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Ultrasonic studies of molecular interactions in 1,4-dioxane+water mixture at different concentrations

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ABSTRACT

The densities, viscosities, and ultrasonic speeds of 1,4-dioxane + water mixtures have been measured at three different concentrations (0.568M, 1.136M, 1.705M) and at a constant temperature 308.15 K. The results are discussed in terms of different theories of propagation of ultrasonic waves. From the velocity, density and viscosity data values, various acoustical parameters namely, adiabatic compressibility(β_{ad})*, intermolecular free length*(L_f)*, free volume*(V_f)*, Rao's constant(R), Wada's constant(W), relaxation time*(τ)*, specific acoustic impedence(Z), classical sound absorption*$(\alpha/f^2)_{class.}$*, internal pressure*(π_i)*, molar cohesive energy(MCE), relative association*(R_A)*, Gibb's free energy*(ΔG)*, solvation number*(S_n) *have been calculated. All these parameters have been discussed separately to throw light on the solute–solvent and solute–solute interactions. The viscosity data have been analyzed in terms of solute–solvent and solute–solute interactions. The compressibilities obtained from the data supplemented with their ultrasonic speeds indicate the electrostriction of the solvent molecules around the ions.*

Keywords: Solute-solvent interactions, free volume, relaxation time, classical sound absorption, Gibb's free energy.

INTRODUCTION

Studies involving density and viscosity measurements are important for elucidation of ion-solvent, ion-ion and solvent-solvent interactions in solutions. The study of intermolecular interaction plays an important role in the development of molecular sciences. The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been studied by the ultrasonic method [1-2]. For interpreting solute-solvent, ion-solvent interaction in aqueous and non-aqueous medium, ultrasonic velocity measurements have been proved very helpful [3-4]. These interactions provide a better understanding of the nature of the solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent. In the present work, an attempt has been made to provide an interpretation of solute–solvent and solute–solute interactions prevailing in the studied aqueous solutions. Several workers have reported volumetric, viscometric and ultrasonic studies of this compound in aqueous solutions [5–8], but such studies in pure 1,4-dioxane and its aqueous mixtures are still scarce. Because of its use as a polymerization catalyst and the unique dipole-dipole interactions of its oxygen centres with surrounding water molecules, the present study appears relevant.

MATERIALS AND METHODS

1,4-dioxane (Merck, India) was kept several days over potassium hydroxide (KOH), refluxed for 24 h, and distilled over lithium aluminium hydride ($LiAlH_4$) as described earlier [1]. Deionised doubly distilled water was used. The densities (ρ) were measured using specific gravity bottle. The desired temperature 308.15 K was maintained by means of a mercury-in-glass thermo regulator. The viscosity measurements have been carried out using a viscometer. Sound speeds were determined using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 3 MHz which was calibrated with water. A number of acoustical parameters have been computed from ultrasonic velocity, density and viscosity values using standard equations [9-10] which are summarized below.

The adiabatic compressibility (β_{ad}) has been estimated from the relation,

$$\beta_{ad} = (\rho C_u)^{-1} \qquad (1)$$

where C_u is the ultrasonic velocity & ρ is the density of the liquid under consideration measured as described elsewhere [5].

The intermolecular path length (L_f) of the liquid was determined by using the relation,

$$L_f = K_T \sqrt{\beta_{ad}} \qquad (2)$$

Where K_T is the temperature dependent constant called Jacobson constant and is equal to 2.095×10^{-6}

Free volume(V_f) has been estimated by using the relation,

$$V_f = \left[\frac{M_{eff}\times C_u}{K\times\eta}\right]^{3/2} \qquad (3)$$

Where M_{eff} is the effective molecular weight, $K = 4.28\times10^9$ and η is the viscosity of the solution under consideration.

Molar sound speed or Rao's constant(R) has been calculated using relation,

$$R = C_u^{1/3}\times V \qquad (4)$$

where V is molar volume and is calculated using relation, $V = M_{eff}/\rho$

Molar compressibility or Wada's constant(W) has been calculated using the relation,

$$W = \beta_{ad}^{-1/7}\times V \qquad (5)$$

Shear relaxation time(τ) has been calculated using the relation,

$$\tau = \frac{4}{3\beta_{ad\times\eta}} \qquad (6)$$

Specific acoustic impedance(Z) has been calculated using the relation,

$$Z = C_u\times\rho \qquad (7)$$

Classical sound absorption $(\alpha/f^2)_{\text{class}}$ can be estimated from the relation,

$$(\alpha/f^2)_{\text{class}} = \frac{8\pi^2\eta}{3\rho C_u^3} \qquad (8)$$

Internal pressure (π_i) was estimated by using the relation,

$$\pi_i = bRT\left(\frac{K\eta}{C_u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \qquad (9)$$

where b is cubic packing which is assumed to be 2 for all liquids.

