
Ultrasonic studies of N-(2-hydroxybenzylidene)-3-substituted pyridine -2-amine Schiff bases in binary mixture of 1,4-dioxane-water at 293, 297 and 300 K

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ABSTRACT

Ultrasonic velocity and density of N-(2-hydroxybenzylidene)-3-substituted pyridine -2- amine Schiff bases have been measured in binary mixture of dioxane-water at 293, 297 and 300 K. From the experimental recordings, various acoustic parameters like apparent molar compressibility (ϕ_k), specific acoustic impedance (Z) and relative association (R_A) have been evaluated for dioxane-water system of different concentrations. It helps in understanding the molecular interactions occurring inbetween water molecules and organic solvent molecules with substituted Schiff bases.

Keywords: Ultrasonic, binary mixture, acoustic, molecular interaction, substituted Schiff bases.

1. Introduction

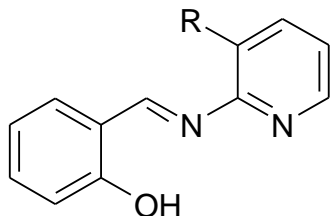
Elastic waves, whose frequency exceeds the range within which they cause sound sensation in human ear, are called ultrasonic waves. Ultrasonic studies furnish the information regarding nature and strength of the molecular interactions occurring in the solutions. The interactions help in better understanding of the nature of solute and solvent, whether the solute modifies or distorts the structure of the solvent [1-3]. Applications of ultrasonic are emerging in the field of forensic sciences, medicines [4-5], space research and in wars. Ultrasonic measurements have been used to relate even weak intermolecular interactions with excess thermodynamic and acoustical parameters. Number of researchers have made ultrasonic study of electrolytic solutions and discussed about the variation of ultrasonic velocity with ion concentration [6-9].

Schiff bases are an important class of ligands in the field of co-ordination chemistry [10]. A large number of Schiff bases have been found to possess important biological and catalytic activities [11-12] and have a large number of synthetic uses in organic chemistry. Therefore, it was found worth to investigate various Schiff bases for their acoustical parameters. Many researchers have observed close relation between ultrasonic speed and chemical or structural characteristic properties of Schiff bases in solution and molecular and structural properties were studied by determination of various acoustical parameters which helps to study solute-solute and solute-solvent interactions in pure solvents and their solutions[13-15].

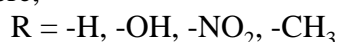
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Present Study is an attempt to determine solute-solvent, solute-solute and ion-solvent interactions measured in terms of acoustic parameters like apparent molar compressibility (ϕ_k), specific acoustic impedance (Z) and relative association (R_A) occurring in following substituted Schiff base ligands in the suitable percentage of 1,4-dioxane – water mixture at different temperatures.

Following is the structure of the ligand –



Where,



N - (2 - hydroxybenzylidene)
pyridine - 2 - amine

1. N-(2'-hydroxybenzylidene) pyridine-2-amine (A_1)
2. N-(2'-hydroxybenzylidene)-3-hydroxy pyridine-2-amine (A_2)
3. N-(2'-hydroxybenzylidene)-3-nitropyridine-2-amine (A_3)
4. N-(2'-hydroxybenzylidene)-3-methylpyridine-2-amine (A_4)

2. Experimental and Instrumentation

2.1 Experimental

The chemicals used for synthesis were of L.R. grade. The ligands (A_1 - A_4) 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. The 0.01M solution of each ligand was prepared in different percentage (75%, 80%, 85%, 90%, 95% and 100%) of 1,4-dioxane-water mixture. The density and the ultrasonic velocity measurements of the ligand solutions were done at 293, 297 and 300 K following the standard protocol.

2.2 Instrumentation

All the weighing in the present study was made on Citizen CY 104 one pan digital balance. The densities of the solution were determined by standardize capillary pycnometer having a bulb of volume of about 10 cm^3 and capillary having an internal diameter of 1 mm. A variable path ultrasonic interferometer from Mittal enterprises, New Delhi, Model MX-3 was used to measure the ultrasonic velocity in liquid mixtures and solutions, having the working frequency of 1 MHz with accuracy of $\pm 0.03\%$.

