Ultrasonic investigation of molecular interaction in aqueous solution of 1,4-dioxane

Vijayta Gupta, Amit Kumar Sharma and Meena Sharma

Abstract: The aim of this paper is to reveal the nature and extent of interaction in the aqueous solution of 1,4-dioxane by computing the various acoustic parameters such as adiabatic compressibility (βad), intermolecular free length (Lf), acoustical impedance (Z), relaxation time (τ), Rao's constant (RM), Wada's constant (W), free volume (Vf), absorption coefficient (α/f 2), Gibb's free energy (ΔG), relative association (RA) and available volume (Va) at 6 MHz using a multi frequency ultrasonic interferometer at temperature 308.15 K. The experimental data for ultrasonic velocity (u), viscosity (η) and density (ρ) of the solutions for various concentrations have been used to calculate these parameters. The variations of sound speed with concentration plays the key role to accomplish the changes in these parameters. The results are depicted in terms of molecular interaction between the components of the solutions.

Key words: Acoustic parameters; density; molecular interaction; sound speed; viscosity.

1. Introduction

In recent years, the studies of acoustical properties of aqueous solutions have been found to be useful in understanding the molecular interaction in solutions. The central and primary role of the molecular details of the solvent species was exposed by many researchers in order to determine the specific interactions. These interactions are accountable for macroscopic thermodynamic and other associated properties in non-electrolyte solutions. Since ultrasonic velocity is basically related to the binding forces between the constituents of the medium, so it is extremely responsive to the structure and interactions present in the liquid system[1]. Ultrasonic studies are widely employed to assess the thermodynamic properties and predict the intermolecular interactions in pure liquid[2], liquid mixtures[3-6] and ionic interactions in electrolytic solutions[7,8]. The measurement of ultrasonic velocity of sound in liquids enables determination of some useful acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions[9]. The great stimulation in the need for extensive information on acoustic and physico-chemical properties of aqueous solutions of 1,4 dioxane is due to increased use of 1,4-dioxane in various industrial processes.

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Dioxane is chiefly used as a stabilizer for 1,1,1-trichloroethane for storage and transportation in aluminium containers. Moreover, it is used in a range of applications as a solvent, e.g. in inks and adhesives. In the present work an effort has been made to study the behaviour of aqueous solution of 1,4-dioxane with regard to adiabatic compressibility, intermolecular free length, acoustical impedance, relaxation time, Rao's constant, Wada's constant, free volume, absorption coefficient, Gibb's free energy, relative association and available volume from viscosity, density and ultrasonic measurements at 308.15 K.

2. Materials and Methods

In the present study, 1,4-dioxane used was of analytical grade (AR) and was redistilled before use. In all systems, the various concentrations of the aqueous solutions were prepared in terms of % (w/w). Water used was prepared by distilling ordinary water thrice over alkaline KMnO4 in all glass apparatus. The specific conductance of water so obtained was 1.3 x 10-4 Ωcm-1. Density was determined with using 10 ml specific gravity bottle. The density was determined with an error of one in 104 at a fixed temperature. Ultrasonic velocity was measured at frequency of 6MHz by using a multi-frequency ultrasonic interferometer provided by Mittal enterprises, New Delhi as shown in figure 1. The temperature of the solution was maintained constant with a precision of + 0.1oC by circulating water from thermostatically regulated bath around the sample holder with double wall. The viscosity of the aqueous solutions was measured using an Ostwald's viscometer calibrated with doubly distilled water.

Figure 1. Ultrasonic interferometer

2.1 Theory and calculations

Using the measured density (ρ), viscosity (η) and ultrasonic velocity (u) values, the derived parameters have been calculated employing the following relations:

Adiabatic compressibility was calculated by using the equation,

$$\beta_{ad} = \frac{1}{u^2 \rho} \quad (kg^{-1}ms^{-2}) \qquad \ldots\ldots (1)$$

Where, u = velocity & ρ = density

Intermolecular free length is determined using the following formula given by Jacobson,

$$L_f = K_T \beta_{ad}^{1/2} \quad (m) \qquad \ldots\ldots (2)$$

Acoustic impedance is determined from equation,

$$Z = u \times \rho \quad (kg\, m^{-2}s^{-1}) \qquad \ldots\ldots (3)$$

The relaxation time (τ) can be calculated from the relation,

$$\tau = (\tfrac{4}{3})\beta\eta \quad (s) \qquad \ldots\ldots (4)$$

Rao's constant is calculated by using following equation,

$$R_M = \left(\frac{M_{eff}}{\rho}\right) u^{1/3} \quad (m^{10}/3s^{-1}/3mol^{-1}) \qquad \ldots\ldots (5)$$

