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COMPARATIVE STUDY OF INTERMOLECULAR INTERACTIONS OF S-TRIAZINE AND TRIAZINOTHIOCARBAMIDES BY ULTRASONIC INTERFEROMETRIC TECHNIQUE

S. S. MISHRIKOTKAR* and P. B. RAGHUWANSHI

Department of Chemistry, Brijlal Biyani Science College, AMRAVATI – 444604 (MS) INDIA

ABSTRACT

The ultrasonic velocity and density measurement of s-triazine and triazinothiocarbamides were carried out in two different solvents, ethanol and dioxane, respectively for investigating solute-solvent interactions. The measurements of 0.01M solutions were carried out at 303.15 K. The aim of the study was to find the effect of protic/aprotic nature, polarity/non-polarity, dielectric constant, hydrogen bonding of solvent with resonance stabilization, structure, different substituents and their effect on ligands in solute-solvent interactions. The data obtained during the study were used for determining the most significant acoustic parameters like adiabatic compressibility (β_s), apparent molar volume (Φ_v) and apparent motor compressibility (Φ_k). These parameters explore solute-solvent interactions in different solvents. In this investigation, the comparative study of effect of solvent and effect of substituents in the solute are studied on molecular interaction of matter.

Key words: Interferometry, Acoustic parameters, Solute-solvent interactions.

INTRODUCTION

The ultrasonic waves have proved to be useful probe for generating more information about the structure and properties of matter[1]. The unique feature of sound wave property is that it gives direct and precise information of the adiabatic properties of solution. The use of ultrasound is one of the well recognized approaches for the study of molecular interactions in fluids. The ultrasonic velocity plays an important role in the investigation of intermolecular interactions. Weak molecular interactions can also be studied by ultrasonic technique. The structural arrangements are influenced by the shape of the molecules as well as their mutual interactions. The ultrasonic velocity and other acoustic parameters like

*Author for correspondence; E-mail: samru1811@gmail.com

adiabatic compressibility can be measured with great accuracy and consequently provides a powerful way to determine intermolecular interaction.

Literature survey reveals that much work has been done in water and organic solvent mixtures[2-7], but rare work is found in pure ethanol or dioxane solvent and comparison of interactions in these different solvents[8]. Also the review doesn't show any attempt made on ultrasonic interferometric study of substituted triazine and triazinothiocarbamides in pure solvents. Hence, it was intended to have a comparative study of these solutes in ethanol and dioxane solvents, related to protic-aprotic nature, polarity-nonpolarity, hydrogen bonding, dielectric constant and density of solvent on intermolecular interactions. Therefore, in the present work, an attempt has been made to understand the behaviour of 2-amino-4-hydroxy-6-methyl-s-triazine (L_1), 1-(4-hydroxy-6-methyl)-s-triazino-3-phenylthiocarbamide (L_2) and 1-(4-hydroxy-6-methyl)-s-triazino-3-tert-butylthiocarbamide (L_3) compounds in ethanol and dioxane solvents separately. The densities and ultrasonic velocities of 0.01M solutions of L_1, L_2 and L_3 were determined. From these values, adiabatic compressibility (β_s), apparent molar volume (Φ_v) and apparent compressibility (Φ_k) were calculated.

EXPERIMENTAL

All the chemicals used were of A.R. grade. Double-distilled water was used during the study. The three ligands were synthesized in our laboratory by reported methods[9]. The solvents were purified by standard procedure[10]. Densities were measured with the help of bicapillary pyknometer. 0.01M solutions of ligands in ethanol and dioxane solvents were prepared separately. Weighing was done on Mechaniki Zaktady Precyzyjnej Gdansk Balance, made in Poland (± 0.001g). Temperature variation was maintained within ± 0.1°C with the help of Elite thermostatic water bath. Single crystal interferometer from Mittal Enterprises, Model MX-3 with accuracy of ±0.03% and frequency of 1 MHz was used in the present work. The densities and ultrasonic velocities of ligands, L_1 to L_3 in ethanol and 1,4-dioxane were measured at 303.15 K.

