# Excess Acoustical properties and Molecular interactions of ternary liquid mixtures of N, N-dimethyl formamide(N,N-DMF), 1 propanol and n- hexane at different temperatures using ultrasonic techniques

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## Abstract

*The physical parameters like density (ρ), ultrasonic velocity (U) and viscosity (η) have been experimentally measured for the Ternary Liquid Mixture of N, N-dimethyl formamide (N,N-DMF) and 1 propanol in n-hexane at different temperatures viz. 303 K, 308 K, 313 K. The thermodynamic and acoustical parameters such as adiabatic compressibility(β), Gibb's free energy($\Delta G^0$), entropy($\Delta S$), absorption coefficient ($\alpha/f^2$), internal pressure($\pi_i$), cohesive energy(CE), free volume($V_f$), free length($L_f$), acoustic impedance(z), available volume($V_a$), viscous relaxation time and Lennard - Jones potential have been calculated from the experimental data.*

*The various excess properties including excess Ultrasonic velocity, excess acoustic impedance, excess free length, excess adiabatic compressibility, excess free volume and excess internal pressure were also computed. The variation of these parameters with respect to concentration and temperatures has been discussed in the light of molecular interaction.*

**Keywords**: Molecular interactions, ultrasonic velocity, ternary liquid mixture, excess adiabatic compressibility, internal pressure, excess acoustic impedance.

## Introduction

In recent years, the measurements of the ultrasonic velocity have been adequately employed for understanding the nature of molecular systems and physio-chemical behavior in liquid mixtures [10,12]. A number of empirical, semi-empirical and statistical theories have been developed by several workers. The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic methods[3]. These interactions help to understand the nature of the solute and solvent i.e. whether the solute modifies or distorts the structure of the solvent.

The measurement of ultrasonic speed enables the accurate determination of some useful acoustical and thermodynamic parameters and their excess functions which are highly sensitive to molecular interactions in liquid mixtures[1,7]. Thermodynamic and transport properties of binary and ternary mixtures with different organic liquids have been studied by many authors [14].

Although a large number of investigations are carried in liquid mixtures having DMF (or) benzene as one of the components, it is found that no work has been made so for to measure the ultrasonic velocity for the ternary liquid mixtures of N, N-DMF +1 propanol+n hexane. N, N-DMF is a polar molecule used in wide variety of reactions including electrophilic substitution, nucleophilic substitution, oxidation and reduction. N, N DMF is a versatile solvent, used in the separation of saturated and unsaturated hydrocarbons and serves as a solvent for many polymers [2,18].

Molecular interaction is associated with 1-alkanol hybrids which are one of the most unique components since the alkanol group is very polar [13]. Alcohols are associated organic liquids and are widely used as basic organic compounds for the synthesis of other organic compounds. Branching of the alkyl group attached to the hydroxyl group results in abnormal behavior of alcohols. In this present study, the authors report the acoustical properties namely absorption coefficient ($\alpha/f^2$), internal pressure($\pi_i$), cohesive energy(CE), free volume($V_f$), free length($L_f$), acoustic impedance(z), available volume($V_a$), adiabatic compressibility(β) etc., these are calculated from the experimental data from which the properties like excess ultrasonic velocity ($U^E$), excess acoustic impedance ($Z^E$), excess adiabatic compressibility($\beta^E$), excess intermolecular free length ($L^E_f$ ), excess internal pressure($\pi_i^E$) and excess free volume were computed.

This study emphasises with the aim of analysing the disruption or association in 1-propanol and the breaking or rupture or formation of bonds due to the dipole-dipole interactions or dipole-induced dipole interactions of N,N-DMF along with the interaction between the n hexane and the hydroxyl group of alcohol molecule. n-hexane is a good non polar solvent used in the separation techniques and in preparation of organolithiums etc. since it is very difficult to deprotonate.

Therefore, the present study has been undertaken to provide useful information regarding the molecular interactions possessed by the system of N,N-DMF, 1 propanol and n-hexane.

## Material and Methods

The ternary liquid mixture (N,N-DMF+1 propanol+n hexane) of various equimolar concentrations was prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9% obtained from E.Merck Ltd. (India). All the component liquids were purified by the standard methods. The density, viscosity and ultrasonic velocity were measured for various concentrations at different temperatures viz. 303 K, 308 K and 313 K keeping constant frequency of 2 MHz. Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model F-81, supplied by M/s Mittal Enterprises, New Delhi) with the accuracy of $\pm 0.1 ms^{-1}$. Water at desired temperature is circulated through the outer jacket of the double-walled measuring cell containing the experimental liquid.

