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ARTICLE

Study of Acoustic Behaviour of Thiamin Hydrochloride with Methanol at 303K

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Abstract: In the present study, ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured at 2 MHz frequency in the binary mixtures of thiamin hydrochloride and methanol in the concentration range 0 to 0.1 molar concentration at 303K using ultrasonic interferometer technique. From the basic experimental data, various acoustic and thermodynamic parameters; namely, adiabatic compressibility, free length, free volume and internal pressure, were calculated, with a view to investigate the nature and strength of molecular interaction in the binary liquid mixture of thiamin hydrochloride and methanol. The obtained results support the occurrence of molecular interaction through hydrogen bonding in the binary liquid mixture.

Keywords: Ultrasonic velocity, Binary liquid mixture, Molecular interaction, Hydrogen bonding.

Introduction

The field of ultrasonic technique has grown enormously in scientific studies and has become a subject of active interest during the recent years [1]. Ultrasonic technique is most important and universally accepted to study the physical and chemical properties of solutions [2-6]. Ultrasonic velocity helps to provide qualitative information about the nature of molecular interactions in pure and binary liquid mixtures [7-9]. Literature study shows that a lot of work has been performed on pure and binary liquid mixtures [10-15].

Vitamins are in general biologically active compounds which are needed by cells and organs to sustain good health; so, they are essential dietary components [16-17].

Acoustical properties are important tool to study the behaviour of solute and solvent interaction. The study of acoustical behaviour in liquid mixtures was reported by various researchers. Thirumaran *et al.* [18] determined the acoustical properties of N, N-Dimethyl formamide, (DMF) acetophenone with 1-alkanols. Khan and Bhise [19] measured the acoustical studies of sucrose in aqueous and non-aqueous media. Vanathi, Mullainathan and Nithiyanantham [20] conducted an acoustical study on 1,4-dioxane with chloroform and cyclohexane. Shinde *et al.* [21] studied the acoustical properties of aqueous manganese chloride solutions. Wasnik [22] reported the acoustic properties of prochlorperazine melate drug in 20% DMF-water solution. In literature survey, it has been found that no effort has been made to investigate the acoustical behaviour of binary liquid solution of thiamin hydrochloride with methanol at 303K.

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In this communication, we reported the ultrasonic velocity, density and viscosity of binary liquid mixture of thiamin hydrochloride and methanol at a fixed temperature of 303K over 0.00 to 0.1 molar concentrations. From these experimental values of ultrasonic velocity, density and viscosity, a number of other thermodynamic parameters; namely, adiabatic compressibility, free length, free volume and internal pressure, have been calculated using standard equations. The variation of these parameters with molar concentration was found to be useful in understanding the nature of interactions between the components.

Experimental Methods

The chemicals thiamin hydrochloride and methanol used in the present study were products from E-Merck. These products were highest commercial and therefore, used without further purification. The binary mixtures of these chemicals were prepared immediately before use by mixing appropriate volume. Double distilled water was used in the preparation of experimental solutions. The solutions of each composition were prepared fresh and all the properties were measured at the same day. The ultrasonic velocities of liquid mixture of thiamin hydrochloride and methanol were measured using an ultrasonic interferometer (Model F-05, with digital micrometer) at a fixed frequency of 2 MHz. The measurements were made at different concentrations from 0 to 0.1 molar at a fixed temperature of 303K. The temperature of liquid mixture can be maintained constant at 303K with an accuracy of 0.1K using a digitally controlled water bath. The viscosity of the liquids was measured by an Ostwald viscometer. The viscometer was suspended in a thermostatic water bath. An electronic digital stopwatch with uncertainty of ±0.01 s was used for flow time measurements. At least three repetitions of each data reproducible to ±0.05 s were obtained and the results were averaged. The density of the pure components and their liquid mixtures was measured with a single-capillary pycnometer made up of borosil glass with a bulb of 8cm^3 and capillary with an internal diameter of 0.1 cm, chosen for the present work. The liquid mixtures were prepared by mass in an air-tight stopped bottle using an electronic balance accurate to ±0.1 mg. The accuracies of density and velocity data were ± 0.02% and ± 0.01%, respectively.

