ACOUSTICAL PROPERTIES OF SCHIFF BASES & THEIR COMPLEX BY ULTRASONIC VELOCITY MEASUREMENTS IN 70% DIOXANE-WATER MIXTURE AT DIFFERENT TEMPERATURES

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ABSTRACT:- The present work deals with the study of acoustic parameters like ultrasonic velocity (Us), adiabatic compressibility (βs), apparent molar volume (Øv) and intermolecular free length (Lf) by ultrasonic interferometric measurements which reflects structural interaction of water molecules and organic solvent molecules with substituted Schiff bases & their comples. The study of Schiff bases & their complex were carried in 70% 1,4-dioxane-water medium, at 298^0K, 303^0K, 308^0K, 315^0K, 318^0K & 323^0K to evaluate the thermodynamic parameters. The ultrasonic velocity of data obtained can be used to evaluate the apparent molal volme & adiabatic compressibility..

Keywords: Acoustic, Substituted Schiff bases,Ligands, Pr(III) complex, densities etc.

1. Introduction

Ultrasounds are sound waves with frequencies higher than the upper audible limit of human hearing. Ultrasound is used in many different fields like ultrasonic devices are used to detect objects and measure distances. Ultrasound imaging is often used in quality control and medicine [1-2]. In the nondestructive testing of products and structures, ultrasound is used to detect invisible flaws. Industrially, ultrasound is used for cleaning, mixing, and to accelerate chemical processes. Scientists are also studying ultrasound using graphene diaphragms as a method of communication [3]. The unique feature of sound wave property is that it gives direct and precise information of adiabatic properties of solution. The anomalous behavior of non-electrolytic solutions and the properties of liquid systems, which are otherwise not easily deduced directly, can be determined from speed of sound and density data in conjunction with equation of state. Ultrasonic technology has been adequately employed to investigate the properties of any substance to understand the nature of molecular interactions in pure liquid [4], liquid mixtures [5-7] and ionic interactions in electrolytic solutions [8]. As ultrasonic technique can reveal very weak intermolecular interactions due to its useful wavelength range, many researchers have made important advancements in understanding the nature of molecular interaction and physicochemical behaviour of liquid mixtures by studying the acoustics at different concentrations and temperatures and results were interpreted in terms of solute-solvent and solvent-solvent interaction [9-18].

Schiff bases have high synthesis flexibility, varied coordinating ability and medicinal utility and are an important class of ligands in the field of co-ordination chemistry [19]. A large number of Schiff bases have been found to possess important biological and catalytic activities [20-21] and their acoustical parameters were reported [22-24]. Hence in the present study, attempt has been made to study the molecular interactions of the following substituted Schiff bases ligands & their complex in 70% 1,4-dioxane-water mixture at different temperatures by acoustical investigations in 2’-Hydroxy,,5-Chloro-Chalcone dibromide(HCCDB)-L_3 as well as complex of Pr(III) with 2’-Hydroxy,,5’Chloro,4-methoxy chalcone dibromide(HCMCDB)-L_4.

2. Experimental and Instrumentation

2.1 Experimental

The chemicals used for synthesis were of L.R. grade. The ligand (L_3) & Pr (III)-L_4 complex were recrystallized before use. The solvent 1,4-dioxane was purified using standard procedure. All the working solutions were freshly prepared from the deionized water. To avoid any ionic contamination, deionized water was used for all the purpose in this study. The 0.01M solution of each ligand was prepared in 70% of 1,4-dioxane-water mixture. The density and the ultrasonic velocity measurements of the ligand & complex solutions were done at 298^0K, 303^0K,308^0K,315^0K,318^0K & 323^0K following the standard protocol.

2.2 Instrumentation

The densities of the solution were determined by standardize capillary pyknometer having a bulb of volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. All the weighing was made on ‘K” Roy one pan electronic balance. In the present investigation, a variable path ultrasonic interferometer from Mittal enterprises, Model F-80 was used to measure the ultrasonic velocity in liquid mixtures and solutions, having the working frequency of 2 MHz with accuracy of ±0.03%.

3. Result and Discussion

The study of ultrasonic velocity (Us), adiabatic compressibility (βs), apparent molar volume(Øv) and intermolecular free length (Lf) gives structural interaction of solvent with solute. It gives information regarding internal structure, molecular association, complex formation and stability of ligands under study. The acoustic parameters for ligand L_3 & Pr (III)-L_4 complex in 70% dioxane-water, studied at six different temperatures are calculated from the ultrasonic velocity obtained. The results are given in table 1& 3.

Adiabatic compressibility plays important role in the study of solute-solvent interactions by explaining the simple association or closed packing or clinging of molecules. It depends on the structure of the liquid which considers the geometrical fit of the solute into the ordered form of the aqueous solvent surrounding the solutes [25].

From table 1 & 3, it is observed that the value of adiabatic compressibility of ligands & complex mostly increases with increase in temperature, there is slight increase in the βs values of ligand (L_3) as well as complex Pr (iii)-L_4[26].