The densities of the mixture were measured using a 10 ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 kgm^{-3}$. An ostwald viscometer (10 ml) with an accuracy of $\pm 0.001 Nsm^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ±0.1s.

## Theory and Calculations

Intermolecular free length ($L_f$), is calculated using the standard expression:

$$L_f = KT \beta^{1/2} \quad (1)$$

where KT is a temperature dependent constant known as Jacobson constant $\{K = (93.875 + 0.375 T) \times 10^{-8}\}$ and β is the adiabatic compressibility that can be calculated from the speed of sound (U) and the density of the medium (ρ) as:

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

The relation for free volume in terms of ultrasonic velocity and the viscosity (η) of liquid is:

$$V_f = (M_{eff}\, U / k\eta)^{1/2} \quad (3)$$

Expression for the determination of internal pressure $\pi_i$ by the use of free volume is:

$$\pi_i = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6}{}_{eff}) \quad (4)$$

where b stands for cubic packing which is assumed to be 2 for liquids and K is a dimensionless constant independent of temperature and nature of liquids and its value is $4.281 \times 10^9$, T is the absolute temperature and $M_{eff}$ is the effective molecular weight of the mixture. The viscous relaxation time was obtained by using the relation:

$$\tau = (4/3)\, \beta\, \eta \quad (5)$$

Gibbs free energy is calculated from the relation:

$$\Delta G = KT\ln(KT\tau/h) \quad (6)$$

where τ is the viscous relaxation time, K is the Boltzman constant, T is the absolute temperature and h is the Planck's constant.

The acoustic impedance is given by:

$$Z = U\rho \quad (7)$$

Absorption coefficient or attenuation coefficient is given by:

$$\alpha / f^2 = 8\pi^2\eta / 3\rho U^2 \quad (8)$$

where η, U and ρ are the viscosity, velocity and density of liquid respectively.

In order to study the non-ideality of the liquid mixtures, namely excess parameters (AE) of all the acoustic parameter were computed by:

$$AE = Aexp - Aid \quad (9)$$

where $Aid = \sum nAiXi$,

where Ai is any acoustical parameter and Xi is the mole fraction of the liquid components i.e. the excess parameters of the ultrasonic velocity, acoustic impedance and intermolecular free length were calculated using the equations:

$$U^E = u - (x_1u_1 + x_2u_2 + x_3u_3) \quad (10)$$

$$Z^E = (\rho u) - (x_1u_1\rho_1 + x_2u_2\rho_2 + x_3u_3\rho_3) \quad (11)$$

$$L_f^E = \frac{k}{(u^2\rho)^{1/2}} - \left[\frac{x_1k}{(u_1^2\rho_1)^{1/2}} + \frac{x_2k}{(u_2^2\rho_2)^{1/2}} + \frac{x_3k}{(u_3^2\rho_3)^{1/2}}\right] \quad (12)$$

where u and ρ denote the ultrasonic velocity and density for the mixture, $u_1$, $u_2$ and $u_3$ and $\rho_1$, $\rho_2$ and $\rho_3$ denote the ultrasonic velocities and densities for the pure components. k is Jacobson's constant.

The values of $U^E$, $Z^E$ and $L_f^E$ for each mixture have been fitted to the Redlich – Kister polynomial equation[16]:

$$Y^E = x(1-x)\sum_{i=1}^{10} a_i(1-2x)^{i-1} \quad (13)$$

The values of the coefficients $a_i$ were calculated by the method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficients i is an adjustable parameter for the best fit of the excess functions.

$$\sigma(Y^E) = \left[\frac{\sum(Y_{expt} - Y_{cal})}{n-p}\right]^{1/2} \quad (14)$$

where n is the number of experimental points, p is the number of parameters and $Y_{expt}$ and $Y_{cal}$ are the experimental and calculated excess parameters.

The values of $V_f^E$ is calculated using the following relation:

$$V_f^E = x_1M_1\left(\frac{1}{\rho}-\frac{1}{\rho_1}\right)+x_2M_2\left(\frac{1}{\rho}-\frac{1}{\rho_2}\right)+x_3M_3\left(\frac{1}{\rho}-\frac{1}{\rho_3}\right) \tag{15}$$

where $x_1M_1, x_2M_2, x_3M_3$ are mole fractions and molecular weights of components (N,N DMF,1 propanol and n hexane) respectively and $\rho_1$, $\rho_2$ and $\rho_3$ are densities of pure components (N, N DMF,1 propanol and n hexane) respectively and ρ is the density of the system under investigation.