3 Result and Discussion

The sound velocities of substituted Schiff's bases were measured in different concentration of 1,4-dioxane-water solvent system at 293 K, 297 K and 300 K. The results have been discussed in the light of molecular interactions obtained from the acoustic parameters like apparent molar

compressibility (ϕ_k), specific acoustic impedance (Z) and relative association (R_A). The experimental data is tabulated as follows.

Table 1: Acoustic Parameters at different percentages of dioxane-water mixture.

System: Ligand - A₁

Temp. = 293 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.99882	2.014	16643.00	1.1946	2.0116
80	0.99859	1.763	21789.27	1.1995	1.7605
85	0.99855	1.674	15406.38	1.0941	1.6716
90	0.99703	1.7982	14408.97	1.1063	1.7929
95	0.99562	1.739	1956.79	1.0081	1.7314
100	0.99547	1.6566	26590.97	1.2350	1.6491

Table 2: Acoustic Parameters at different percentages of dioxane-water mixture.

System: Ligand - A₂

Temp. = 293 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	1.00168	2.0528	15583.71	1.1904	2.0562
80	1.0007	1.9326	16255.13	1.1658	1.9340
85	1.00052	1.8012	10403.48	1.0698	1.8021
90	0.99907	1.788	14642.03	1.1107	1.7863
95	0.99714	1.8176	-959.90	0.9948	1.8124
100	0.99599	1.7808	21602.69	1.2062	1.7737

Table 3: Acoustic Parameters at different percentages of dioxane-water mixture.

System: Ligand - A₃

Temp. = 293 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.99903	1.9814	17465.21	1.2014	1.9795
80	0.99878	1.794	20683.82	1.1928	1.7918
85	0.99863	1.7886	10967.41	1.0703	1.7861
90	0.99744	1.824	13522.06	1.1015	1.8193
95	0.99577	1.785	260.93	0.9995	1.7774
100	0.99535	1.9552	16214.85	1.1685	1.9461

Table 4: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₄

Temp. = 293 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\Phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	1.00086	1.8872	19971.20	1.2233	1.8888
80	0.9993	2.1456	11259.88	1.1243	2.1441
85	0.99795	1.9966	4788.31	1.0310	1.9925
90	0.99667	1.9938	8614.62	1.0685	1.9872
95	0.99655	1.8464	-1869.79	0.9890	1.8400
100	0.99552	1.9472	16415.42	1.1703	1.9385

Table 5: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₁

Temp. = 297 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\Phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	1.0013	2.2452	11707.08	1.1550	2.2481
80	0.9989	2.2288	9675.74	1.1097	2.2264
85	0.9986	2.1714	856.73	1.0032	2.1684
90	0.9973	2.1710	4612.21	1.0392	2.1651
95	0.9972	2.1760	-10188.91	0.9370	2.1700
100	0.9962	2.1804	10983.94	1.1277	2.1721

Table 6: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₂

Temp. = 297 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\Phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.9990	1.7930	23115.56	1.2420	1.7912
80	0.9984	1.6592	25984.09	1.2237	1.6565
85	0.9974	1.7716	11640.50	1.0724	1.7671
90	0.9966	1.6688	19464.73	1.1338	1.6632
95	0.9953	1.7914	58.42	0.9978	1.7829
100	0.9947	1.6326	27747.00	1.2401	1.6239

Table 7: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₃

Temp. = 297 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	1.0061	2.2282	11827.30	1.1635	2.2419
80	1.0012	2.3592	7428.85	1.0914	2.3620
85	0.9990	2.2534	-674.13	0.9914	2.2512
90	0.9964	2.2160	3796.73	1.0313	2.2081
95	0.9956	1.9656	-5290.23	0.9677	1.9569
100	0.9948	1.9972	15141.91	1.1596	1.9868

