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Thermo-Acoustical and Excess Thermodynamic Studies of Binary Liquid Mixtures, Statistical Analysis of Liquid State Theories

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Abstract: ***The observed experimental parameters such as density (ρ), and ultrasonic velocity (U) of butanol, toluene and pyridine were measured over the entire range of composition at different temperatures 303,313,323 K. The observed experimental data have been utilized to evaluate some of the excess thermo-acoustical parameters such as excess volume (V^E), excess adiabatic compressibility (β_a^E) and excesses free length (L_f^E). Thermo-acoustic parameters are also calculated theoretically by applying Jacobson's free length theory and Kalidoss revised free length theory, statistical Chi-square (χ^2) test applied to both the theories, applicability of liquid theories promptly discussed.***

Keywords: Thermoacoustic parameters, Chi-square (χ^2) test

1. Introduction

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures[1-3]. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids[4-6]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components[7-8] as well as strongly interacting components. Jacobson's free length[9] (flt) have been applied by many workers [10-11] to evaluate ultrasonic velocities in liquids. Revised free length theory (rflt) suggested by kalidoss[12] can predict ultrasonic velocities in mixtures better, and the approach can very well be use to incorporate thermostatic state, associative and shape factors[13] The present study reports the results of the variation of thermo-acoustic parameters with mole fraction at different temperature in binary systems and the statistical analysis analysis has been done by applying Chi-square (χ^2) test.

2. Materials and Methods

In the present work, we have used chemicals, which are analytical reagent (AR) grade minimum assay of 99.9% obtained from EMerk, and the purities of the above chemicals were checked by the density measurements at different temperature and were compared with available literature values. The binary liquid mixtures of different known composition were prepared by mole fraction basis. The density and ultrasonic velocity were measured as a function of the binary liquid mixture at 303, 313,323K. The densities of liquid mixtures are measured by employing monopan balance. Fixed frequency ultrasonic interferometer (2MHz) has been used to measure the ultrasonic velocity with an accuracy of $\pm 0.01 ms^{-1}$. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell make up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1K.

3. Theory and Calculation

By using velocity and density data, thermodynamic parameters such as adiabatic compressibility and free length of binary liquid mixtures have been calculated, is given by relation,

$$\beta_a = (\rho u^2)^{-1} \quad \text{.....1.}$$

$$L_{Mix} = 2(V_m - X_1 V_0^{\,1} + X_2 V_0^{\,2} / X_1 Y_1 + X_2 Y_2) \quad \text{.....2.}$$

Molar volume of the binary mixtures is calculated by,

$$V_m = (X_1 M_1 + X_2 M_2)/ \rho \quad \text{.....3.}$$

Where X_1, X_2 represents the molar concentration of 1 and 2 liquid.

Excess parameters have been calculated by using formula,

$$A^E = A_{Exp} - A_{Ideal} \quad \text{.....4.}$$

According to kalidoss revised free length theory (rflt) intermolecular free length is given by relation,

$$Lf_{(rflt)} = 2\,(\sum XiAiMi/ \rho_{mix} - \sum XiAiV_{oi}) / X_i A_i F_i Y_i \quad \text{.....5.}$$

Where A_i and F_i are association and shape factors of i^{th} component in the mixtures. A_i = 1,2,3… refers to the monomeric , dimetic, trimeric.. of molecules X_i is mole fraction and M_i represents molecular weight of the i^{th} components in liquid mixtures.

Ultrasonic velocity using flt and rflt have been obtained by,

$u = K/\rho^{1/2} L_f$ ……..6.

$\chi^2 = \sum \{\frac{(O-E)2}{E}\}$ …… 7.