The values of $\beta^E$ is calculated using the following relation:

$$\beta^E = \beta_s\text{-}(x_1\beta_1 + x_2\beta_2 + x_3\beta_3) \tag{16}$$

where $x_{1,}\, x_2$ and $x_3$ are mole fractions, $\beta^E$ *is the* excess adiabatic compressibility, $\beta_1, \beta_2$ and $\beta_3$ are the adiabatic compressibilities of pure components (N,N-DMF,1 propanol and n hexane respectively), $\beta_s$ is the adiabatic compressibility of the mixture.

Similarly excess internal pressures will also be calculated using the following relation:

$$\begin{aligned}\pi_i^E = {} & bRT\left(K_\eta/U\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \\ & -\left\{bRT\left(K_\eta/U_1\right)^{1/2}\left(\frac{\rho_1{}^{2/3}}{M_{1eff}^{7/6}}\right)+bRT\left(K_\eta/U_2\right)^{1/2}\left(\frac{\rho_2{}^{2/3}}{M_{2eff}^{7/6}}\right)+\right. \\ & \left. bRT\left(K_\eta/U_3\right)^{1/2}\left(\frac{\rho_3{}^{2/3}}{M_{3eff}^{7/6}}\right)\right\}\end{aligned} \tag{17}$$

where U $\rho$ M are velocity, density and molecular weight of the system respectively and $U_1\ \rho_1\ M_1$, $U_2\ \rho_2\ M_2$, $U_3\ \rho_3\ M_3$ are velocity, density and molecular weight of the pure components respectively.

## Results and Discussion

The experimentally measured values of density, viscosity and ultrasonic velocity for the mixture at 303K, 308K and 313 K were presented in table 1. Table 2 represents the excess values of acoustic impedance, adiabatic compressibility and free volume. Similarly, table 3 depicted the excess values of free length, ultrasonic velocity and internal pressure for the mixtures. In order to understand more about the interaction between the components of liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than the acoustical parameters like acoustic impedance, free length, adiabatic compressibility etc. These were calculated from the experimental values and the values were tabulated from tables 4 to 8 respectively for which limited discussions are provided in this study.

They (excess parameters) can yield an idea about the non-linearity/linearity of the system as association or other type of interactions. Table 9 revealed experimental values of density, viscosity and ultrasonic velocity for each pure component present in the ternary mixture and those values are found to be in good agreement with theoretical values.

From the table 1, it was observed that the ultrasonic velocity of the ternary liquid mixtures decreases with increasing temperature of the mixture with particular concentration while at the same temperature, it is noted that the ultrasonic velocity increases with respect to increase in concentration of the mixture. However, viscosity increases while the temperature increases and the density shows irregular trend with increasing the concentration as well as with increase in temperature.

From table 2 the excess acoustic impedance increases (considering the magnitude alone) with increasing the concentration of the mixture for the particular temperature and the same acoustic impedance decreases with rise in temperature at higher concentration of the mixture.

**Table 1**
**Experimental values of velocity, viscosity and Density for N, N-DMF+1 Propanol+n Hexane**

| S.N. | Conc. (M) X$10^{-3}$ | Velocity (U) $ms^{-1}$ | | | Viscosity (η)$Nsm^{-2}$ X$10^{-4}$ | | | Density (ρ) $Kgm^{-3}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 303 K | 308 K | 313 K | 303 K | 308 K | 313 K | 303 K | 308 K | 313 K |
| 1 | 1 | 1059.52 | 1035.12 | 1017.28 | 4.913 | 5.084 | 5.263 | 801 | 806 | 811 |
| 2 | 2 | 1060.22 | 1036.52 | 1017.92 | 4.927 | 5.097 | 5.274 | 801 | 806 | 811 |
| 3 | 3 | 1062.13 | 1037.22 | 1018.27 | 4.927 | 5.112 | 5.287 | 802 | 806 | 811 |
| 4 | 4 | 1063.27 | 1038.62 | 1018.66 | 4.991 | 5.129 | 5.251 | 808 | 807 | 811 |
| 5 | 5 | 1065.92 | 1039.13 | 1019.62 | 4.987 | 5.102 | 5.265 | 808 | 813 | 812 |
| 6 | 6 | 1066.16 | 1040.77 | 1019.92 | 4.956 | 5.171 | 5.265 | 802 | 813 | 811 |
| 7 | 7 | 1066.98 | 1041.70 | 1020.22 | 4.997 | 5.146 | 5.340 | 808 | 807 | 818 |
| 8 | 8 | 1067.22 | 1042.40 | 1020.66 | 4.989 | 5.196 | 5.229 | 808 | 819 | 812 |
| 9 | 9 | 1068.65 | 1042.86 | 1021.52 | 5.040 | 5.133 | 5.346 | 814 | 807 | 818 |
| 10 | 10 | 1068.96 | 1043.32 | 1021.80 | 5.053 | 5.227 | 5.409 | 814 | 817 | 818 |

