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# Study of Thermoacoustic Parameters and Statistical Analysis of Liquid State Therories

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**Abstract:** *Molecular interaction in binary liquid mixtures can be evaluated from the thermodynamic properties of the liquid mixture. Nature of interaction of liquid molecules can be explain by various liquid state theories, such as Collision factor theory, Free length theory, Eyring's significant structure theory, Flory theory etc., In present work experimental parameters such as ultrasonic velocity (U), density (ρ) of binary mixtures of p-Xylene-Piperidine and Tolune-Piperidine has been measured over the entire range of composition at different temperatures 303,313,323K. The observed experimental data have been utilized to evaluate thermo-acoustical parameter ie. adiabatic compressibility βa, free length $L_f$ molar volume V etc., Theoretical ultrasonic velocities calculated by applying Jacobson's free length theory and Kalidoss revised free length theory, statistical analysis carried out by applying Chi-square ($\chi^2$) test for both the liquid systems to verify the applicability of liquid state theories..*

**Keywords:** Thermo acoustic parameters, Chi-square ($\chi^2$) test.

## I. INTRODUCTION

The molecular behavior of can be studied in the liquid state which is having importance in the activities of various leaving and non leaving things. There are various methods to study the molecular behavior of liquid. Ultrasonic interferometric study have played very important role and found easier way to investigate the characteristics of the molecules in the pure liquids and their mixture. Ultrasonic velocity depends on the intermolecular distance that is free length, and it varies with the concentration of solvent in case of binary or ternary liquid system, it also changes with the temperature. Therefore it provides the nature of intermolecular behavior existing between the components of the liquid and its mixtures. The organic liquids like p-Xylene, Tolune, and Piperidine are having many applications in the different fields like paint, rubber and chemical industries. To understand the molecular interaction between liquid mixtures of these organic compound, ultrasonic velocity by interferometric method, and density of binary mixture at different temperature find out and these data has been used to calculate thermo acoustic parameters like free length adiabatic compressibility and molar volume . Jacobson's free length theory (flt)[1] Eyring significant structure theory [2] has been applied to various liquid mixtures by many workers [3-7] to evaluate ultrasonic velocities in liquids. Kalidoss incorporated thermodynamic state and shape factor, Revised Jacobson free length theory found helpful to predict ultrasonic velocities in liquid mixtures better as compare to free length theory.

## II. EXPERIMENTAL METHOD

The chemicals p-Xylene, Tolune, and Piperidine are used are of AR grade (E-Merk) with 99-99.5 % purity, which is verified by the density measurements at different temperature and were compared with available literature values. Fixed frequency ultrasonic (M-81) interferometer (2MHz) has been used to measure the ultrasonic velocity with an accuracy of $\pm 0.01 ms^{-1}$ at different temperature by circulating constant temperature water from double wall glass cell. The densities of liquid mixtures are measured at different temperature by employing monopan balance. The accuracy in the temperature measurement is $\pm 0.1^0$C.

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

$$L_f = (\beta_a)^{-1/2}$$

Where, $K = (93.875 + 0.375\ T) \times 10^{-8}$, K – is temperature dependent constant

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$L_{f\,(Mix)}=2(V_m-X_1V_0^1+X_2V_0^2/X_1Y_1+X_2Y_2)$

Molar volume of the binary mixtures is calculated by,

$V_m=(X_1M_1+X_2M_2)/\rho$

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

Excess parameters of binary liquid mixtures have been calculated by using formula,

$A^E=A_{Exp}-A_{Ideal}$

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

$L_{f\,(rflt)}=2\,(\sum XiAiMi/\rho_{mix}-\sum XiAiV_{oi})/X_iA_iF_iY_i$

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, dimeric, 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,