Statistical Chi-square (χ^2) test is given by relation,

Table 1: Experimental and theoretical velocity (u) m/s at temp 303K-323K
System:1-Butanol+Pyridine

		303K			313K			323K	
X	u(expt)	u(flt)	u(rflt)	u(expt)	u(flt)	u(rflt)	u(expt)	u(flt)	u(rflt)
0.1	1310.55	1352.28	1313.05	1269.85	1311.11	1274.3	1229.05	1269.43	1234.94
0.2	1321.1	1383.17	1312.67	1279.7	1341.49	1275.19	1238.6	1299.29	1237.02
0.3	1331.65	1410.19	1316.57	1289.55	1368.14	1279.91	1248.15	1325.55	1242.49
0.4	1342.2	1432.73	1324.43	1299.4	1390.43	1288.17	1257.7	1347.59	1251.13
0.5	1352.75	1450.2	1336.01	1309.25	1407.79	1299.78	1267.25	1364.84	1262.77
0.6	1363.3	1462.07	1351.15	1319.1	1419.69	1314.61	1276.8	1376.77	1277.31
0.7	1373.85	1467.91	1369.78	1328.95	1425.68	1332.6	1286.35	1382.93	1294.7
0.8	1384.4	1467.38	1391.87	1338.8	1425.43	1353.72	1295.9	1382.96	1314.91
0.9	1394.95	1460.29	1417.45	1348.65	1418.74	1378.02	1305.45	1376.67	1337.99
		^{2}=43.63	χ^2=1.19		χ^2=46.83	χ^2=1.10		χ^2=47.85	χ^2=1.25

System: Toluene + Pyridine

		303K			**313K**			**323K**	
X	u(expt)	u(flt)	u(rflt)	u(expt)	u(flt)	u(rflt)	u(expt)	u(flt)	u(rflt)
0.1	1266.6	1378.85	1326.65	1258	1336.13	1287.93	1219	1293.17	1248.88
0.2	1309.5	1435.52	1335.49	1266	1389.29	1296.96	1229	1343.03	1257.89
0.3	1321.5	1486.77	1345.51	1279	1437.36	1307.06	1242.5	1388.14	1268.04
0.4	1334	1529.8	1356.68	1291.5	1477.83	1318.19	1253.5	1426.22	1279.11
0.5	1342.5	1561.48	1368.97	1303	1507.84	1330.33	1263	1454.66	1291.08
0.6	1355.5	1578.47	1382.36	1313	1524.35	1343.44	1272	1470.71	1303.93
0.7	1366.5	1577.57	1396.82	1323	1524.4	1357.53	1285	1471.62	1317.64
0.8	1379.5	1556.13	1412.35	1332.5	1505.51	1372.57	1296	1455.06	1332.23
0.9	1390	1512.54	1428.95	1345	1466.02	1388.58	1307	1419.37	1347.67
		χ^2=209.89	χ^2=7.85		χ^2=193.58	χ^2=7.43		χ^2=172.35	χ^2=6.99

Table: 2.Experimental and theoretical free length (L_f) 10^{-10}m at temp 303K-323K
System: 1-Butanol+Pyridine

		303K			**313K**			**323K**	
X	L_f(expt)	L_f(flt)	L_f(rflt)	L_f(expt)	L_f(flt)	L_f(rflt)	L_f(expt)	L_f(flt)	L_f(rflt)
0.1	0.5325	0.5161	0.5315	0.5643	0.5466	0.5624	0.5977	0.5787	0.5949
0.2	0.5228	0.4993	0.5262	0.5541	0.5285	0.556	0.5867	0.5593	0.5887
0.3	0.5134	0.4848	0.5293	0.5441	0.5129	5482	0.576	0.5424	0.5687
0.4	0.5044	0.4725	0.5111	0.5345	0.4995	0.5392	0.5857	0.528	0.5577
0.5	0.4956	0.4623	0.5018	0.5253	0.4885	0.5291	0.5557	0.516	0.5458
0.6	0.4871	0.4542	0.4914	0.5163	0.4797	0.518	0.5461	0.5064	0.5458
0.7	0.4788	0.4481	0.4802	0.5075	0.4731	0.5061	0.5367	0.4992	0.5332
0.8	0.4708	0.4442	0.4683	0.4991	0.4687	0.4936	0.5276	0.4944	0.52
0.9	0.4631	0.4423	0.4557	0.4909	0.4666	0.4804	0.5188	0.492	0.5062