**Table 2**
**Computed values of excess acoustic impedance adiabatic compressibility and free length for N, N-DMF+1 Propanol+n Hexane**

| S.N. | CON (M) X$10^{-3}$ | Excess Acoustic Impedance($Z^E$) Kg/($m^2$s) | | | Excess Adiabatic compressibility($\beta^E$) x$10^{-7}N^{-1}m^2$ | | | Excess Free length ($L^E_f$ ) x$10^{-10}$ $m^3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Temperature (K) | | | Temperature (K) | | | Temperature (K) | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 65486.6 | 81493.9 | 98692 | -0.34 | -0.452 | -0.56 | -6.33 | -6.51 | -6.70 |
| 2 | 2 | -6754.4 | 22158.5 | 48538 | -0.71 | -0.939 | -1.18 | -6.03 | -6.23 | -6.44 |
| 3 | 3 | -67509.5 | -30089.5 | 3393.7 | -1.07 | -1.423 | -1.80 | -5.75 | -5.98 | -6.21 |
| 4 | 4 | -117191 | -75429.7 | -36743 | -1.45 | -1.936 | -2.44 | -5.51 | -5.75 | -6.01 |
| 5 | 5 | -165914 | -110794 | -70660 | -1.84 | -2.459 | -3.10 | -5.30 | -5.55 | -5.82 |
| 6 | 6 | -217572 | -147927 | -103990 | -2.25 | -2.998 | -3.78 | -5.10 | -5.37 | -5.66 |
| 7 | 7 | -251886 | -187432 | -125245 | -2.66 | -3.556 | -4.48 | -4.92 | -5.21 | -5.51 |
| 8 | 8 | -289450 | -205805 | -157843 | -3.10 | -4.132 | -5.21 | -4.76 | -5.06 | -5.37 |
| 9 | 9 | -315750 | -246453 | -175131 | -3.54 | -4.728 | -5.96 | -4.62 | -4.92 | -5.25 |
| 10 | 10 | -347196 | -262716 | -197398 | -4.01 | -5.345 | -6.74 | -4.48 | -4.80 | -5.13 |

**Table 3**
**Computed values of excess free volume, ultrasonic velocity and internal pressure for N, N-DMF+1 Propanol+n Hexane**

| S.N. | CON(M)X$10^{-3}$ | Excess Free Volume($V_f^E$) x$10^{-8}$ ($m^{3/}$mol) | | | Excess ultrasonic velocity($U^E$) (m/s) | | | Excess Internal Pressure x$10^{+7}Nm^{-2}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Temperature (K) | | | Temperature (K) | | | Temperature (K) | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 10.5 | 7.42 | 4.89 | -62.538 | -52.363 | -39.023 | -1.75 | -0.45 | 1.39 |
| 2 | 2 | 7.24 | 5.04 | 3.14 | -102.061 | -79.917 | -59.304 | -1.53 | 0.22 | 2.53 |
| 3 | 3 | 6.93 | 4.55 | 2.65 | -135.650 | -104.77 | -77.417 | -2.01 | -0.21 | 2.17 |
| 4 | 4 | 6.59 | 4.63 | 3.07 | -166.069 | -126.09 | -93.442 | -2.04 | -0.49 | 1.75 |
| 5 | 5 | 6.80 | 4.86 | 3.02 | -191.661 | -145.91 | -107.17 | -2.53 | -0.83 | 1.47 |
| 6 | 6 | 6.66 | 4.08 | 2.69 | -216.843 | -162.57 | -120.09 | -3.17 | -0.83 | 1.21 |
| 7 | 7 | 7.00 | 4.93 | 2.84 | -239.027 | -178.20 | -131.76 | -3.09 | -1.41 | 1.47 |
| 8 | 8 | 7.37 | 4.86 | 3.87 | -259.701 | -192.55 | -142.20 | -3.47 | -1.16 | 0.66 |
| 9 | 9 | 6.25 | 4.62 | 2.40 | -277.370 | -205.84 | -151.27 | -3.33 | -1.99 | 1.07 |
| 10 | 10 | 6.15 | 3.96 | 2.01 | -294.568 | -217.98 | -160.07 | -3.57 | -1.60 | 1.09 |