The adiabatic compressibility of solvent (β_o) and solution (β_s) are given by-

$$\beta_o = 1/(V_o^2 d_o) \quad \ldots(1)$$

$$\text{and } \beta_s = 1/(V_s^2 d_s) \quad \ldots(2)$$

V_o, d_o, V_s and d_s are the velocities and the densities of the solvent and solution, respectively.

Apparent molar volume has been calculated from the relation-

$$\Phi_v = 1000(d_o - d_s)/C\, d_s\, d_o + M/\, d_s \quad \ldots(3)$$

M = Molecular weight of ligand and C = Molarity of the solution.

Apparent molar compressibility was obtained from-

$$\Phi_k = 1000\, (\beta_s\, d_o - \beta_o\, d_s)/C\, d_s\, d_o + \beta_s\, M/\, d_s \quad \ldots(4)$$

All these acoustic parameters were computed for all the three ligands in ethanol as well as in 1,4-dioxane.

RESULTS AND DISCUSSION

A study of β, Φ_k and Φ_v directly relate the structural interaction of solvent with solute and provides the information regarding complex formation, stability, internal structure, molecular association and internal pressure. The values of acoustic parameters are given in Table 1. It was observed that β_s values in ethanol are considerably higher than in 1,4-dioxane. This may be due to the nature of the solvents.

Table 1

Acoustic	Ethanol			1,4-Dioxane		
Parameters	**L_1**	**L_2**	**L_3**	**L_1**	**L_2**	**L_3**
Density (d_s) (Kg^{-3})	797	801.5	796	1006.7	1007.4	1006.3
U. S. velocity (v) ($m.\ sec^{-1}$)	1796.62	748.2	511.85	2239.36	817.062	990.98
Adiabatic compressibility (β_s) (Pa^{-1})	0.38871	2.22755	1.79514	0.19808	1.48692	1.011912
Apparent molar volume (Φ_v) ($m^3\ mol^{-1}$)	0.39379	-0.143112	0.696089	-0.092395	-0.102749	0.061419
Apparent molar compressibility (Φk) ($m^3 mol^{-1} Pa^{-1}$)	-86.7449	-63.7635	-31.2426	8.0639×10^{-8}	4.7644×10^{-8}	4.5956×10^{-8}

The parameters of the solvent, which directly affect the values of β are protic nature, polarity, high dielectric constant (24.6) and lower density of ethanol as compared to aprotic nature, non-polarity and low dielectric constant (2.2) and higher density of dioxane. In ethanol, hydrogen bonding is also possible, while it is not observed in dioxane.