Theory

Adiabatic Compressibility

From the ultrasonic velocity (U) and density (ρ) of the medium, the adiabatic compressibility values of the solution were calculated as [23]:

$$\beta_a = \frac{1}{U^2 \rho} \ (\mathbf{Kg^{-1}.m.sec^2}) \qquad (1)$$

where:

U: Ultrasonic velocity of the solution (m.Sec^{-1}) at fixed experimental temperature.

ρ: Density of the solution (kg.m^{-3}) at fixed experimental temperature.

Free Length

Jacobson [24] in 1951 established a semi-empirical relation to achieve the concept of intermolecular free length in order to explain the ultrasonic velocity in liquids.

$$L_f = K(\beta_a)^{1/2} \ (\mathbf{m}) \qquad (2)$$

where:

K is a temperature-dependent constant known as Jacobson's constant. K= 2.131×10^{-6}.

β_a is adiabatic compressibility.

Free Volume

The dimensional relation given by Suryanarayana and Kuppusamy [25] based on ultrasonic velocity (U) and viscosity (η) data is given below.

$$V_f = \left(\frac{M.U}{K\eta}\right)^{3/2} \ (\mathbf{m^3/mole}) \qquad (3)$$

where:

U: Ultrasonic velocity of the solution (m.Sec^{-1}) at fixed experimental temperature.

η: Viscosity of the solution (Pa.Sec) at fixed experimental temperature.

K: Temperature-independent constant = 4.28 x 10^9.

M: Effective molecular weight of the mixture = $\Sigma(m_i x_i)$

where: m_i and x_i are the molecular weight and mole fraction of individual constituents, respectively.

Internal Pressure

On the basis of statistical thermodynamics, Suryanarayana [26] derived an expression for the determination of internal pressure by the use of free volume concept as:

$$P_i = bRT \left(\frac{K_j.\eta}{U}\right)^{1/2} \left(\frac{\rho^{2/3}}{M^{7/6}}\right) (\mathbf{N/m^2}) \qquad (4)$$

where:

b: Cubic packing factor (assumed to be 2 for all liquids and solutions).

R: Universal gas constant.

T: Absolute temperature (in Kelvin).

K_j: Temperature-independent constant = 4.28 x 10^9.

η: Viscosity of the solution (Pa.Sec) at fixed experimental temperature.

U: Ultrasonic velocity of the solution (m.Sec^{-1}) at fixed experimental temperature.

ρ: Density of solution (kg.m^{-3}) at fixed experimental temperature.

M: Effective molecular weight of the mixture = $\Sigma(m_i x_i)$

where: m_i and x_i are the molecular weight and mole fraction of individual constituents, respectively.

Results and Discussion

With a view to understand the effects of concentration, nature of solvent and the structure of thiamin hydrochloride on structure forming and breaking tendency, various acoustical parameters, like adiabatic compressibility, free length, free volume and internal pressure, were determined using experimental data of ultrasonic velocity, density and viscosity of binary liquid solution of thiamin hydrochloride and methanol at 303 K using standard Eqs. 1 to 4. The ultrasonic velocity and related acoustical parameters at 303K are shown in Figs.1 to 5.

The measured experimental values of density (ρ),viscosity (η) and ultrasonic velocity (U) of pure solvent methanol are compared with the available literature data [27-30] at 303 K. These values are reported in Table 1 and a satisfactory agreement was found.

Fig. 1 shows the variation of ultrasonic velocity with increase in molar concentration of thiamin hydrochloride. Initially, the ultrasonic velocity of binary mixture of thiamin hydrochloride and methanol increases and attains a maximum value at a particular concentration of 0.02 M. This is due to the fact that as the density of solution increases, the number of particles in a given region increases leading to quick transfer of sound energy and disrupting the methanol structure with the addition of thiamin hydrochloride [31]. Methanol is monohydric alcohols having a hydroxyl group (OH), which may form hydrogen (O-H..O) bond with thiamin hydrochloride, thus association may be possible between thiamin hydrochloride and methanol molecules through hydrogen bonding. The increase of intermolecular hydrogen bonding between the molecules increases the ultrasonic velocity, which results in structure-making behavior of thiamin hydrochloride.

TABLE 1. Comparison of experimental measured density (ρ), viscosity (η) and ultrasonic velocity (U) values of methanol with literature data at 303 K.