$u=(K/\rho)^{1/2}L_f$

Statistical Chi-square ($\chi^2$) test is given by relation,

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

**Table 1:** Experimental and theoretical velocity (u) m/s at temp 303K-323K

**a. System: p-Xylene-Piperidine**

| | | 303K | | | 313K | | | 323K | |
|---|---|---|---|---|---|---|---|---|---|
| x | u(expt) | u(flt) | u(rflt) | u(expt) | u(flt) | u(rflt) | u(expt) | u(flt) | u(rflt) |
| 0.1 | 1367.5 | 1382.9 | 1370.7 | 1326.8 | 1346.2 | 1332.7 | 1295.5 | 1308.9 | 1294.4 |
| 0.2 | 1364.5 | 1387 | 1365 | 1323.2 | 1350.8 | 1326.6 | 1291.4 | 1314.1 | 1287.9 |
| 0.3 | 1361.5 | 1389.6 | 1360.4 | 1319.5 | 1353.9 | 1321.6 | 1287.4 | 1317.5 | 1282.6 |
| 0.4 | 1368.5 | 1390.7 | 1356.8 | 1315.9 | 1355.2 | 1317.7 | 1283.3 | 1318.9 | 1278.4 |
| 0.5 | 1355.5 | 1390.1 | 1354.1 | 1312.2 | 1354.4 | 1314.7 | 1279.3 | 1318.2 | 1275.1 |
| 0.6 | 1352.5 | 1387.3 | 1352.1 | 1308.6 | 1351.4 | 1312.5 | 1275.2 | 1314.9 | 1272.6 |
| 0.7 | 1349.5 | 1382.4 | 1350.1 | 1304.9 | 1345.9 | 1311.1 | 1271.2 | 1308.8 | 1270.9 |
| 0.8 | 1346.5 | 1374.9 | 1350.6 | 1301.3 | 1337.5 | 1310.4 | 1267.1 | 1299.6 | 1270.1 |
| 0.9 | 1343.5 | 1364.6 | 1350.5 | 1297.6 | 1326 | 1310.4 | 1263.1 | 1286.8 | 1269.8 |
| | | $\chi^2$=5.3 | $\chi^2$=0.06 | | $\chi^2$=8.4 | $\chi^2$=0.27 | | $\chi^2$=6.7 | $\chi^2$=0.12 |

**b. System: Tolune + Piperidine**

| | | 303K | | | 313K | | | 323K | |
|---|---|---|---|---|---|---|---|---|---|
| X | u(expt) | u(flt) | u(rflt) | u(expt) | u(flt) | u(rflt) | u(expt) | u(flt) | u(rflt) |
| 0.1 | 1291.9 | 1327.8 | 1339.8 | 1249.9 | 1288.5 | 1271.2 | 1211.3 | 1248.7 | 1232.1 |
| 0.2 | 1297.3 | 1335.6 | 1304.6 | 1254.8 | 1296.1 | 1266.3 | 1216.6 | 1256.1 | 1227.4 |
| 0.3 | 1302.7 | 1342.31 | 1302.8 | 1259.7 | 1302.6 | 1264.6 | 1221.9 | 1262.4 | 1225.8 |
| 0.4 | 1308 | 1347.8 | 1303.8 | 1264.6 | 1303.9 | 1265.5 | 1227.2 | 1267.6 | 1226.7 |
| 0.5 | 1313.5 | 1352.1 | 1307.2 | 1269.5 | 1312.1 | 1268.8 | 1232.5 | 1271.6 | 1229.8 |
| 0.6 | 1318.9 | 1355.1 | 1312.6 | 1274.4 | 1314.9 | 1274 | 1237.8 | 1274.3 | 1234.8 |
| 0.7 | 1324.3 | 1356.5 | 1319.9 | 1279.3 | 1316.3 | 1280.9 | 1243.1 | 1275.6 | 1241.5 |
| 0.8 | 1329.7 | 1356.4 | 1328.8 | 1284.2 | 1316.2 | 1289.6 | 1248.4 | 1275.4 | 1249.7 |
| 0.9 | 1335.1 | 1354.7 | 1339.4 | 1289.1 | 1314.4 | 1299.6 | 1253.7 | 1273.6 | 1259.3 |
| | | $\chi^2$=8.056 | $\chi^2$=0.39 | | $\chi^2$=10.25 | $\chi^2$=0.59 | | $\chi^2$=8.904 | $\chi^2$=0.5 |

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**Table 2:** Experimental and theoretical free length ($L_f$) $10^{-10}$m at temp 303K-323K

**a. System: p-Xylene-Piperidine**

| | 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 | 0.5040 | 0.4983 | 0.5028 | 0.5333 | 0.5256 | 0.5309 | 0.5598 | 0.5541 | 0.5603 |
| 0.2 | 0.5044 | 0.4962 | 0.5042 | 0.5339 | 0.5229 | 0.5325 | 0.5605 | 0.5508 | 0.5620 |
| 0.3 | 0.5048 | 0.4946 | 0.5052 | 0.5345 | 0.5209 | 0.5336 | 0.5612 | 0.5484 | 0.5633 |
| 0.4 | 0.5052 | 0.4935 | 0.5059 | 0.5351 | 0.5196 | 0.5343 | 0.5619 | 0.5467 | 0.5641 |
| 0.5 | 0.5057 | 0.4931 | 0.5062 | 0.5357 | 0.5190 | 0.5347 | 0.5626 | 0.5460 | 0.5645 |
| 0.6 | 0.5061 | 0.4934 | 0.5062 | 0.5363 | 0.5193 | 0.5347 | 0.5633 | 0.5463 | 0.5645 |
| 0.7 | 0.5065 | 0.4945 | 0.5060 | 0.5370 | 0.5206 | 0.5344 | 0.5641 | 0.5478 | 0.5642 |
| 0.8 | 0.5070 | 0.4965 | 0.5055 | 0.5376 | 0.5231 | 0.5339 | 0.5648 | 0.5507 | 0.5635 |
| 0.9 | 0.5074 | 0.4996 | 0.5048 | 0.5383 | 0.5268 | 0.5330 | 0.5656 | 0.5551 | 0.5626 |