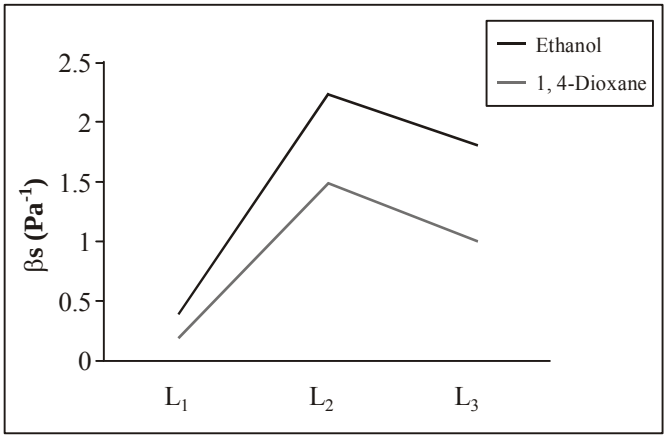

Fig. 1: Variation of adiabatic compressibility with L_1, L_2 and L_3

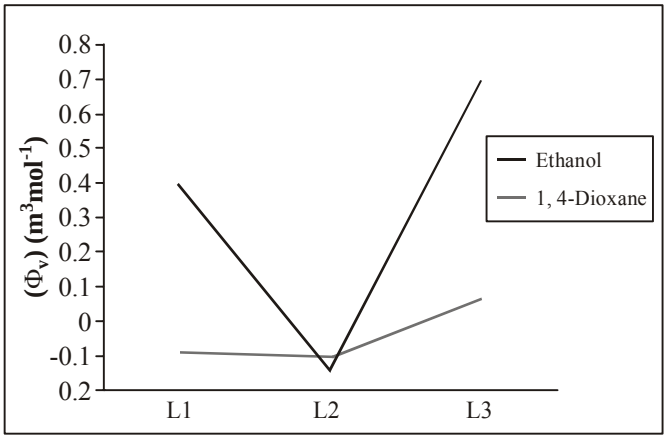

Fig. 2: Variation of apparent molar volume with L_1, L_2 and L_3

β_s values are increasing from L_1 to L_2. This is due to the change in structure of the ligands. L_1 contains symmetrical triazino nucleus having three carbon atoms and three nitrogen atoms, arranged alternately in the hetrocyclic ring. In L_2, more stable phenyl isothiocyanate group is substituted on amino group while L_3 contains electron donating tert-butyl group. The tert-butyl group is a bulky group, which blocks the amino group. Amino group is free in L_2 and hence, β_s value is lower for L_3 than L_2.

Φ_v values of L_2 are lower than L_1 and negative. This may be due to the presence of more stable phenyl ring in L_2 increasing the compactness of the medium and closer packing of the molecules increases the clinging. Whereas in dioxane solvent, the negative values obtained for L_1 and L_2 again indicate the compactness of the medium and the clinging. Φ_v for L_3 are the highest in both the solvents. This is due to the presence of the electron donating nature of the ligand. In dioxane, negatively charged oxygen is present and so there is weak solute-solvent interaction whereas in ethanol, increase in the molecular weight increases the Φ_v of L_3.

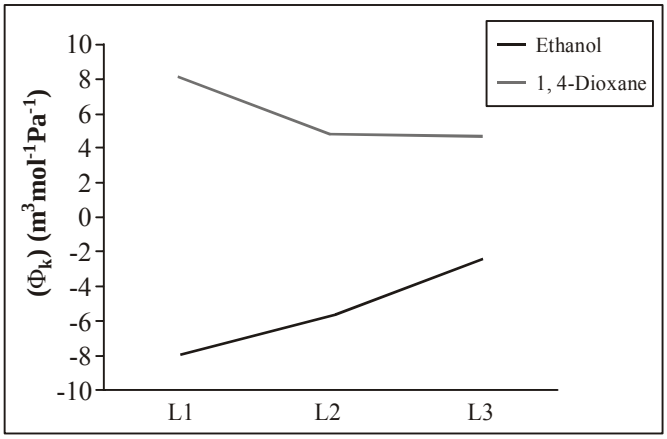

Fig. 3: Variation of apparent molar compressibility with L_1, L_2 and L_3

Apparent molar compressibility Φ_k also explains the intermolecular interactions like β_s. The structure of the solute and the number of the atoms present in it will directly affect the Φ_k values. It is observed that the Φ_k values in ethanol are lower than that in dioxane. This reverse trend than β_s shows the difference between adiabatic and apparent molar compressibility clearly. β_s just explains the simple association whereas Φ_k explains the molecular interactions like structure making and structure breaking nature of the solute.

Ethanol is a polar solvent having profuse hydrogen bonding due to which molecules are arranged in such a way that the void spaces may be available. Thus, in ethanol, stucturedness is already present, which may break on the addition of polar solute and form the bulk of solute-solvent as indicated by lower Φ_k values.

On the other hand, dioxane is a non-polar solvent having higher density and no hydrogen bonding. When a polar solute is added to it, a weak interaction between positive charge on the solute and negative charge on the oxygen of dioxane developes resulting in

weak Vander Waal's forces, which introduces structuredness in the solution. Thus, void spaces may be created and solution becomes more compressible possessing higher Φ_k values.

Thus, it may be predicted from β_s and Φ_k values that β_s can detect gross changes in interaction but minute changes due to change in structure may only be noticed by Φ_k values.

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