Wada's constant is calculated by following equation,

$$W = \left(\frac{M_{eff}}{\rho}\right) \beta_{ad}^{-1/7} \quad (m^3/mole(N/m^2)1/7) \ldots\ldots (6)$$

Free volume is calculated by following equation,

$$V_f = \left(\frac{M_{eff}\, u}{K\eta}\right)^{3/2} \quad (m^3) \qquad \ldots\ldots (7)$$

where Meff is the effective molecular weight, which is expressed as Meff = Σ M=mixi where, x and m are the mole fraction and molecular weight of the individual component in the mixture respectively. K is the temperature independent constant and its value is 4.28 x 109.

Absorption coefficient can be calculated using the relation,

$$\left(\frac{\alpha}{f^2}\right) = \frac{4\pi^2\tau}{2u} \quad (s^2m^{-1}) \qquad \ldots\ldots (8)$$

Gibbs free energy is calculated from acoustic relaxation time (τ) as follows,

$$\Delta G = kT \ln\left(kT\tau/h\right) \, Jmol^{-1}) \qquad \ldots\ldots (9)$$

Relative association is a function of ultrasonic velocity and is calculated by the equation,

$$R_A = \frac{\rho}{\rho_0}\left(\frac{u_0}{u}\right)^{1/3} \qquad \ldots\ldots (10)$$

The available volume is a direct measure of compactness in the liquid and the strength of attraction between the molecules of a liquid or a liquid mixture. It can be calculated from Schaaf's relation,

$$V_a = V_m\left(1 - \frac{u}{u_\infty}\right) \, (m^3) \qquad \ldots\ldots (11)$$

4. Results and discussion

Velocities, densities, ultrasonic velocities and acoustical parameters for different concentration of 1,4-dioxane at 308.15K are given in Table 1, 2 & 3 and the variation in these acoustical properties with dioxane are shown in Figure (2-5). According to the model proposed for sound propagation by Eyring and Kincaid[10], ultrasonic velocity should increase, if the inter molecular free length decreases and vice versa. This fact was noticed in the present study. The ultrasonic velocity (u) data summarized in table 1 shows that velocity increases with increase in concentration of 1,4-dioxane. In fact, the molecular association increases ultrasonic velocity (u) and acoustic impedance (Z), decreases intermolecular free length (L_f) and adiabatic compressibility (β_{ad}). Same trend was noticed by earlier workers in their liquid mixtures[11-13]. Acoustic impedance (Z) of a material is the opposition exerted by the medium to displacement of the medium's particles by the sound energy. The behaviour of acoustic impedance becomes accountable for the transmission of ultrasonic waves.

Table 1. Experimental parameters (ρ, η and u) for both the systems at 308.15 K.

Concentration (c)	$\rho \times 10^3$ /kgm^{-3}	$\eta \times 10^{-3}$ /kgm^{-1}s^{-1}	$u \times 10^3$ /ms^{-1}
5%	0.9972	0.7737	1.5348
10%	1.0016	0.8425	1.5432
15%	1.0071	0.9212	1.5612
20%	1.0153	1.0308	1.5661
25%	1.0193	1.1407	1.5720

The increasing trends of Rao's constant or molar sound velocity and Wada's constant or molar compressibility with concentration suggest the availability of more number of components in a given region thus leads to a close packing of the medium and thereby increase the interactions. The values of Wada's constant increase with increasing concentration indicate that there must be tight packing of the medium and hence interaction is increasing.

Thus there may be solute-solvent interaction occurring. A decrease in free volume with increase in concentration is notice din the present system. The decrease in free volume shows that the strength of interaction increases steadily with the increase in 1,4-dioxane concentration. The values of absorption coefficient, Gibb's free energy and relative association listed in the table show increasing trend with concentration whereas the values of available volume decreases with increase in concentration of 1,4-dioxane. The increasing value of Gibb's free energy with concentration shows appreciable interaction between solute and solvent molecules. The absorption coefficient trend and available volume trend confirms the earlier conclusions. Relative association evaluate the extent of association of the component in the mixture. The value of relative association increases with increase in concentration signifying strong solute-solvent interaction.

