A STUDY OF ACOUSTIC PROPERTIES OF SUBSTITUTED HYDROXY CHALCONEIMINE IN DIFFERENT PERCENTAGE AND CONCENTRATION OF DIOXANE-WATER MIXTURES

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ABSTRACT

Ultrasonic velocity and density measurements of 2^1-hydroxy – 5^1 – bromo – N – (m - hydroxyphenyl) - chalconeimines HBN3HPCU) in DIOXANE – Water mixtures, have been carried out in the concentration range 1×10^{-2} -5×10^{-2} mol dm^{-3} and in different percentage of dioxane – water mixtures. The experimental data have been used to calculate various acoustical parameters such as velocity, adiabatic compressibility (B_s), apparent molal volume (Φ_v), apparent molal compressibility ($\Phi_{k(s)}$), intermolecular free length (L_f), Specific acoustic impedance (Z_s) and relative association (R_A). The results so obtained are very much comparable and are in good agreement. A molecular interaction study has also been made successfully in the light of these acoustical properties.

KEYWORDS : Acoustical impedance, velocity, mixed solvents, Dioxane-WATER MIXTURES substituted hydroxyl chalconeimine.

INTRODUCTION

Excess – acoustical properties are very helpful in predicting the physico-chemical behaviors and molecular interactions occurring in a DIOXANE-Water mixtures.

Successful attempt have been done made by Thirumaran et al (2009) to estimate ultrasonic study of intermolecular association through hydrogen bonding in ternary liquid mixtures. Over a wide range of compositions which indicates that there exist a strong molecular interaction existing between the unlike molecules.

Agrawal,(2010) predict Acoustical and allied property of situated Isoxazole in difft co solvent at 293.15 k.,Bhandakkar et al (2010) have been studied ultrasonic study of molecular interactions in some bio-liquids. Successful attempts have been made by several workers like Pal et al (2003) and Aminabhavi et al (2006) on the measurements and theoretical prediction of various thermo-acoustical properties of liquid binary and ternary mixtures over a wide range of composition and still in progress. In a chemical industry, these properties are very significant in design calculations, heat transfer and mass transfer ets. There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the interactions in liquid mixtures. Extensive work has been done earlier by Pandey et al (1999), Pal et al (1998) and Tamura et al (2000) to estimate the acoustical properties of liquid mixtures which are helpful in assessing the molecular size and shape, contribution to steric hindrance coupling of torsional oscillations and extent of non-ideal behaviors. The latter, in fact depends on the molecular structure and intermolecular interactions in different combinations. The role of internal pressure in liquid-solution thermodynamics was qualitative but recently its usefulness has been explored for quantitative study of intermolecular forces. Pioneer attempts have been made by Pandey et al (1993) to show the significance and its correlation with other properties in which the internal pressure has been computed from the knowledge of viscosity (n) density (p), and ultrasonic velocity (u) using an indirect method. In the present investigation. Ultrasonic velocity (u) and density for substituted chalconeimines have been measured over a wide range of compositions. As for as our knowledge is concerned, no one has attempted in predicting the various acoustical properties for substituted hydroxy chalconeimines so for due to scarcity of experimental data, its theoretical applicability could not be done. Also prediction of solubility parameter of 2^1- hydroxy – 5^1 – bromo – N – (-m-hydroxy phenyl)- chalconeimines for 70% DIOXANE-water at 307.15 K using experimentally determined value of density, and ultrasonic velocity.

EXPERIMENTAL

Component liquid DIOXANE obtained from the BDH chemical Ltd., Poole, England of Anal R Grade, were purified and dried by usual procedure. Selected substituted hydroxy chalconeimines was : 2^1-hydroxyl -5^1- Bromo – N – (m-hydroxy phenyl)- chalconeimines. Densities & ultrasonic velocities were measured at determined -307.15 k over a wide range of compositions. Densities were with a bicapillary pyknometer with an estimated error of ±0.001 g/ml. The ultrasonic velocity measurements were made using a crystal controlled variable path ultrasonic interferometer (Mittal Enterprise, Model F-05) of 2 MHz with accuracy of ± 0.03 %.