Molar cohesive energy(MCE) has been estimated using the relation,

$$\text{MCE} = \pi_i\times V \qquad (10)$$

Relative association (R_A) from the relation,

$$R_A = \left(\frac{\rho}{\rho_o}\right)\left(\frac{C_{u_o}}{C_u}\right)^{1/3} \qquad (11)$$

Where C_{u_o} is the ultrasonic velocity of the solvent and ρ_o is the density of solvent.

Gibb's free energy(ΔG) has been calculated from specific relaxation time (τ) following Eyring rate process theory,

$$\Delta G = RT\ln\left(\frac{kT\tau}{h}\right) \qquad (12)$$

where $k = 1.23\times10^{-23}$, $h = 6.626\times10^{-34}$, R is the gas constant and T is the absolute temperature.

Solvation number(S_n) has been calculated using the relation,

$$S_n=\frac{n_s}{n_i}\,(1-\frac{\beta}{\beta_o}) \qquad (13)$$

where n_s is the number of moles of solvent and n_i is the number of moles of solute in mol kg^{-1}, β is the adiabatic compressibility of solution at a particular temperature and β_o is the adiabatic compressibility of solvent at a particular temperature.

RESULTS AND DISCUSSION

The object of these studies is to identify the molecular interaction between a heterocyclic organic compound and solvent. The present study was taken under acoustical behaviour of aqueous solutions of 1,4-dioxane at several concentrations.

The necessary data of observed and calculated acoustic parameters at three different concentrations(0.568M, 1.136M, 1.705M) and at a constant temperature 308.15K has been summarised in Tables 1 & 2 and some of the important parameters have been plotted against different concentrations of 1,4-dioxane as shown in figures 1-4.

Table 1. Ultrasonic velocity(C_u), density(ρ), viscosity(η), adiabatic compressibility(β_{ad}), intermolecular free length(L_f), free volume(V_f), Rao's constant(R) and Wada's constant(W) of aqueous solutions of 1,4-dioxane at different concentrations and at a constant temperature 308.15K.

Concentration(c)	C_u×10^3 (ms^{-1})	ρ×10^3 (kgm^{-3})	η×10^{-3} (kgm^{-1}s^{-1})	β_{ad} × 10^{-7} (N^{-1}m^2)	L_f×10^{-13} (m)	V_f×10^{10} (m^{3}mol^{-1})	R×10^{-4} (m$^{10/3}$s$^{1/3}$mol^{-1})	W×10^{-4} (m^{5}mol^{-1}N^{-1})
0.568M	1.535	0.9972	0.7737	4.2559	4.3219	2.5665	2.1189	1.5335
1.136M	1.543	1.0016	0.8425	4.1935	4.2901	2.4178	2.1999	1.5930
1.705M	1.561	1.0047	0.9190	4.0847	4.2341	2.3121	2.3035	1.6679

Table 2 Shear relaxation time(τ), specific acoustic impedance(Z), classical sound absorption($(\alpha/f^2)_{class.}$), internal pressure(π_i), molar cohesive energy(MCE), relative association(R_A), Gibb's free energy(ΔG), and solvation number(S_n) of aqueous solutions of 1,4-dioxane at different concentrations and at a constant temperature 308.15K.

Concentration(c)	τ×10^{10} (s)	Z×10^6 (kgm^{-2}s^{-1})	$(\alpha/f^2)_{class}$×10^{-15} (s^{2}m^{-1})	π_i×10^{12} (Nm^{-2})	MCE×10^{-8} (KJ mol^{-1})	R_A	ΔG × 10^{-19} (J mol^{-1})	S_n
0.568M	0.4049	1.5307	5.5858	7.9424	1.4948	0.9978	1.9512	3.6517
1.136M	0.3774	1.5455	6.0201	7.9529	1.5516	0.9868	1.9486	2.3504
1.705M	0.3552	1.5683	6.3226	7.8775	1.6031	0.9820	1.9462	2.1588

