. The temperature of the liquid mixture was kept constant within an accuracy of  $\pm 0.1^{\circ}\text{C}$  by using thermostat U-10. The experimental temperature was maintained constant by circulating water with the help of thermostatic water bath. Viscosity measurements were taken using Ostwald's viscometer with an accuracy of  $\pm 0.1\text{Kg/m}^3$ . The flow of time was measured by a digital stop watch capable of registering time accurate to  $\pm 0.1\text{sec}$ . An average of three sets of flow of time for each solution was taken for the purpose of calculation of viscosity. The density of the solution was determined accurately using 10ml specific gravity bottle and electronic balance and accuracy in the density measurement is  $\pm 1 \times 10^{-5}\text{gm/cm}^3$ . An average of triple measurements was taken into account.

Ultrasonic velocity is noted by an ultrasonic multi frequency interferometer (Mittal enterprises , New Delhi) operating at a frequency range 1MHz to 10MHz with an accuracy of  $\pm 0.01\text{ m/s}$ . The source of ultrasonic waves was a quartz crystal excited by a radio frequency oscillator. The cell was filled with desired solution and water at constant temperature was circulated in the outer jacket.

The velocity of ultrasonic wave in the binary mixture have been measured using multi-frequency ultrasonic Interferometer. The densities of the mixture were measured using a 10ml specific gravity bottle. The specific gravity bottle with the experimental mixture was immersed in a temperature controlled water bath. The density was measured using the formula

$$\rho_2 = (w_2/w_1) \cdot \rho_1$$

Where,  $w_1$  = weight of distilled water,  $w_2$  = Weight of experimental liquid,  $\rho_1$  = Density of water,  $\rho_2$  = Density of experimental liquid

Viscosities of the binary mixtures were measured using an Ostwald's viscometer calibrated with double distilled water. The Ostwald's viscometer with the experimental mixture was immersed in a temperature controlled water bath. The time of flow was measured using a digital racer stop watch with an accuracy of 0.1 sec. The viscosity was determined using the relation,

$$\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$$

Where,  $\eta_1$  = Viscosity of water,  $\eta_2$  = Viscosity of mixture,  $\rho_1$  = Density of water,  $\rho_2$  = Density of mixture,  $t_1$  = Time of flow of water,  $t_2$  = Time of flow of mixture.

#### Theoretical Aspect

The following parameters are estimated for further studies.

*(i) Adiabatic Compressibility ( $\beta$ )*

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It is calculated from the speed of sound ( $U$ ) and the density ( $\rho$ ) of the medium by using the equation of Newton Laplace as,

$$\beta = 1/U^2 \cdot \rho$$

*(ii) Intermolecular free length ( $L_f$ )*

The intermolecular free length is the distance between the surfaces of the neighboring molecules. It is calculated by using the relation

$$L_f = K_T \beta / 2$$

Where  $K_T$  is the temperature dependent constant and ' $\beta$ ' is the adiabatic compressibility.

*(iii) Free Volume ( $V_f$ )*

Free volume in terms of ultrasonic velocity ( $U$ ) and the viscosity ( $\eta$ ) of liquid is

$$V_f = (M_{eff} \cdot U / K \cdot \eta)^{1/2}$$

Where ' $M_{eff}$ ' is the effective mass of the mixture, ' $K$ ' is a dimensionless constant independent of temperature and liquid. Its value is  $4.281 \times 10^9$ .

*(iv) Internal Pressure  $\pi_i$* 

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant force of attraction and force of repulsion between the molecules. It is calculated by using the relation,

$$\pi_i = bRT (K \cdot \eta / U)^{1/2} (\rho^2 / 3 / M_{eff})^{7/6}$$

Where, ' $b$ ' stands for cubic packing, which is assumed to be '2' for all liquids, ' $K$ ' is a dimensionless constant independent of temperature and nature of liquids. Its value is  $4.281 \times 10^9$ . ' $T$ ' is the absolute temperature in Kelvin, ' $M_{eff}$ ' is the effective molecular weight, ' $R$ ' is the Universal gas constant, ' $\eta$ ' is the viscosity of solution in N.S.m<sup>-2</sup>, ' $U$ ' is the ultrasonic velocity in m.s<sup>-1</sup> and ' $\rho$ ' is the density in Kg.m<sup>-3</sup> of solution.

*(v) Relaxation time ( $\tau$ )*

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. The relaxation time can be calculated from the relation,

$$\tau = 4/3 \cdot (\beta \cdot \eta)$$

Where ' $\beta$ ' is the adiabatic compressibility and ' $\eta$ ' is the viscosity of the mixture.

*(vi) Acoustic impedance ( $Z$ )*

The specific acoustic impedance is given by,

$$Z = U \cdot \rho$$

Where ' $U$ ' is the velocity and ' $\rho$ ' is the density of the mixture.