Table 2. Derived parameters (β_{ad}, L_f, Z, τ and R_M) for both the systems at 308.15 K.

| Concentration (c)	$\beta_{ad} \times 10^{-10}/N^{-1}m^2$	$L_f \times 10^{-11}/m$	$Z \times 10^6/Kgm^{-2}s^{-1}$	$\tau \times 10^{-12}/s$	$R_M \times 10^{-3}/m^{10/3}s^{-1/3}mol^{-1}$
5%	4.2571	4.3226	1.5305	0.4392	0.2168
10%	4.1924	4.2896	1.5457	0.4709	0.2256
15%	4.0739	4.2285	1.5723	0.5004	0.2354
20%	4.0163	4.1985	1.5900	0.5144	0.2448
25%	3.9700	4.1742	1.6023	0.5306	0.2563

Table 3. Derived parameters (W, V_f, α/f^2, ΔG, R_A, V_a) of the two systems at 308.15 K.

| Concentration (c)	$W \times 10^{-3}/m^3/$ mole $(N/m^2)^{1/7}$	$V_f \times 10^{-8}/m^3mol^{-1}$	$\alpha/f^2 \times 10^{-15}/s^2m^{-1}$	$\Delta G \times 10^{-21}/Jmol^{-1}$	(R_A)	$V_a \times 10^{-7}/m^3$
5%	0.4113	2.5610	5.6429	4.4075	0.9956	7.6603
10%	0.4268	2.4211	6.0172	4.7039	0.9982	6.9311
15%	0.4454	2.3024	6.3204	4.9623	0.9998	4.9214
20%	0.4637	2.0410	6.4774	5.0797	1.0069	4.4801
25%	0.4856	1.9458	6.6558	5.2116	1.0096	3.8575
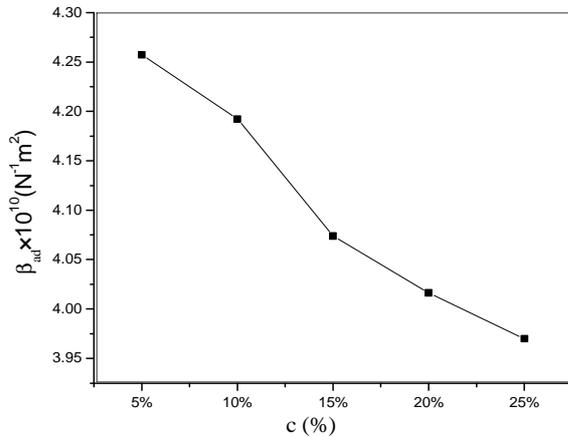
Figure 2: A plot of adiabatic compressibility versus concentration of aqueous solution of 1, 4-dioxane at 308.15K.
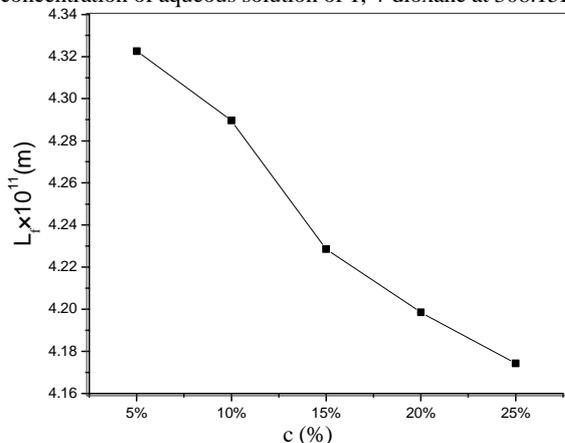
Figure 3. A plot of intermolecular free length versus concentration of aqueous solution of 1,4-dioxane at 308.15K.