As the investigated systems are characterized by hydrogen bonds, the solute–solvent and solute–solute interactions can be interpreted in terms of structural changes, which arise due to hydrogen bond interactions present between various components of the solvent and solution systems. The ultrasonic velocity(C_u) is found to increase with the increase in solute concentration. This increase indicates the maximum association among the molecules of solution. The maximum association is due to the hydrogen bonding between the solute and solvent molecules. The density(ρ) increases with increasing concentration which may be due to the cohesive forces and thus molecular association is responsible for the observed values. Viscosity(η) is an important parameter in understanding the structure as well as molecular interactions occurring in these solutions. From the data, it is observed that the values of η increases with increase in solute concentration in all the systems and this trend indicates the existence of molecular interactions occurring in these systems. Adiabatic compressibility(β_{ad}) decreases with increase in concentration which confirms the presence of solute-solvent interactions through dipole-dipole interactions of the oxygen centres of 1,4-dioxane with surrounding water molecules. Intermolecular free length(L_f) decreases with increase in solute concentration suggesting that there is a significant interaction between solute and solvent molecules and thereby suggests a structure promoting behaviour on addition of solute. Increase in free length results decrease in ultrasonic velocity on the basis of sound propagation in the liquid [11-12]. These results showed that there is weak solute-solvent interaction. The decrease in free volume(V_f) with rise in concentration also confirms the ion-solvent interactions. The increasing trends of R and W with increasing solute 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 relaxation time(τ) should increase linearly with increase in 1,4-dioxane concentrations because of the structure forming nature of the solute in water and reinforcement of hydrogen bonds in water which leads to the increase in shear relaxation time but in the present study, a reverse trend is observed because the temperature is slightly higher and at higher temperature the hydrogen bonds become weak due to the thermal vibrations and structure breaking effect predominates over the formation through hydrogen bonding. As a result, τ value decreases in aqueous 1,4-dioxane solutions. The product of $C_u$and ρ is known as specific acoustic impedence(Z). This factor is governed by the inertial and elastic properties of the medium. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density of the liquid shows a periodic variation with distance from the source along the direction of propagation. Specific acoustic impedence increases with increasing concentration of solute which indicates that molecular interactions are associative in nature. The classical sound absorption $(\alpha/f^2)_{\mathrm{class}}$ increase gradually with increasing 1,4-dioxane concentrations because of the stronger interactions between solute and solvent medium through H-bonding. Internal pressure(π_i) in a liquid system is a measure of intermolecular cohesive forces. The values of internal pressure can be used to study the nature of molecular interactions in liquids. It is observed from the data that the increase in internal pressure with solute concentration confirms the formation of intermolecular hydrogen bonding between 1,4-dioxane and water molecules and the structure enhancement trend in aqueous 1,4-dioxane solutions at various concentrations. The increase in internal pressure with increase in 1,4-dioxane concentration confirms the presence of solute–solvent interactions through dipole–dipole interactions of the oxygen centres of 1,4-dioxane with the surrounding water molecules. But at higher temperature with increasing concentration, the hydrogen bonds break up due to thermal vibrations in solvent and also the thermal vibrations between solute and solvent molecules. As a result, the weakened intermolecular forces lead to a decrease in internal pressure. It is pertinent to mention here that increase in π_i and decrease in V_f with increasing concentration of 1,4-dioxane suggests ordered arrangement in the system due to decrease in entropy. Molar cohesive energy(MCE) increases with increasing solute concentration which indicates the strengthening of cohesive forces perhaps due to making up the structure of solvent. The data suggests that the relative association(R_A) decreases with increasing solute concentration. This decrease indicates the weakening of molecular association between the solute and solvent with the addition of solutes. The Gibb's free energy(ΔG) reveals closer packing of the molecules due to the H-bonding of unlike molecules in the solutions. The Gibb's free energy decreases with concentration rise suggesting that less time is required for the cooperative process or the rearrangement of molecules in the solution decreases the energy that leads to dissociation. The hydration number or solvation number(S_n) is the number of water molecules rigidly bound to the ions. The decreasing values of $S_n$reveal that there are significant interactions between solute and solvent molecules due to which structural arrangement in the surrounding is affected. It also suggests that the hydration sphere of solute-solvent interaction is not more intensive than solvent-solvent interactions.