Table 8: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₄

Temp. = 297 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	1.0020	1.7830	23276.79	1.2481	1.7866
80	1.0004	1.6828	24822.91	1.2205	1.6834
85	0.9982	1.7870	11039.19	1.0702	1.7838
90	0.9973	1.6594	19828.59	1.1366	1.6549
95	0.9953	1.7652	995.37	1.0028	1.7570
100	0.9946	1.5474	32058.70	1.2622	1.5390

Table 9: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₁

Temp. = 300 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.9975	1.5988	31279.86	1.2884	1.5948
80	0.9969	1.3500	44778.64	1.3090	1.3459
85	0.9959	1.5150	23563.46	1.1280	1.5088
90	0.9952	1.6942	18484.88	1.1264	1.6860
95	0.9946	1.7888	188.97	0.9976	1.7791
100	0.9944	1.6196	28379.72	1.2429	1.6105

Table 10: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₂

Temp. = 300 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.9973	1.6088	30814.21	1.2855	1.6044
80	0.9970	1.6032	28684.59	1.2362	1.5984
85	0.9965	1.5508	21511.64	1.1200	1.5453
90	0.9960	1.5938	23007.19	1.1505	1.5874
95	0.9953	1.6444	5940.97	1.0267	1.6367
100	0.9948	1.6406	27372.77	1.2381	1.6320

Table 11: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₃

Temp. = 300 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.9992	1.8520	21153.39	1.2290	1.8506
80	0.9984	1.9984	14643.10	1.1502	1.9952
85	0.9976	1.8050	10460.30	1.0660	1.8007
90	0.9975	1.9626	9394.00	1.0750	1.9576
95	0.9972	1.9994	-6253.52	0.9638	1.9939
100	0.9964	1.8240	20098.44	1.1970	1.8173

Table 12: Acoustic Parameters at different percentages of dioxane-water mixture.System: Ligand – A₄

Temp. = 300 K

% 1,4-Dioxane	$d_s \times 10^3$ (kg m ⁻³)	$V \times 10^3$ (m sec ⁻¹)	$\phi_k \times 10^{-10}$ (m ³ mol ⁻¹ pa ⁻¹)	R_A	$Z \times 10^6$ (kg m ⁻² sec ⁻¹)
75	0.9988	2.0264	16347.74	1.1921	2.0239
80	0.9983	1.7850	21017.51	1.1943	1.7820
85	0.9970	1.7768	11480.46	1.0709	1.7715
90	0.9962	1.6696	19458.37	1.1331	1.6633
95	0.9961	1.7514	1460.66	1.0061	1.7445
100	0.9957	1.7784	21707.34	1.2064	1.7707

3.1 Apparent Molar Compressibility (ϕ_k)

Apparent molar compressibility (ϕ_k) is an important acoustic parameter, which explains the solute-solvent and solute-solute interactions in solutions. Thus, the structure of solute and the number of atoms present in it will have direct effect on ϕ_k values. From table 1-12 and fig. 1-3, it is observed that the ϕ_k values are negative for ligand solution in 95% dioxane medium. Negative value of ϕ_k shows that interactions are insensitive to solvent. This interprets in terms of loss of compressibility of solute due to strong electrostatic solvation of ions [16]. This weak interaction of the Vander Wall forces is expected to introduce structurdness in the solution. Thus spaces may be

created making the solution more compressible as it appears from the higher apparent molar compressibility values in dioxane solvent.

