FTIR Spectroscopic Analysis in Comparison with Acoustical Nature in Mono, Di and Tri Methyl Substituent Liquid Mixtures

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Abstract. FTIR spectroscopic study is a useful method to identify the functional groups and to know the nature of bond between different liquid mixtures. In the present case it is paid much interest towards the variation in the acoustical parameters with the bond strength in binary liquid mixtures. The work was keenly performed to study the acoustical variations bond strength with methyl group substituent in a liquid mixture containing aniline + toluene (mono methyl group), aniline + o-xylene (di methyl group) and aniline + mesitylene (tri methyl group) at ratio of different mole fractions. Ultrasonic velocities, and densities in binary liquid mixtures containing (aniline + toluene), (aniline + o-xylene) and (aniline + mesitylene) along with their acoustical parameters are studied at room temperature (T= 303.15 K) with different mole fractions of aniline. The results obtained are compared and discussed in terms of molecular associations between the component molecules in terms of bond strength (C-N, C-H & N-H) of the binary liquid mixtures. The results thus derived are verified by using Hooke's law.

Keywords: toluene; o-xylene; mesitylene; aniline; absorbance; wave number; IR spectra.

1. Introduction
In elucidating the structural associations amid the constituents of liquid mixture the study of thermo-acoustical parameters in binary liquid mixture has proved to be useful. Recent investigations on temperature dependant acoustical parameters are available in this technology with variation of composition and temperature. FTIR Studies with thermo-acoustical parameters are useful to understand different kinds of association, the molecular packing, typical behavior and various types of intermolecular interactions in the liquid mixtures. In the present paper, values of thermo-acoustical parameters and their variations with mole fraction of aniline in binary liquid mixtures containing (aniline + toluene), (aniline + o-xylene) and (aniline + mesitylene) at room temperature T= 303.15K have been reported. An attempt is also made to identify the groups that will involve in interactions by FTIR analysis.

2. Materials and Methods
In the present work using the binary solutions, the blends of different compositions 8:0, 6:2, 5:3, 4:4, 3:5, 2:6, 0:8 were prepared. The complete vacuum dried cast films were employed. The spectra were recorded using Alpha T (Bruker) FTIR spectrophotometer. The chemicals used SDFCL chemicals (aniline) and MERCK chemicals (Toluene, o-xylene and Mesitylene) are purified by standard procedure.
3. Theory
Thermo-acoustical parameters such as adiabatic compressibility (β), intermolecular free length (Lₐ), acoustical impedance (Z) and relaxation strength (r) have been calculated from the experimentally measured values of ultrasonic velocities, viscosities and densities by using the following relations.

\[ \beta = \frac{1}{U^2 \rho} \quad \text{m}^2/N \quad \text{-------- (1)} \]
\[ L_a = \frac{k \beta^{1/2}}{A} \quad \text{-------- (2)} \]
\[ Z = \frac{U \rho}{Kg.m^2.s^{-1}} \quad \text{-------- (3)} \]

Where, U is the ultrasonic velocity and ρ is the density of the solution. Where, k is Jacobson’s constant.

\[ r = 1 - \frac{U}{U_{\infty}} \quad \text{-------- (4)} \]

Where \( U_{\infty} = 1.6 \times 10^7 \) m/s.

Hooke’s law:-
\[ \varphi = \frac{1}{2 \kappa} \left[ \frac{\left(m_1 + m_2\right)}{m_1 m_2} \right]^{1/2} \quad \text{cm}^{-1} \quad \text{-------- (5)} \]

f = force constant or bond strength, m = masses of atoms.

4. Results and Discussions
The experimental values of Ultrasonic velocities (U) and Densities (ρ) of the three binary liquid mixtures over the mole fraction of aniline at T=303.15 K are given in the Table 1.

| Table 1. Ultrasonic Velocities and Densities of three liquid mixtures at T = 303.15K. |
|---------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Aniline + Toluene Mixture       | Aniline + o-Xylene Mixture                       | Aniline + Mesitylene Mixture                     |
| Mole fraction (X)              | Ultrasonic Velocity (U)                         | Density (ρ)                                    |
| 0.0000                         | 1273.52                                         | 867.11                                          |
| 0.1145                         | 1303.82                                         | 880.49                                          |
| 0.2254                         | 1332.45                                         | 895.72                                          |
| 0.3328                         | 1361.76                                         | 915.69                                          |
| 0.4369                         | 1392.23                                         | 935.69                                          |
| 0.5379                         | 1423.36                                         | 954.89                                          |
| 0.6358                         | 1453.47                                         | 974.89                                          |
| 0.7309                         | 1488.10                                         | 991.69                                          |
| 0.8232                         | 1527.73                                         | 1005.16                                         |
| 0.9129                         | 1567.36                                         | 1014.39                                         |
| 1.0000                         | 1614.15                                         | 1020.14                                         |
|                                  | 1339.93                                         | 870.72                                          |
|                                  | 1370.23                                         | 882.49                                          |
|                                  | 1398.86                                         | 897.72                                          |
|                                  | 1428.17                                         | 913.69                                          |
|                                  | 1458.64                                         | 930.69                                          |
|                                  | 1489.77                                         | 944.89                                          |
|                                  | 1519.88                                         | 957.89                                          |
|                                  | 1544.51                                         | 974.69                                          |
|                                  | 1574.14                                         | 989.40                                          |
|                                  | 1574.92                                         | 1003.97                                         |
|                                  | 1575.55                                         | 1017.20                                         |
|                                  | 1614.15                                         | 1020.14                                         |