System: Toluene + Pyridine

		303K			**313K**			**323K**	
X	L_f(expt)	L_f(flt)	L_f(rflt)	L_f(expt)	L_f(flt)	L_f(rflt)	L_f(expt)	L_f(flt)	L_f(rflt)
0.1	0.5316	0.501	0.5207	0.563	0.5301	0.5499	0.5947	0.5996	0.5805
0.2	0.5228	0.4769	0.5126	0.5544	0.5052	0.5411	0.5844	0.592	0.571
0.3	0.5135	0.4564	0.5043	0.5438	0.4839	0.5322	0.5729	0.5839	0.5613
0.4	0.5042	0.4397	0.4958	0.5339	0.4666	0.5231	0.5628	0.5754	0.5516
0.5	0.4968	0.4271	0.4872	0.5246	0.4533	0.5138	0.5538	0.5663	0.5417
0.6	0.4879	0.419	0.4784	0.5162	0.4446	0.5045	0.5452	0.5566	0.5318
0.7	0.4799	0.4157	0.4695	0.508	0.4409	0.4951	0.5351	0.5462	0.5219
0.8	0.4716	0.418	0.4606	0.5003	0.4428	0.4857	0.5262	0.5351	0.5119
0.9	0.4643	0.4266	0.4516	0.4916	0.4511	0.4762	0.5175	0.5232	0.5019