All the measurements were carried out using a water bath thermo statistically controlled to ± 0.01 K.

Theory and Calculation :- The apparent molal volumes (ϕv) and apparent molal adiabatic compressibilities $\phi k_{(s)}$ in solutions are determined respectively, from density (ds) and adiabatic compressibility (ßs) of solution using the equation,

$$\phi v = (M/ds) + [(do - ds)10^3] / m\,ds\,do \qquad (1)$$

and

$$\phi k(s) = [1000\,(\beta s\,do - \beta o\,ds) / m\,ds\,do] + (\beta s\,M/ds) \qquad (2)$$

where, do is the density of pure solvent, m is molality, M is the molecular weight of solute,

βo is adiabatic compressibility of pure solvent and βs is adiabatic compressibility of solution.

βs is calculated from ultrasonic velocity using the equations–

$$\beta s = 100 / (Us^2 ds) \text{ and } \beta_o = 100 / Uo^2\,do$$

where, Us is the ultrasonic velocity in the solution in m/s. ßs is in bar^{-1} and ϕk(s) is in cm3 mol^{-1} bar^{-1}.

The values of ϕk(s) and ϕv were plotted versus √molality of solutes. The curves represent the least square and ϕ v can be given as–

$$\phi v = \phi^0 v + Sv\sqrt{m} \qquad (3)$$

and

$$\phi\, k(s) = \phi^0 k(s) + S\,k(s)\sqrt{m} \qquad (4)$$

where, $\phi^0 v = v^0$ and $\phi^0 k(s) = k^0$ are the infinite dilution apparent molal volumes and apparent molal adiabatic compressibilities respectively. Sv and $Sk_{(s)}$ are the experimental slopes representing ion-ion interactions.

The intermolecular free length (L_f), specific acoustic impedance (z) and relative association (R_A) are calculated by using the following equation-

$$Lf = K \times \sqrt{\beta s} \qquad (5)$$

Where, K is the Jackbson's constant.

$$Z = Us \times ds \qquad (6)$$

$$R_A = \frac{d_s}{d_o} \left(\frac{U_o}{U_s} \right)^{1/3} \qquad (7)$$

Table No. 1(A)
Acoustic parameters of HBN3HPCI (L_5) in DIOXANE at different percentage of DIOXANE

% DIOXANE	Mole fraction of DIOXANE	Ultrasonic Velocity (u_s) (m/sec)×10^3	Density (ds) (g/m^2)× 10^6	Adiabatic compressibility βs (bar^{-1}) ×10^{-10}	Intermolecular free length L_f (A^0))×10^2	Apparent molal volume Φ_v(m^3/mole)×10^{-6}	Apparent molal Compressibility ($\Phi_{k(s)}$)(m^{3}mol^{-1} bar^{-1})×10^{-10}	Relative association (R_A)	Specific acoustic impedance Z_s (kg m^{-2} s-1) ×10^6
100	1	1.3274	1.0305	5.5096	4.7159	228.701	-19.0485	0.9955	1.3679
90	0.6563	1.3957	1.0319	4.9804	4.4836	110.4355	-26.9288	0.9945	1.4401
80	0.4584	1.4681	1.0334	4.6459	4.3307	5.6125	-0.9614	0.9978	1.5171
75	0.3883	1.5204	1.0345	4.1825	4.1090	-17.296	-27.7469	0.9952	1.5729
70	0.3305	1.5714	1.0361	3.9141	3.9751	-137.465	-30.011	0.9954	1.6270
60	0.2409	1.6197	1.0376	3.7267	3.8786	-244.61	-24.4864	1.0017	1.6688

Table 1(B)
Acoustic parameters of HBN3HPCI (L_5) in DIOXANE at different concentrations of solute in DIOXANE-Water mixtures.