From figure 2 & 3, it is apparent that adiabatic compressibility and intermolecular free length decreases with increase in concentration of 1, 4-dioxane respectively. In the figures 4 and 5 are presented the values for the free volume and Gibb's free energy for aqueous solutions of 1,4-dioxane versus concentration respectively. Free volume decreases whereas Gibb's free energy increases with increase in concentration of 1,4-dioxane.
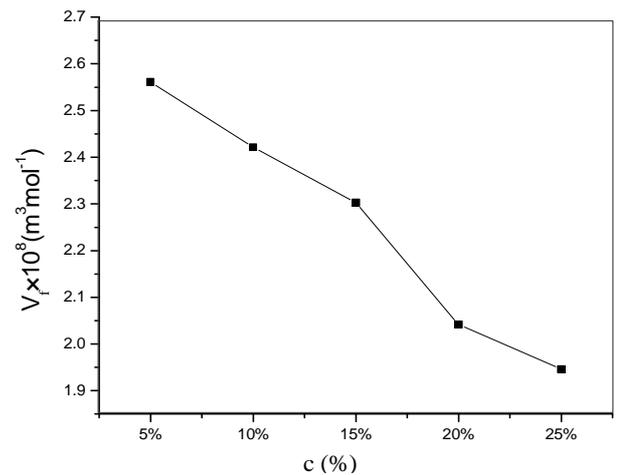

Figure 4. A plot of free volume versus concentration of aqueous solution of 1,4-dioxane at 308.15K.

Conclusion

The results of the present study signify that the ultrasonic velocity and other derived acoustic

parameters depend on composition of the solution, which is indicative of the presence of molecular interaction. The computed acoustical parameters and their values point to the presence of specific molecular interaction in the mixtures. Solute-solvent interactions are more favorable than other interactions.
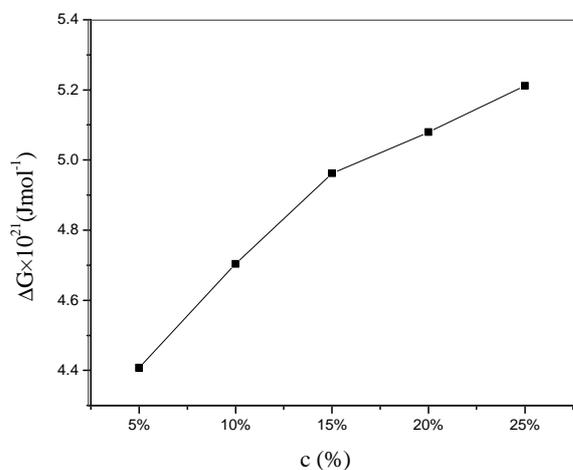
Figure 5. A plot of Gibb's free energy versus concentration of aqueous solution of 1,4-dioxane at 308.15K.

References

1. Arul, G.; Palaniappan, L.; *Indian J. Pure Appl. Phys.* 2001, *39*, 561-564.
2. Nithiyanantham, S.; Palaniappan, L.; *Acta Ciencia Indica* 2005, *36*, 533-538.
3. Palaniappan, L.; Karthikeyan, V.; *Indian J. Phys.* 2005, *79*, 155. Nithiyanantham, S.; Palaniappan, L.; *Acta Ciencia Indica* 2006, *37*, 382-392.
4. Nithya, R.; Mullainathan, S.; Nithiyanantham, S.; Rajasekaran, R.; *E. J. Chemistry* 2009, *6*, 138.
5. Nithiyanantham, S.; Palaniappan, L.; *Metals Materials and Processes* 2008, *20*, 203-356.
6. Satya Narayanamurthy, M.; *Curr. Sci.* 1964, *33*, 364.
7. Soitkar, V. S.; Jajoo, S. N.; *Acoust. Lett.* 1984, *7*, 1991.
8. Nath, G.; *Chem. Sci. Trans.* 2012, *1*, 516-521.
9. Eyring, H.; Kincaid, J. F.; *J. Chem. Phys.(USA)* 1938, *6*, 620-629.
10. Pandey, J. D.; Sanguri, V.; Yadav, M. K.; Singh, A.; *Indian J. Chem.* 2008, *74A*, 1020-1025.
11. Kumara Sastry, S. V.; Babu, S. H. A.; Tiong, S.; Sastry, S. S.; *J. Chem. Pharm. Res.* 2012, *4*, 2122-2125.
12. Shinde, B. R.; Suresh; Jadhav, S.; Sangita; Shinde, U.; Shengule, D. R.; Jadhav, K. M.; *J. Chem. Pharm. Res.* 2011, *3*, 432-438.