Fig. 1

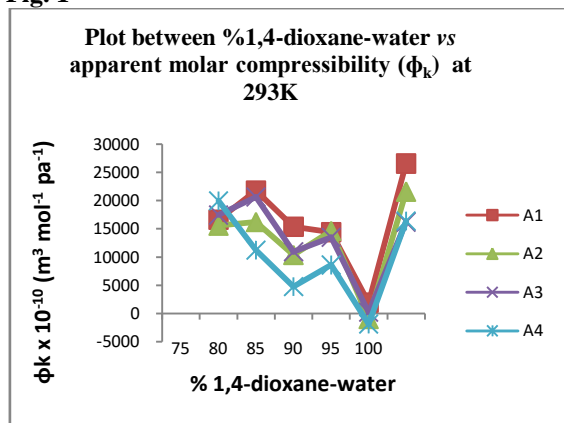


Fig. 2

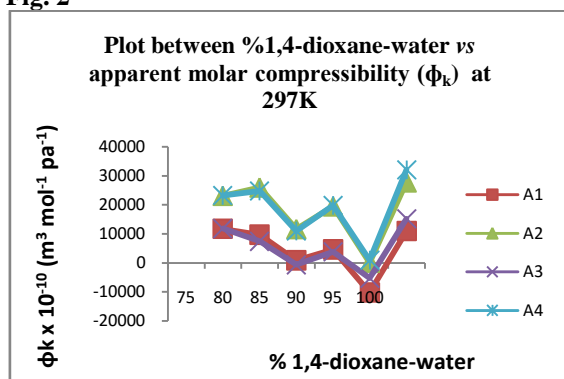
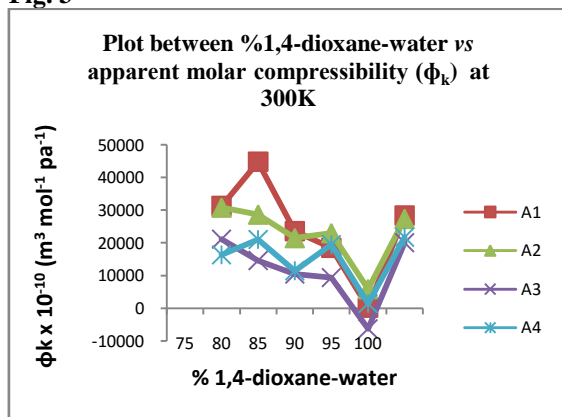


Fig. 3



3.2 Specific acoustic impedance (Z)

Specific acoustic impedance is the complex ratio of the effective sound pressure at a point to the effective particle velocity at that point [17]. It constitutes an additional probe for studying molecular interactions. As the specific acoustic impedance depends upon the various structures of the liquid and the molecular packing in the medium, from table 1-12 and fig. 4-6, it can be seen that the values of Z changes on changing the structures of ligands. The value of acoustic impedance varies with increase in concentrations indicating significant interactions in the systems.

Fig. 4

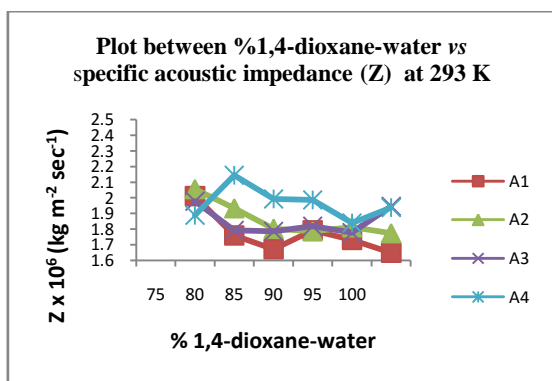


Fig. 5

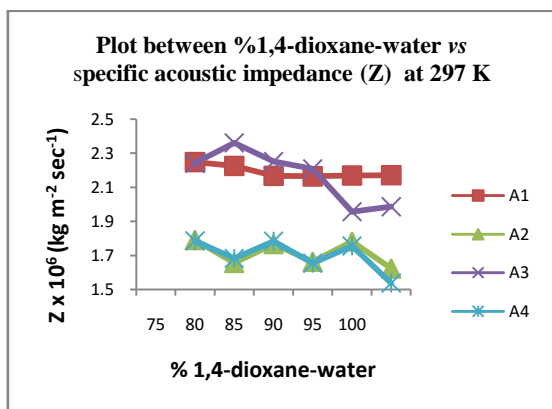
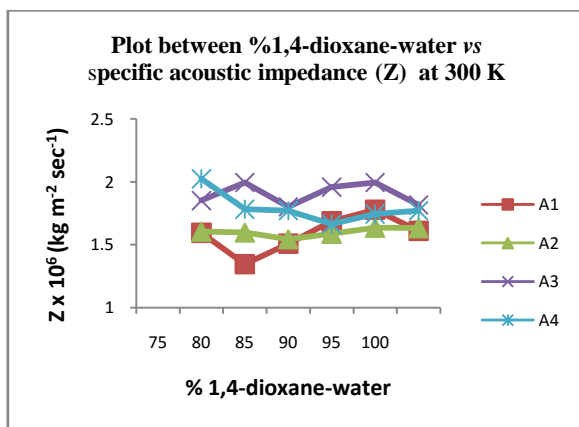