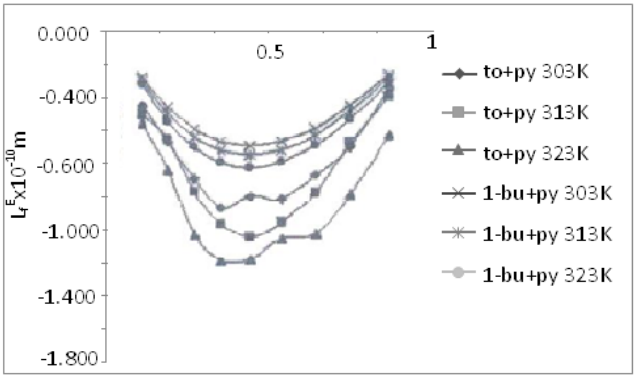

Figure 1: Mole fraction Vs excess free length

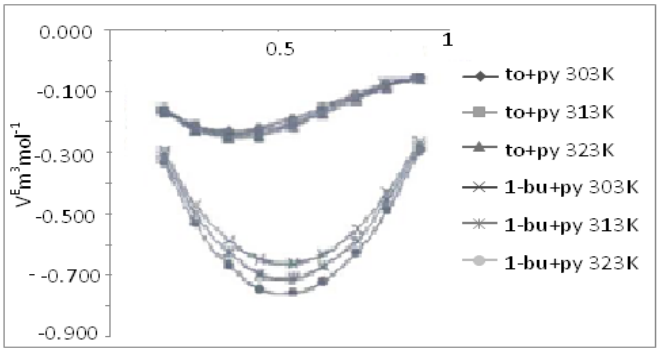

Figure 2: Volume fraction Vs excess adiabatic compressibility

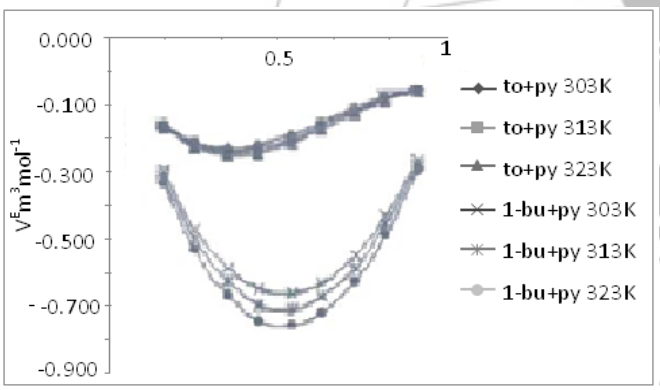

Figure 3: Volume fraction Vs excess molar volume

4. Result and Discussion

The tables 1 and 2 provide the experimentally and theoretically determined ultrasonic velocity (u) for the binary systems of 1-butanol+pyridine and toluene+pyridine at 303,313and 323K.The variation of ultrasonic velocity in a mixture depends up on the increase (or) decrease of intermolecular free length after mixing the components. On the basis of a model, for sound propagation proposed by Eyring and Kincaid[14] ultrasonic velocity should decrease, if the intermolecular free length increase and vice-versa. This is in fact observed in the present investigation for both the liquid systems. The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures.

Ultrasonic velocity in both the systems is increased and almost linear with mole concentration of pyridine, flt and rflt are applied to both the systems at three different temperatures. Theoretical sound velocities have been calculated by using Jacobson's free length theory (flt) and Kalidoss revised free length theory (rflt) (table1) shows the variation of $u_{(expt)}$ $u_{(flt)}$ and $u_{(rflt)}$ with mole fraction. While applying revised free length theory, different shape combination and thermostatic state of liquid are considered such as monomer, dimer, trimer. In case of 1-butanol-pyridine system, minimum Chi-square (χ^2) value has been obtained by considering spherical + spherical combination and thermostatic state as toluene in monomer state and pyridine in dimer state. In both the systems cluster of pyridine may be reducing the volume giving negative $V^{E.}$.By considering minimum χ^2 value of thermostatic state theoretical ultrasonic velocity u(rflt) have been calculated. In both the systems it reveals that there is close agreement between theoretical ultrasonic velocity calculated according to revised free length theory and from the experiment. The deviation in sound velocities is large due to flt than rflt. From table 1. It has been observed that, in case of 1-butanol-pyridine system, χ^2 value at 303K for u(flt) is 43.63 and for (rflt) it is 1.19 . Similarly toluene- pyridine system χ^2 value at 303K for u(flt) is 209.89 and for u(flt) is 7.85, it reveals that u(rflt) values closely agree with u(expt) compared to u(flt) values . Also other values Chi-square (χ^2) shows that revised free length theory (rflt) is applicable than free length theory in binary mixtures of 1-butanol, toluene with pyridine.

The sign and magnitude of deviation of excess properties depend on strength of interaction between unlike molecules. That is in order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The negative values of β^E is associated with a structure-forming tendency, while positive values are an indication of structure-breaking tendency due to heteromolecular interaction between the component molecules of the mixtures. The positive values of excess adiabatic compressibility which indicates the loosely packed molecules in the mixtures resulting due to shape and size. The sign of the V^E depends on the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are (i) specific interactions between the component molecules and (ii) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavourable geometric fitting and electrostatic repulsion. The negative values of excess free volume in both the systems assert that the combined effect of the factors responsible for volume contraction and vice-versa, negative values of excess free volume suggesting the specific interactions among unlike molecules. From fig 2 & 3, in1-butanol-pyridine thermodynamic parameters β_a^E ,V^E decreases with the mole fraction and the minima in both figures lie at X= 0.5 such variation indicate an attractive heteromolecular AB interaction leading to association of the molecules, in toluene+pyridine system both are negative, predicts

association with attractive interaction. As the minima in both the graphs lie in the first half part, it predicts that AA interaction must be stronger than AB interaction and dipole-induce dipole intermolecular forces exist between them. L_f^E indicate that sound waves cover long distances due to decrease in intermolecular free length describing the dominant nature of hydrogen bond interaction between unlike molecules. Excess negative (fig.1) values of free length L_f^E support the attractive interaction in the mixture.

5. Conclusion

Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interactions in the liquid mixtures. The evaluated ultrasonic excess values of binary mixtures of 1-butanol-pyridine at 303, 313 and 323K which may eventually concluded that there exist AB type molecular interaction between 1-butanol & pyridine and AA type interaction between toluene+pyridine mixtures. From the result chi-square (χ^2) test our present study also predicts revised free length theory (rflt) is applicable to both the liquid systems.

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