The evaluated values of thermo-acoustical parameters such as adiabatic compressibility (β), intermolecular free length (Lₐ), acoustical impedance (Z) and relaxation strength (r) for the above
binary liquid mixtures over the mole fraction range of aniline at room temperature $T= 303.15 \text{ K}$ are given in the Table- 2, 3 & 4.

Table 2. Aniline + Toluene at $T= 303.15\text{K}$.

| Mole fraction X | Adiabatic Compressibility ($\beta$) | Inter molecular Free length ($L_f$) | Acoustic Impedance ($Z$) | Relaxation Strength ($r$) |
|-----------------|-------------------------------------|------------------------------------|--------------------------|--------------------------|
| 0.0000          | 71.1073                             | 0.1672                             | 1.1043                   | 0.910784                 |
| 0.1145          | 66.8098                             | 0.1621                             | 1.1480                   | 0.909729                 |
| 0.2254          | 62.8819                             | 0.1572                             | 1.1935                   | 0.908743                 |
| 0.3328          | 58.8912                             | 0.1522                             | 1.2470                   | 0.907745                 |
| 0.4369          | 55.1374                             | 0.1472                             | 1.3027                   | 0.906719                 |
| 0.5379          | 51.6913                             | 0.1426                             | 1.3592                   | 0.905681                 |
| 0.6358          | 48.5548                             | 0.1382                             | 1.4170                   | 0.904689                 |
| 0.7309          | 45.5365                             | 0.1338                             | 1.4757                   | 0.90356                  |
| 0.8232          | 42.6257                             | 0.1295                             | 1.5356                   | 0.902285                 |
| 0.9129          | 40.1289                             | 0.1256                             | 1.5899                   | 0.901025                 |
| 1.0000          | 37.6229                             | 0.1216                             | 1.6467                   | 0.899559                 |

Table 3. Aniline + o-Xylene at $T= 303.15\text{K}$.

| Mole fraction X | Adiabatic Compressibility ($\beta$) | Inter molecular Free length ($L_f$) | Acoustic Impedance ($Z$) | Relaxation Strength ($r$) |
|-----------------|-------------------------------------|------------------------------------|--------------------------|--------------------------|
| 0.0000          | 63.9672                             | 0.1586                             | 1.1667                   | 0.908487                 |
| 0.0146          | 60.3536                             | 0.1540                             | 1.2092                   | 0.907458                 |
| 0.0323          | 56.9260                             | 0.1496                             | 1.2558                   | 0.906497                 |
| 0.0541          | 53.6588                             | 0.1452                             | 1.3049                   | 0.905522                 |
| 0.0816          | 50.5009                             | 0.1409                             | 1.3575                   | 0.90452                  |
| 0.1176          | 47.6848                             | 0.1369                             | 1.4077                   | 0.903506                 |
| 0.1667          | 45.1924                             | 0.1333                             | 1.4559                   | 0.902536                 |
| 0.2373          | 43.0083                             | 0.1300                             | 1.5054                   | 0.901749                 |
| 0.3478          | 40.7888                             | 0.1266                             | 1.5575                   | 0.900811                 |
| 0.5455          | 38.8157                             | 0.1235                             | 1.6094                   | 0.899976                 |
| 1.0000          | 37.6229                             | 0.1216                             | 1.6467                   | 0.899559                 |

Table 4. Aniline + Mesitylene at $T= 303.15\text{K}$.

| Mole fraction X | Adiabatic Compressibility ($\beta$) | Inter molecular Free length ($L_f$) | Acoustic Impedance ($Z$) | Relaxation Strength ($r$) |
|-----------------|-------------------------------------|------------------------------------|--------------------------|--------------------------|
| 0.0000          | 67.62                               | 0.1630                             | 1.13                     | 0.909372                 |
| 0.0166          | 63.33                               | 0.1578                             | 1.18                     | 0.908536                 |
| 0.0367          | 59.86                               | 0.1534                             | 1.22                     | 0.907529                 |
| 0.0613          | 55.91                               | 0.1483                             | 1.28                     | 0.906533                 |
| 0.0922          | 52.41                               | 0.1435                             | 1.34                     | 0.905548                 |
| 0.1322          | 49.18                               | 0.1391                             | 1.40                     | 0.904572                 |
| 0.1860          | 46.61                               | 0.1354                             | 1.44                     | 0.903607                 |
The computed wave number values from Hooke’s law along with experimentally observed values from IR Spectra are given in Table -5.