**Table 4**
**Calculated values of acoustic impedance, adiabatic compressibility and free volume for N, N-DMF+1 Propanol+n Hexane**

| S.N. | CONC(M) X$10^{-3}$ | Acoustic impedance(Z) x$10^{+5}$ Kg/($m^2$s) | | | Adiabatic compressibility($\beta$) x$10^{-9}$ $N^{-1}m^2$ | | | Free Volume($V_f$) x$10^{-7}$ $m^3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Temperature (K) | | | Temperature (K) | | | Temperature (K) | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 8.49 | 8.34 | 8.25 | 1.11 | 1.16 | 1.19 | 3.68 | 3.375 | 3.122 |
| 2 | 2 | 8.49 | 8.35 | 8.26 | 1.11 | 1.15 | 1.19 | 2.75 | 2.530 | 2.340 |
| 3 | 3 | 8.52 | 8.36 | 8.26 | 1.11 | 1.15 | 1.19 | 2.76 | 2.522 | 2.332 |
| 4 | 4 | 8.59 | 8.38 | 8.26 | 1.09 | 1.15 | 1.19 | 2.71 | 2.514 | 2.358 |
| 5 | 5 | 8.61 | 8.45 | 8.28 | 1.09 | 1.14 | 1.18 | 2.73 | 2.536 | 2.352 |
| 6 | 6 | 8.55 | 8.46 | 8.27 | 1.10 | 1.14 | 1.19 | 2.75 | 2.492 | 2.353 |
| 7 | 7 | 8.62 | 8.41 | 8.35 | 1.09 | 1.14 | 1.17 | 2.72 | 2.513 | 2.304 |
| 8 | 8 | 8.62 | 8.54 | 8.29 | 1.09 | 1.12 | 1.18 | 2.73 | 2.479 | 2.380 |
| 9 | 9 | 8.70 | 8.42 | 8.36 | 1.08 | 1.14 | 1.17 | 2.69 | 2.527 | 2.305 |
| 10 | 10 | 8.70 | 8.52 | 8.36 | 1.08 | 1.12 | 1.17 | 2.68 | 2.461 | 2.266 |

**Table 5**
**Calculated values of free length, ultrasonic velocity and internal pressure for N, N-DMF+1 Propanol+n Hexane**

| **S.N.** | **CONC(M) X10$^{-3}$** | **Free length (L$_f$ ) x10$^{-11}$ m$^3$** | | | **Internal Pressure x10$^{+8}$ Nm$^{-2}$** | | | **K dm$^{-3}$mol$^{-1}$** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **Temperature (K)** | | | **Temperature (K)** | | | **Temperature (K)** | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 6.62 | 6.75 | 6.85 | 2.79 | 2.88 | 2.97 | 50.1 | 47.5 | 45.9 |
| 2 | 2 | 6.56 | 6.69 | 6.79 | 3.49 | 3.61 | 3.72 | 22.9 | 21.7 | 20.9 |
| 3 | 3 | 6.54 | 6.68 | 6.78 | 3.49 | 3.61 | 3.72 | 28.8 | 27.4 | 26.5 |
| 4 | 4 | 6.51 | 6.67 | 6.78 | 3.53 | 3.62 | 3.71 | 23.6 | 22.5 | 21.7 |
| 5 | 5 | 6.49 | 6.64 | 6.77 | 3.52 | 3.62 | 3.71 | 20.1 | 19.0 | 18.4 |
| 6 | 6 | 6.52 | 6.63 | 6.77 | 3.49 | 3.65 | 3.71 | 18.4 | 17.5 | 16.9 |
| 7 | 7 | 6.49 | 6.65 | 6.74 | 3.53 | 3.62 | 3.76 | 16.4 | 15.6 | 15.0 |
| 8 | 8 | 6.48 | 6.59 | 6.76 | 3.52 | 3.67 | 3.70 | 15.3 | 14.6 | 14.1 |
| 9 | 9 | 6.45 | 6.64 | 6.73 | 3.56 | 3.61 | 3.76 | 14.2 | 13.5 | 13.0 |
| 10 | 10 | 6.45 | 6.60 | 6.73 | 3.56 | 3.67 | 3.78 | **23.31** | **22.14** | **21.38** |