Concentrations of ligand (m) (mol/dm^3)	$\sqrt{m}$	Ultrasonic Velocity (u_s) (m/sec)×10^3	Density (ds) (g/m3)×10^3	Adiabatic compressibility βs (bar^{-1})×10^{-10}	Intermolecular free length (L_f)(A^0) ×10^2	Apparent molal volume Φ_v(m^3/mole) ×10^{-6}	Apparent molal Compressibility ($\Phi_{k(s)}$)(m^{3}mol^{-1} bar^{-1})×10^{-10}	Relative association (R_A)	Specific acoustic impedance Z_s (kg m^{-2} s^{-1}) ×10^6
0.01	0.1000	1.4694	1.0388	4.4673	4.2454	189.74	32.001	1.0206	1.5265
0.02	0.1414	1.5218	1.0407	3.1627	4.0972	-10.375	1.704	1.0106	1.5838
0.03	0.1732	1.5559	1.0423	3.9778	4.0050	72.165	-5.1960	1.0048	1.6219
0.04	0.2000	1.5881	1.0458	3.8133	3.9207	100.99	-13.2668	1.0000	1.6607
0.05	0.2236	1.6288	1.0478	3.6058	3.8140	92.125	-8.0888	0.9987	1.7066

Results and discussion:-

In the present in vestigation different acoustic parameters such as adiabatic compressibility (β_s), apparent molal volume (Φ_v), apparent molal compressibility ($\Phi_{k(s)}$), acoustic impedance (Z_s), relative association (R_A) and intermolecular free length (L_f) of the solutions in different percentage of DIOXANE and at different concentrations of solute are determined at 307.15 k and presented in table 1(A)& 1(B) .

1. It is observed from the Table that the values of βs decrease with decrease in percentage of DIOXANE. Also βs decrease with increase in concentrations in 70% DIOXANE - water mixture (1×10^{-2}) As concentration increases, number of ions or particles increases in a given volume leading to the decrease in the gap between two species. This indicates that there is a strong interaction between ion and solvent molecules, suggesting a structure promoting behavior of the added solute. This may also imply the decrease in number of free ions, showing the occurrence of ionic association due to strong ion-ion interactions. This fact is again supported from the decrease of β_s with the concentration. When an ion is added to the solvent, it attracts certain solvent molecules towards itself by wrenching the molecule species from the bulk of the solvent. Hence less number of solvent molecules will be made available for the next incoming species. This is known as compression. The decreasing trend of β_s with the concentration may be due to aggregation of solvent molecules around ions supporting the strong ion-solvent interaction.

   It could be observed that the values of (Φ_{ks}) are found to be decreasing with increase in the concentration of solute. The negative value of (Φ_{ks}) may be due to loss of compressibility of solute due to strong electrostatic salvations of ions.

   Density increases with concentration for DIOXANE which is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, the increase in density may be interpreted to the structure former of the solvent due to the added solute.

   As stated earlier, due to the presence of solute, there is shrinkage of volume which reflects in the apparent molal volume (Φ_v) which is found to be decreased with increase in the concentration of solute.

   (L_f) increases with increase in percentage of DIOXANE indicating weak interaction between ion and solvent molecules. This also implies increase in number of free ions showing ionic dissociation but weak ion-ion interactions.

Relative association (R_A) is influenced by two factors:-

i) The breaking up of the solvent molecules on addition of electrolyte to it, and,

(ii) The salvation of ions that is simultaneously present, the former resulting in decrease and later increase of relative association.

As percentage decreases Relative association (R_A) decrease initially & increases later due to breaking up of solvent molecules on addition of electrolyte (decrease) and solvation of ion's predominates over the breaking up of the solvent aggregate on addition of solutes, with increasing concentration.

The specific acoustic impedance (Z_s) Values increases with decrease in percentage of DIOXANE. It also supports weak ion-solvent interactions and electrostatic solvation of ions. Also the acoustic impedance (Z_s) increases with increase in concentration of solute which may be due to lyophobic interaction between solute and solvent molecule.

If decreases linearly with increase in concentration of solute, is due to intermolecular attractive and strong electrostatic forces.

Acknowledgement

The authors are very much thankful to the principal, R.D.I.K. & N.K.D. Badnera (Rly) Amravati. Also thankful to Govt. V.I.S.H. Amravati for providing necessary facilities. One of the authors (NRP) is thankful to UGC for the award of Rajiv Gandhi National fellowship **(RGNF)**

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