Organic liquid (Solvent)	ρ (kg.m^{-3})		η (Pa.Sec)		U (m/Sec^2)	
	Present work	Literature work	Present work	Literature work	Present work	Literature work
Methanol	782.2	781.9[27] 781.8[30]	0.000512	0.000501[28] 0.000515[29]	1100	1087[27] 1103[28]

The ultrasonic velocity attains a maximum value at 0.02 molar concentration, because at this molar concentration, components' molecules show a strong hydrogen bond. Similar increasing trend of variation of ultrasonic velocity with increase in solute concentrations was reported by various co-workers; Chithralekha and Panneerselvam [1], Raju and Rakkappan [32], Magazu *et al.* [33], Rohman and Mahiuddin [34], Badarayani and Kumar [35]. The ultrasonic velocity further decreases up to 0.04 molar concentration, which indicates structure-breaking properties of interacting molecules. Similar decreasing trend was reported by Mehra and Malav [36], Kannapan, Thirumaran and Palani [37], Kannapan and Hemlata [38], Mistry and Bhandakkar [39]. Ultrasonic velocity again shows an increasing trend from 0.04 molar concentration, which indicates structure-making property of thiamin hydrochloride [40].

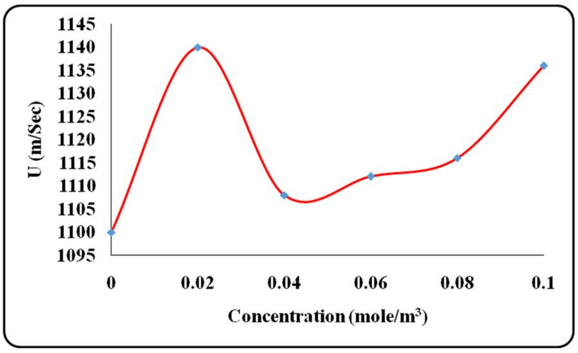

FIG. 1. Variation of ultrasonic velocity with concentration.

The variation of adiabatic compressibility with increase in molar concentration is shown in Fig. 2. The adiabatic compressibility initially decreases up to 0.02 molar concentration and then increases to 0.04 molar concentration. The decrease in adiabatic compressibility implies enhancement in molecular association by increase in thiamin hydrochloride content, as the new entities (formed due to molecular association) become compact and less compressible. It is also suggested that compressibility of the solution will be lesser than that of methanol. As a result, thiamin hydrochloride will have mobility and have more probability of contacting methanol molecules. This may enhance the interaction between thiamin hydrochloride and methanol molecules. Similar kinds of behaviour were observed by researchers at various solute concentrations [41-47]. The increases in adiabatic compressibility up to 0.04 mole concentration suggest molecular dissociation between the thiamin hydrochloride and methanol molecules [48]. Further decrease in adiabatic compressibility from 0.04 molar concentration might be due to aggregation of methanol molecules around thiamine hydrochloride molecules. Nithiyanantham and Palaniappan [49], Hemlata *et al.* [50] and Praharaj and Satapathy *et al.* [51] reported similar trends and observations. The inverse relationship that exists between ultrasonic velocity and adiabatic compressibility clearly indicates association between the thiamin hydrochloride and methanol molecules [52]. The calculated values of ultrasonic velocity and adiabatic compressibility are in good concordance with reported work [53].

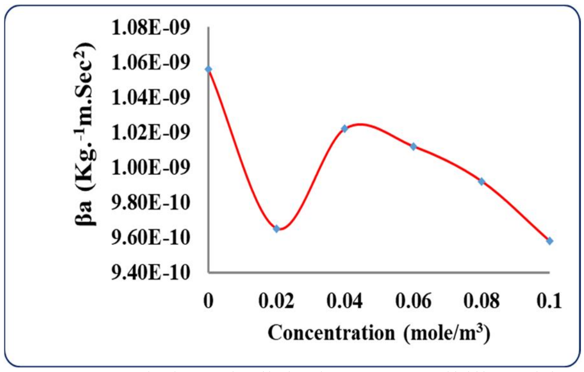

FIG. 2. Variation of adiabatic compressibility with concentration.