3.2 Apparent molar volume (Øv) :- Apparent molar volume is the thermodynamic property of solutions, which express the solute-solvent interactions, and is related to the density, molarity of the solution and the molecular weight of the solute. From table 1 & 3 shows that, the values of apparent molar volume (ϕv) increases with increase in temperature in the70% of 1,4-dioxane-water mixture. \

3.3 Intermolecular free length (Lf) :- Intermolecular free length (Lf) is the distance between the surfaces of the molecules. From Table 1 & 3, it can be noted that the Lf values are positive for all ligands in 0% dioxane-water mixures at different temperatures. The positive value of excess free length shows the existence of dispersive forces between molecules of mixture. Increase in temperature leads to less ordered structure and volume expansion and hence in intermolecular freelength [28]. It reveals that interaction become weaker at higher temperatures. Acoustical properties of L_3 ligand & Pr(III)-L_4 complex have been studied at six different temperatures to evaluate the thermodynamic parameters (Free energy ΔG,Enthapy ΔH & entropy ΔS) as shown in table 1 & 3. It is observed from table 1 & 3 that the values of Us & ØV increases with increasing the temperature and the values of $Ø^0$K(s) decreases with increasing temperatre.The values of ΔG,ΔH & ΔS are determined from table 2 & 4. It is seen from table 2 & 3 that the values of ΔG & ΔS are found to be lower in L_3 system than Pr (III)-L_4 complex.The higher values may be due to association of ligand to metal cation.

Table 1 :- Acoustic Properties of L3 at different Temperatures in 70% Dioxane-water Mixtures

Temp ^oK	1/T K^{-1}	Us (m.Sec^{-1})	ds (g.cm^{-3})	βs (bar^{-1})	Lf (A^0)	Øv (cm^3 mole^{-1})	ØK(s) (cm^3 mole^1 bar^{-1})	Log ØK(s)	RA	Z (cm sec^1 cm^{-3})
298	3.35 x 10-3	1312.65	0.9816	6.23 x 10-4	14.02 x 102	1147.68	21.55	1.33	1.0094	1288.49
303	3.30 x 10-3	1344.15	0.965	5.8 x 10-4	14.58 x 102	1681.97	16.98	1.23	1.0064	1312.56
308	3.24 x 10-3	1374.55	0.9683	5.53 x 10-4	14.16 x 102	2552.80	12.51	1.09	1.0029	1330.97
313	3.19 x 10-3	1394.55	0.9563	5.31 x 10-4	13.8 x 102	3854.12	9.42	0.9	0.9952	1333.60
318	3.14 x 10-3	1425.45	o.9425	5.12 x 10-4	13.62 x 102	5391.63	7.007	0.84	0.9882	1343.48
323	3.09 x 10-3	1450.20	0.9315	5.01 x 10-4	13.48 x 102	6649.87	5..67	0.5	0.9841	1350.86

Table 2- T.D. Parameters of L3

ΔG J Mole^{-1} DEG^{-1}	-32487.54
ΔH J Mole^{-1} DEG^{-1}	5699.81
ΔS J Mole^{-1} DEG^{-1}	-126.03

Table 3 :- Variation of Different Parameters of Pr (III)-L4 Complex with Temperature

Temp ^oK	1/T K^{-1}	Us (m.Sec^{-1})	ds (g.cm^{-3})	βs (bar^{-1})	Lf (A0)	Øv (cm^3 mole^{-1})	ØK(s) (cm^3 mole^1 bar^{-1})	Log ØK(s)	RA	Z (cm sec^1 cm^{-3})
303	3.30 x 10-3	1324.15	0.9839	6.05 x 10-4	14.80 x 102	1380.14	17.04	1.23	1.0240	1302.83
308	3.24 x 10-3	1344.33	0.9750	5.81 x 10-4	14.51 x 102	2316.13	15.95	1.20	1.0171	1310.72
313	3.19 x 10-3	1354.22	0.9685	5.63 x 10-4	14.28 x 102	2996.20	12.99	1.11	1.0130	1311.56
318	3.14 x 10-3	1384.40	0.9520	5.51 x 10-4	14.13 x 102	4815.49	11.37	1.05	0.9880	1317.94
323	3.09 x 10-3	1420.35	0.9430	5.38 x 10-4	13.96 x 102	5826.84	9.55	0.98	0.9936	1339.39

Table 4 - T.D. Parameters of Pr (III)-L4 Complex

ΔG J $Mole^{-1}$ DEG^{-1}	-19702.48
ΔH J $Mole^{-1}$ DEG^{-1}	3957.25
ΔS J $Mole^{-1}$ DEG^{-1}	-7681.73

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5.Conclusion :-

From the present study it can be concluded that ØK(s) and Lf values mostly decreases with increase in temperature of organic solvent while the values of Φv, βs & Z increases at 303.308,313,318 and 323^0K.the higher values may be due to association of ligand metal cation. Thus we can say that these acoustic properties helps in explaining how solute-solvent, solute-solute and ion-solvent interactions occur and are responsible for breaking and making of the structure in the solution.

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