Fig. 6



3.3 Relative association (R_A)

The decrease in R_A values is due to the breaking up of the solvent molecules on addition of electrolyte to it whereas solvation of the solutes in the solution leads to increase in R_A values. As soon as solute is added to dioxane, the probability of solute forming association with dioxane will be greater as the dioxane molecules are not associated [18]. R_A values of the ligands are given in table 1-12 and shown in graph 7-9.

Fig. 7

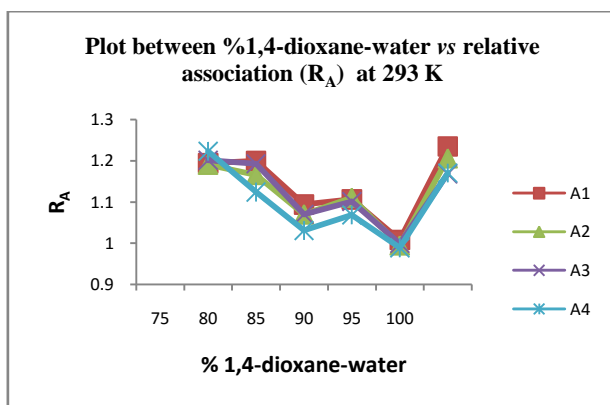


Fig. 8

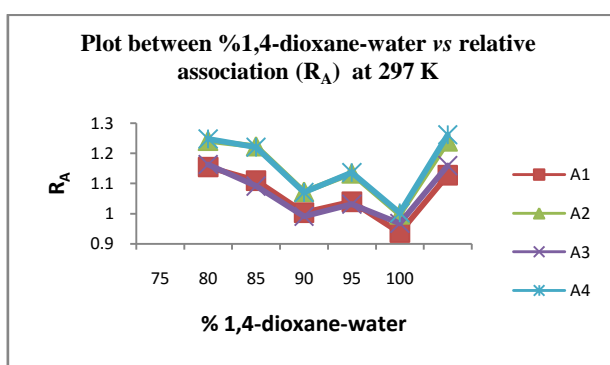
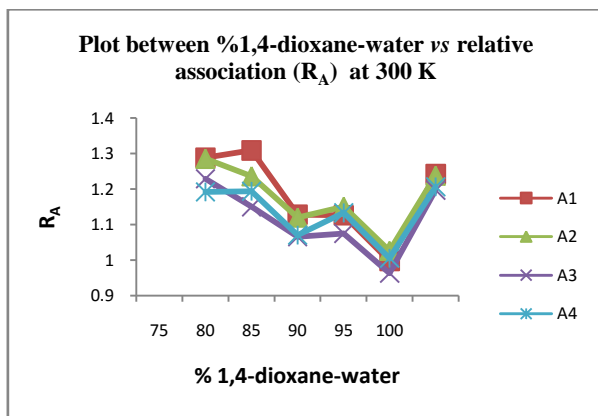


Fig. 9



4. Conclusion

Measurement of ultrasonic velocity is the best tool to investigate solute-solvent, solute-solute and ion-solvent interactions. Therefore, in last four decades ultrasonic interferometric study has created its own identity for determining solute-solvent interactions. In present study, apparent molar compressibility (ϕ_k), specific acoustic impedance (Z) and relative association (R_A) of substituted Schiff base are determined which explain how these interactions occur and responsible for breaking and making of the structure in the solution at 293, 297 and 300 K.

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