The intermolecular free length (L_f) gives the distance between the surfaces of the neighbouring molecules, which mainly affects the sound velocity [54]. The behaviour of free length is analogous to adiabatic compressibility, but inversely reflected by ultrasonic velocity [1]. It has been found that free length initially decreases up to 0.02 molar concentration and then increases to 0.04 molar concentration and again decreases from 0.04 molar concentration. The decrease in free length with increase in concentration of thiamin hydrochloride indicates that there is a significant interaction between thiamin hydrochloride and methanol molecules, suggesting a structure-promoting behaviour on addition of thiamin hydrochloride concentration. This structure-promoting behaviour considerably changed the structural arrangement of interacting molecules of thiamin hydrochloride and methanol. Asghar, Khan and Subramani [55], Thakre and Naik [56], Aswale, Dhote and Tayade [57] reported similar results. The increase in free length with increase in thiamin hydrochloride concentration brings the molecules to a loosely packing, resulting in weakening the molecular association between unlike molecules [48].

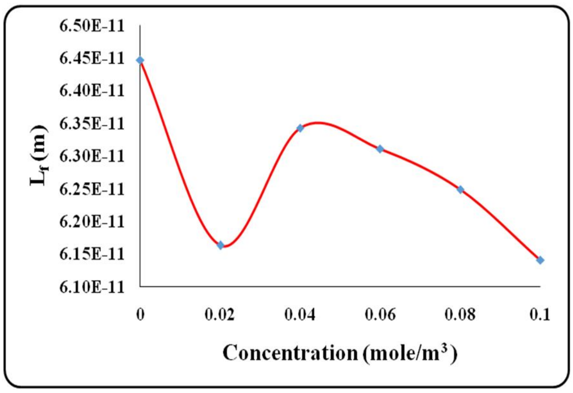

FIG. 3. Variation of free length with concentration.

Free volume gives the measure of cohesive or binding forces between the solute and solvent molecules [58] and internal pressure gives significant information about structural changes in the solution [36]. It has been observed that free volume and internal pressure show no variation up to 0.06 concentration with increase in molar concentration indicating that less amount of intermolecular forces exists during this concentration range. However, from 0.06 M concentration, free volume increases whereas internal pressure decreases. This is due to the fact that at these concentrations, molecules get disordered due to increasing entropy of the system which leads to decrease interactions between molecules of thiamine hydrochloride and methanol [59].

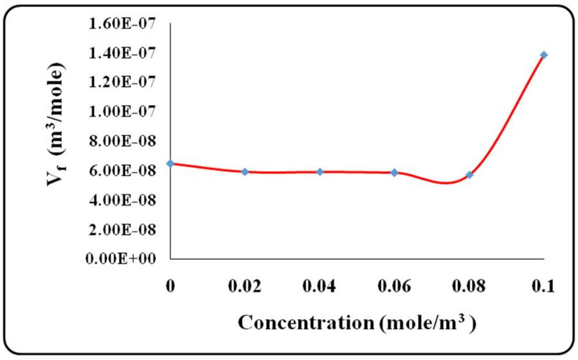

FIG. 4. Variation of free volume with concentration.

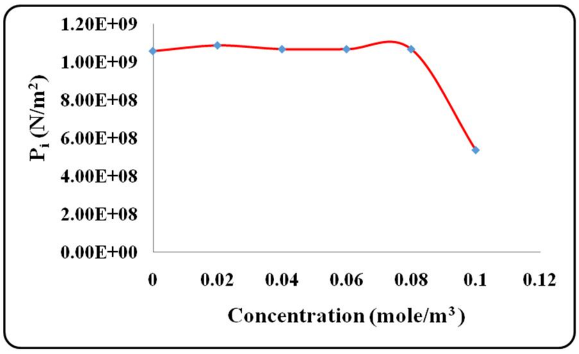

FIG. 5. Variation of internal pressure with concentration.

Conclusion

The results of the present investigation indicate a positive slope of ultrasonic velocity and a corresponding negative slope of adiabatic compressibility (or free length) and *vice versa* with increase in molar concentration of thiamin hydrochloride. The resulting positive slope of ultrasonic velocity is indicated by hydrophobic character, whereas the negative slope is indicated by hydrophilic character. These hydrophobic and hydrophilic characters promote the structure-making and structure-breaking tendency of thiamine hydrochloride due to formation of hydrogen bond between thiamin hydrochloride and methanol molecules.

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