Table 5. Observed and computed wave number values of Bond strength in cm⁻¹.

| Bond Strength | Observed values (IR Spectra) Wave number cm⁻¹ | Computed values (Hooke’s Law) Wave number cm⁻¹ |
|--------------|-----------------------------------------------|-----------------------------------------------|
| C-H          | 3024-3029                                     | 3034.53                                       |
| N-H          | 3469-3220                                     | 3317.74                                       |
| C-N          | 1157-1250                                     | 1150.77                                       |

4.1 Variation of Adiabatic Compressibility:- From Table 2, 3 &4 it is observed that adiabatic compressibility (β) with respect to the mole fraction of aniline ranging from 0 to 1 decrease with increase in mole fraction in all the three binary liquid mixtures. Same kind variations are observed by Ali and Nain in their binary mixtures and reported that there exist strong nature of interactions between the component molecules of liquid mixtures in all the three binary liquid mixtures.

4.2 Variation of Free length:- From the variations of intermolecular free length (Lf) with respect to the mole fraction of aniline in all the three liquid mixtures, it is observed that the value of intermolecular free length decreases with a change in mole fraction of aniline. The decrease in intermolecular free length (Lf) indicates strong intermolecular interactions between the components of the liquid mixture. According to a model proposed by Eyring Kincaid, ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing components. In the present study, similar results are observed.

4.3 Variation of Acoustic Impedance:- According to the variations of acoustical impedance (Z) with respect to the mole fraction of aniline in all the three binary liquid mixtures at room temperature, it is cleared that the value of acoustical impedance increases with the mole fraction of aniline which supports the strong molecular interactions as suggested by Garcia et al and Oswal et al. When an acoustic wave travels in a medium, there is a variation of pressure and instantaneous velocity from particle to particle. This is governed by the inertial and elastic properties of the medium.

4.4 Variation of Relaxation strength:- Relaxation strength is found to decrease with increase in concentration of aniline in all the three binary liquid mixtures. At a fixed concentration, it increases with temperature. In the present case, at lower mole fractions the relaxation strength is predominant than those on higher mole fractions. The increase in ‘r’ suggests the predominance of molecular interactions.

4.5 FTIR Spectra Analysis:- Different functional groups bend stretch and wag at different frequencies. A functional group will absorb light matches the frequency of stretching, bending or wagging. Hence IR spectra show absorption bands that enable to determine if certain functional groups are present in a molecule. The stronger the bond the higher the frequency/wave number and also the lighter the atoms the higher the frequency/wave number for identification of functional group. In the present liquid mixture of aniline with mono, di and tri methyl substituent, it is found that the wave number from
experimentally measured value comes out to be in the range of 3016-3029 cm$^{-1}$ which is in close agreement with the calculated value from Hooke’s law.

4.5.1 C-H Bond Stretching. In the case of mono methyl substituent (toluene) from Figure 1, the C-H bond stretch shows an absorption peak at 3029 cm$^{-1}$, also in the case of di methyl substituent (oxyylene) from Figure 2, the C-H bond stretch shows an absorption peak at 3024 cm$^{-1}$ and in the case of tri methyl substituent (mesitylene) from Figure 3, the C-H bond stretch gives an absorption peak at 3027 cm$^{-1}$.

4.5.2 N-H, C-N Bond bending. It is observed in the functional group region that absorption peaks are also there in the range of 3469-3220 cm$^{-1}$ which indicate the presence of N-H bond stretch of amine group i.e., aniline. The constant absorption peaks in the finger print region suggest that there exists C-N bond bending in the range of 1157-1250 cm$^{-1}$.
Figure 1. IR spectra of Aniline + Toluene liquid mixture.
Figure 2. IR spectra of Aniline + o-Xylene liquid mixture.
Figure 3. IR spectra of Aniline + Mesitylene liquid mixture.
5. Conclusions
In the present study of mono, di and tri methyl substituent liquid mixtures with aniline, ultrasonic velocity, density and viscosity were measured. From the data, acoustical parameters were calculated and observed that there exists more molecular association strength among the component molecules. In addition to that when the liquid mixture with these methyl substituent is screened to IR studies, insists clearly about the stretching, bending and wagging of C-H, N-H and C-N bond in the liquid mixture. Graphically observed values from the components of mono, di, tri methyl substituent liquid mixtures with aniline.

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