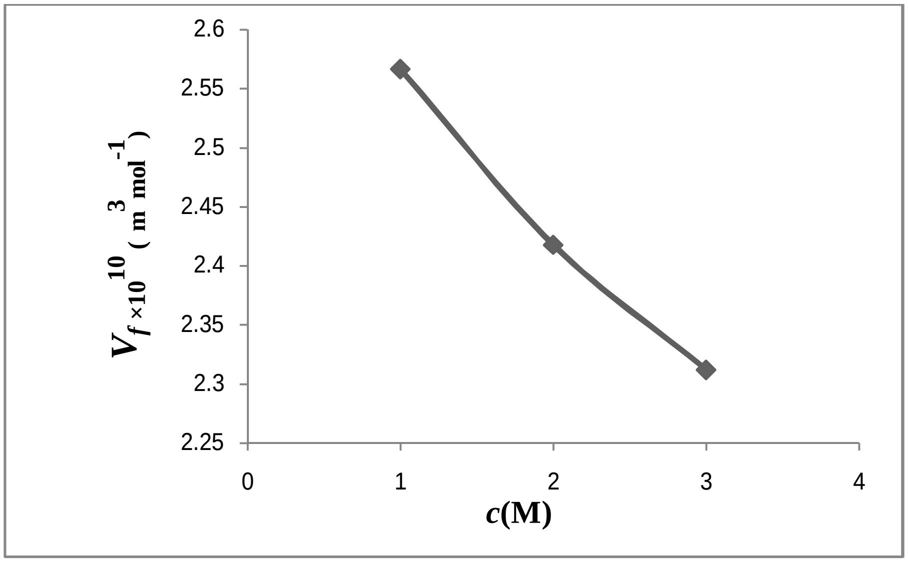
2.6
2.55
2.5
2.45
2.4
2.35
2.3
2.25
0
1
2
3
4
c(M)
$V_f \times 10^{10}$ (m^3 mol^{-1})

Fig. 1

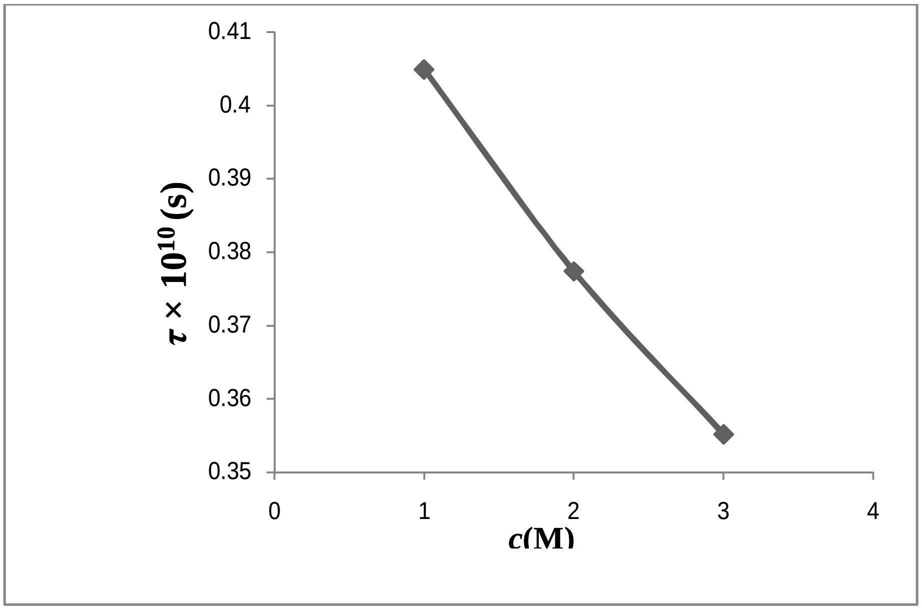
0.41
0.4
0.39
0.38
0.37
0.36
0.35
0
1
2
3
4
c(M)
$\tau \times 10^{10}$ (s)