**b. System: Tolune + Piperidine**

| | 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 | 0.5384 | 0.5238 | 0.531 | 0.5705 | 0.5534 | 0.5609 | 0.6025 | 0.5844 | 0.5923 |
| 0.2 | 0.5349 | 0.5195 | 0.5318 | 0.5668 | 0.5488 | 0.5617 | 0.5983 | 0.5795 | 0.593 |
| 0.3 | 0.5314 | 0.5157 | 0.5313 | 0.5632 | 0.5447 | 0.561 | 0.5941 | 0.5751 | 0.5922 |
| 0.4 | 0.5279 | 0.5123 | 0.5296 | 0.5596 | 0.5411 | 0.5592 | 0.59 | 0.5712 | 0.5902 |
| 0.5 | 0.5245 | 0.5095 | 0.527 | 0.5561 | 0.5381 | 0.5564 | 0.5806 | 0.568 | 0.5872 |
| 0.6 | 0.5211 | 0.5072 | 0.5236 | 0.5526 | 0.5356 | 0.5528 | 0.582 | 0.5653 | 0.5833 |
| 0.7 | 0.5177 | 0.5054 | 0.5194 | 0.5491 | 0.5337 | 0.5484 | 0.578 | 0.5633 | 0.5787 |
| 0.8 | 0.5144 | 0.5043 | 0.5147 | 0.5457 | 0.5324 | 0.5434 | 0.5741 | 0.5619 | 0.5735 |
| 0.9 | 0.5111 | 0.5037 | 0.5095 | 0.5423 | 0.5318 | 0.5379 | 0.5702 | 0.5613 | 0.5676 |

## III. Result and Discussion

Ultrasonic velocity (u) of binary liquid mixtures of p-Xylene-Piperidine and Tolune - Piperidine at temperature 303, 313 and 323K, measured experimentally and theoretically given in table no.1 (a&b) and calculated intermolecular fee length is given in table no.2 (a&b).In present study it has been observed that thermodynamic excess parameters are changes with temperature. Ultrasonic velocity in case of p-Xylene-Piperidine is decreased with mole concentration of Piperidine, and the value of free length is increasing with the mole concentration of Piperidine which supports the interaction between the molecules with the formation of large cluster in the mixture and for the Toluene- Piperidine liquid system ultrasonic velocity is increases with mole concentration and calculated values of free length decreases with increasing mole concentration of Piperidine which predicts the hetromolecular interaction exiting in the mixture. Liquid state theories, ie Jacobson's free length theory (flt) and Kalidoss revised free length theory (rflt) has been applied to both the systems at different temperatures 303K,313K,323K . Theoretical values of ultrasonic velocity of $u_{(flt)}$ $u_{(rflt)}$ given in table-1(a&b) . Revised free length theory applied by considering different shape combination and thermostatic state such as monomer, dimer, trimer of liquid has been considered. In case of both the system, minimum chi-square ($\chi^2$) value has been obtained by considering spherical- spherical shape combination. By considering minimum $\chi^2$ value of thermostatic state theoretical ultrasonic velocity (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 (rft) and experimental velocity. In case of p-Xylene-Piperidine mixture there is quite a good agreement between experimental and theoretical (rflt) sound velocities, giving minimum value of $\chi^2$ is 0.06 at 303K,0.27 at 313K ,0.12

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at323K. Minimum $\chi^2$ is obtained when p-Xylene and Piperidine molecules are assumed to have spherical shape where as p-Xylene is monomer and Piperidine is dimer thermostatic state. In Toluene+ Piperidine system produced good result of new free length theory giving minimum $\chi^2$value 0.39at303K, 0.59 at 313 K , 0.5 at 323K ,by considering spherical shapes combination and Toluene is monomer while Piperidine is dimer thermostatic state.

## V. CONCLUSION

Ultrasonic technique is found very helpful to characterize the thermoacoustic properties of the liquid which gives the information about the molecular interaction in the liquid mixtures,. By considering different shape combination of molecules and by applying statistical chi-square test ($\chi^2$) it has been observed that, revised free length theory (rflt) is applicable to p-Xylene-Piperidine and Tolune-Piperidine systems.

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