*(vii) Gibb's free energy*

The Gibb's free energy is calculated by using the relation

$$\Delta G = kT \cdot \ln(kT\tau/h)$$

Where,  $t$  is the viscous relaxation time, ' $T$ ' is the absolute temperature, ' $k$ ' is the Boltzmann's constant and ' $h$ ' is the Planck's constant.

**RESULTS AND DISCUSSION**

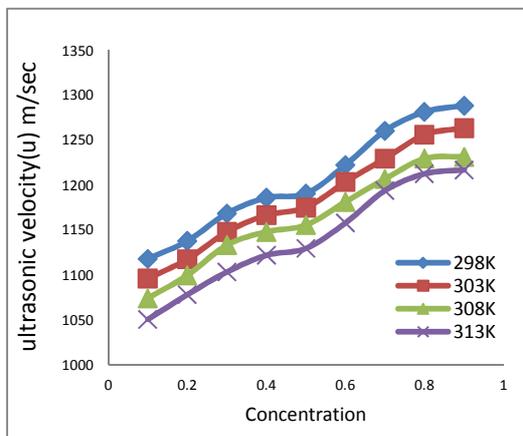


Fig1:- Ultrasonic velocity with concentration

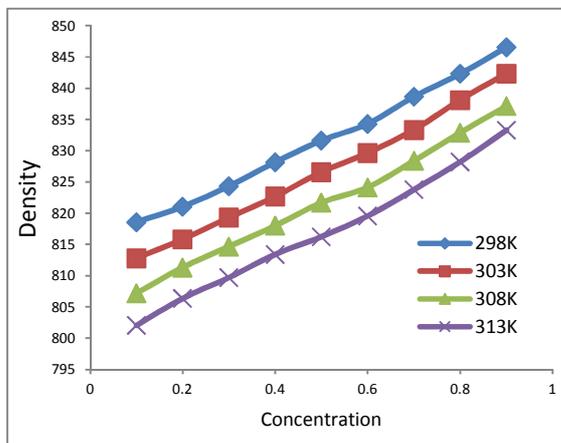


Fig2:- density with molar concentration

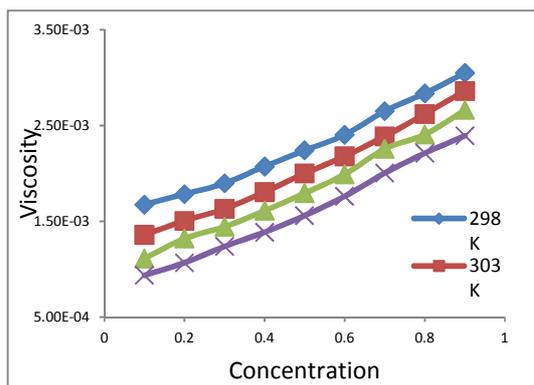


Fig3:- viscosity with concentration

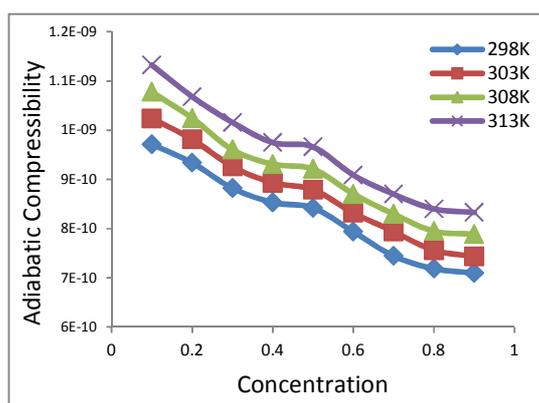


Fig 4 adiabatic compressibility with concentration

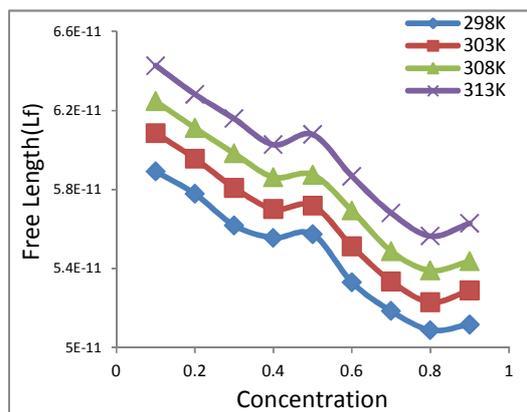


Fig5:- intermolecular free length with concentration

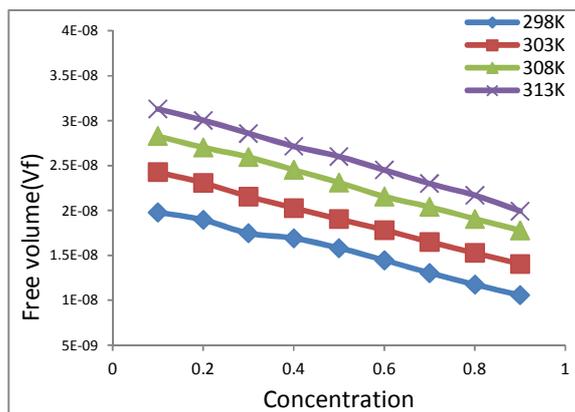


Fig 6:- free volume with concentration

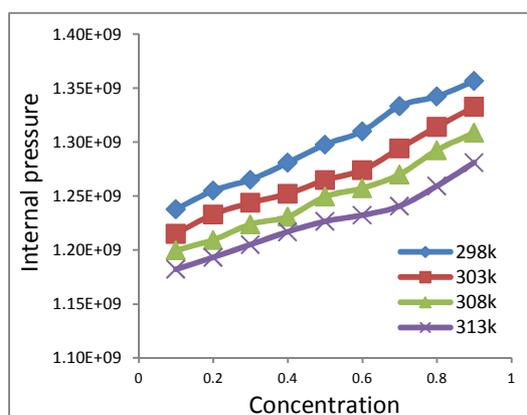


Fig7:- Internal pressure with concentration

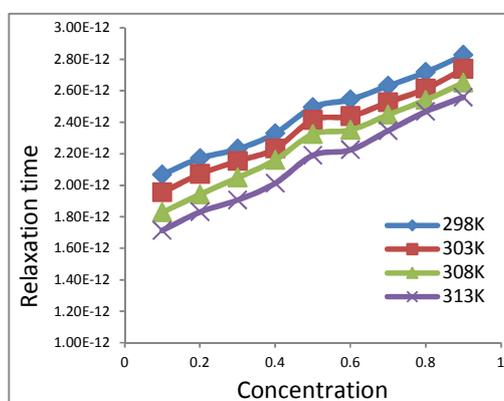


Fig8:-Relaxation time with concentration

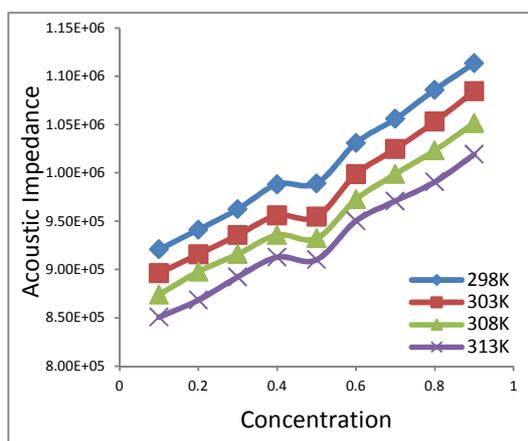


Fig 9:- acoustic impedance with concentration

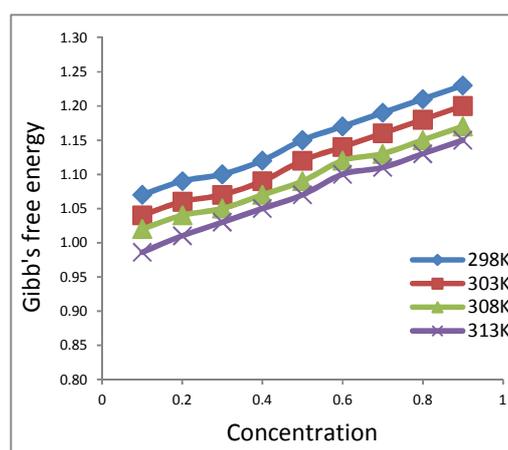


Fig 10:- Gibb's energy with concentration

Fig1 shows that velocity almost linearly increases at a given temperature with increase in concentration. Increase in ultrasonic velocity with increase in concentration is indicative of solute solvent interaction. At a given temperature velocity rises with concentration but as we increase the temperature velocity decreases. Increase in ultrasonic

velocity at higher concentrations may be due to interaction between gallic acid and ethanol but as we go to higher side of temperature scale sound velocity decreases this may happen due to weakening of intermolecular forces between the molecules.

As density increases number of particles in given region is increased, this leads to quick transfer of sound velocity and hence ultrasonic velocity increases with increase in concentration. The density increases with increase in concentration as shown in *fig 2*.

It is observed that viscosity increases with rise in concentration. This indicates that there exists a strong interaction between solute and solvent which is also supported by ultrasonic velocity. The variation of Viscosity with concentration is as shown in *fig*.