Fig. 2

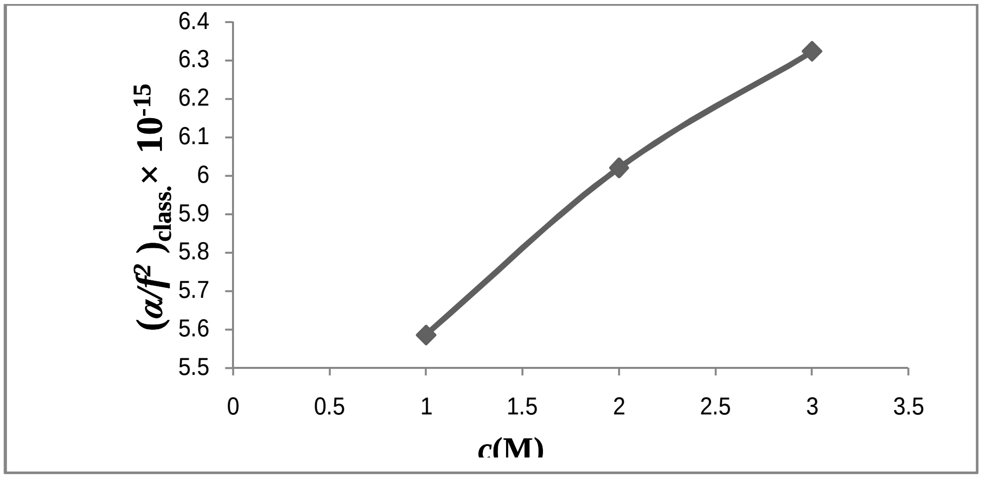

Fig. 3

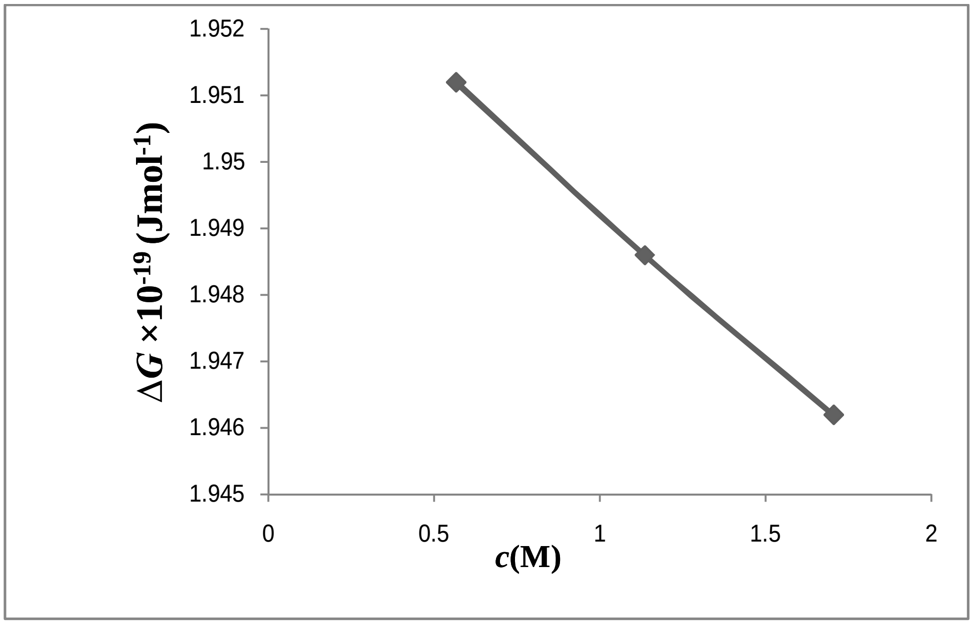

Fig. 4

Fig. 1-4 Effect of increase in concentration on free volume, relaxation time, classical sound absorption and Gibb’s free energy of aqueous 1,4-dioxane.

APPLICATIONS

Ultrasonic waves are used to detect a wide variety of anomalous conditions such as tumors and to study various phenomena such as heart valve action. This ultrasonic wave is more sensitive than X-rays. Due to this, ultrasonic technique is used in the treatment of certain cancer as well as arthritis and related diseases [13]. 1,4-dioxane and its aqueous mixtures are very important solvents that are widely used in various industries. They figure prominently in the high energy battery technology and have also found application in organic synthesis as manifested from the physicochemical studies in these media [14].

CONCLUSIONS

Adiabatic compressibility, free volume, relaxation time, classical sound absorption and related acoustical parameters have been estimated on the basis of Gibb's free energy calculations using data on viscosity and ultrasonic velocity of 1,4-dioxane + water mixtures at different concentrations. The results are useful for studying the molecular interactions between the solute and the solvent in their solutions. The results indicate the presence of a less intense hydration sphere. The calculated acoustical parameters and their values show the presence of specific molecular interactions in the solutions of 1,4-dioxane at different concentrations, hence, it is concluded that, the association in this mixture is the result of H-bonding in the aqueous heterocyclic organic solutions. The dependence of ultrasonic velocity and other derived parameters on composition is an indication of the presence of molecular interactions.

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