The adiabatic compressibility decreases with increase in concentration as shown in *fig4*. Adiabatic compressibility is the property of a substance capable to being reduced in volume by application of pressure; quantitatively, the reciprocal of the bulk modulus. Decrease in adiabatic compressibility might be due to aggregation of solvent molecules around solute molecules. This indicates the existence of solute-solvent interactions. The change in adiabatic compressibility in liquid mixtures indicates that there is a definite contraction on mixing and the variation is may be due to complex formation.

Variation of free length for different value of temperature and concentration is described in *Fig.5*. Since the free length  $L_f$  is proportional to the adiabatic compressibility  $\beta_{ad}$  the same trend of variation is observed.

The molecules of liquid are not closely packed and as such there is always some free space between them. This free space is known as free volume. It is observed that free volume decreases with rise in concentrations as shown in *fig.6* which shows that solute solvent molecules are coming close to each other and the space between them is decreasing with rise in concentration. This supports to the strong solute –solvent interaction in liquid solution.

Internal pressure is the fundamental property of liquid which provides an excellent basis for examining the solution phenomena and studying the various properties of the liquid state. It is a measure of change in internal energy of liquid solution as it undergoes a very small isothermal change. It is a measure of cohesive or binding forces between the solute and solvent interaction. It is found that internal pressure is increasing with increasing concentration as shown in *fig.7*. This shows that binding forces between the solute and solvent in liquid solution are becoming stronger which shows that there exists a strong molecular interaction.

It is observed that in *fig. 8*, the relaxation time increases with increase in concentration and decrease in temperature of solution. The variation of relaxation time is a cumulative effect of the density, viscosity and ultrasonic velocity.

Acoustic specific impedance increase with increase in concentration indicates that there is strong interaction between solute solvent molecules as shown in *fig 9*. The increasing value of acoustical impedance substantiates the possibility of molecular interactions between the dissimilar molecules.

From *fig.1* the increasing positive values of Gibb's function suggest that the closer approach of unlike molecules is due to hydrogen bonding.

## CONCLUSION

1. Increase in ultrasonic velocity with increase in molar concentration in this binary liquid system is due to molecular aggregation between the constituents molecules.
2. Nonlinear variation of thermo acoustics parameters with molar concentration shows the strong intermolecular interactions between the constituent molecules. Decrease in adiabatic compressibility and increase in acoustic impedance with increase in molar concentration is due to association in the constituent molecules.
3. The non linear behavior confirms the presence of solute-solvent interaction.
4. The nonlinear variation of thermo acoustic parameters with molar concentration provides useful information about nature of intermolecular forces existing in binary liquid mixtures.

**Acknowledgement**

M.S. Deshpande is grateful to University grant commission, New Delhi, for providing financial support to this work through Minor research project.

**REFERENCES**

- [1] Mason TJ, Lorimer JP. Applied sonochemistry: uses of power ultrasound in chemistry and Processing. Wiley Europe; **2002**.
- [2] Okuda, T. *Curr. Org. Chem.* **1999**, 3, 609-622.
- [3] G. Nath, Chem Sci Trans., **2012**, 1(3), 516-521 *Chemical Science Transactions* DOI:10.7598/cst**2012**.
- [4] A. Ali and A. K. Nain, Indian Academy of sciences, Vol. 58, No.4 *journal of April physics*, pp.695–701
- [5] M. K. Praharaj, Abhiram Satapathy, *Scholars Research Library, Archives of Applied Science Research*, **2012**, 4 (2):837-845
- [6] Sunanda S. Aswale, Shashikant R. Aswale, *European Journal of Applied Engineering and Scientific Research*, **2012**, 1 (2):73-79
- [7] Alka Tadmalkar, Pravina Pawar and Govind K. Bichile *J. Chem. Pharm. Res.*, **2011**, 3(3):165-168
- [8] Rice, M.E., Ritchard, N.T., Ann E. Hagerman 200.2 Food chem. **1998**, 46 1887-1892.
- [9] Krzysztof Bebek, *Molecular & quantum acoustics* vol.26 (**2005**)
- [10] P. Krishnamurthi and P. A. Thenmozhi, *Journal of Chemical and Pharmaceutical Research*, **2012**, 4(11):4671-4676
- [11] S. Thirumaran and Deepesh George, vol. 4, no. 4, june **2009**, *ARPJ Journal of Engineering and Applied Sciences*
- [12] J M Resa, C Gonzalez, J M Goenaga and M. Iglesias, *Journal of Thermal Analysis and calorimetry*, Vol.87, (**2007**), 1, 237-245
- [13] Ali A. S. M. Zahid, Md A. Alib and Jae Ryang Hahna , *Pelagia Research Library Advances in Applied Science Research*, **2015**, 6(6):65-74
- [14] Reza Maleki Baladi, Sima Moghaddaszadeh-Ahrabi and Mohammad Afrouziyeh, *European Journal of Experimental Biology*, **2014**, 4(2):148-154