**Table 6**
**Calculated values of Lennard jones potential, Delta G and Cohesive energy for N, N-DMF+1 Propanol+n Hexane**

| **S.N.** | **CONC(M) X10$^{-3}$** | **Lennard jones potential n** | | | **Delta G KJmol$^{-1}$** | | | **Cohesive energy KJmol$^{-1}$** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **Temperature (K)** | | | **Temperature (K)** | | | **Temperature (K)** | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 4.765 | 3.998 | 3.476 | 4.215 | 4.421 | 4.593 | 36.131 | 37.296 | 38.474 |
| 2 | 2 | 4.778 | 4.029 | 3.485 | 4.219 | 4.420 | 4.595 | 37.343 | 38.627 | 39.772 |
| 3 | 3 | 4.841 | 4.052 | 3.493 | 4.205 | 4.425 | 4.604 | 37.308 | 38.591 | 39.777 |
| 4 | 4 | 4.876 | 4.091 | 3.507 | 4.215 | 4.423 | 4.581 | 37.806 | 38.770 | 39.702 |
| 5 | 5 | 4.968 | 4.110 | 3.534 | 4.199 | 4.385 | 4.583 | 37.664 | 38.734 | 39.740 |
| 6 | 6 | 4.973 | 4.157 | 3.541 | 4.201 | 4.413 | 4.584 | 37.343 | 39.055 | 39.697 |
| 7 | 7 | 4.999 | 4.185 | 3.549 | 4.199 | 4.416 | 4.596 | 37.877 | 38.843 | 40.313 |
| 8 | 8 | 5.009 | 4.207 | 3.560 | 4.193 | 4.398 | 4.556 | 37.629 | 39.232 | 39.542 |
| 9 | 9 | 5.059 | 4.223 | 3.585 | 4.193 | 4.403 | 4.594 | 38.021 | 38.555 | 40.125 |
| 10 | 10 | 5.069 | 4.235 | 3.594 | 4.199 | 4.416 | 4.623 | 38.128 | 39.306 | 40.473 |

**Table 7**
**Calculated values of Available volume, viscous relaxation time and absorption coefficient for N, N-DMF+1 Propanol+n Hexane**

| **S.N.** | **CONC(M) X10$^{-3}$** | **Available volume X10$^{-5}$** | | | **Viscous relaxation time X10$^{-13}$ s** | | | **Absorption coefficient X10$^{-14}$** | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **Temperature (K)** | | | **Temperature (K)** | | | **Temperature (K)** | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | 4.297 | 4.463 | 4.576 | 7.29 | 7.85 | 8.4 | 1.36 | 1.50 | 1.62 |
| 2 | 2 | 3.546 | 3.679 | 3.777 | 7.30 | 7.85 | 8.4 | 1.36 | 1.49 | 1.62 |
| 3 | 3 | 3.529 | 3.674 | 3.775 | 7.26 | 7.86 | 8.4 | 1.35 | 1.49 | 1.62 |
| 4 | 4 | 3.496 | 3.661 | 3.772 | 7.29 | 7.86 | 8.32 | 1.35 | 1.49 | 1.61 |
| 5 | 5 | 3.478 | 3.630 | 3.761 | 7.24 | 7.75 | 8.32 | 1.34 | 1.47 | 1.61 |
| 6 | 6 | 3.503 | 3.620 | 3.764 | 7.25 | 7.83 | 8.33 | 1.34 | 1.48 | 1.61 |
| 7 | 7 | 3.472 | 3.641 | 3.730 | 7.24 | 7.84 | 8.37 | 1.34 | 1.48 | 1.62 |
| 8 | 8 | 3.470 | 3.583 | 3.755 | 7.23 | 7.79 | 8.24 | 1.34 | 1.47 | 1.59 |
| 9 | 9 | 3.435 | 3.633 | 3.722 | 7.23 | 8.00 | 8.36 | 1.33 | 1.47 | 1.61 |
| 10 | 10 | 3.433 | 3.586 | 3.720 | 7.24 | 7.84 | 8.45 | 1.34 | 1.48 | 1.63 |

**Table 8**
**Calculated values of entropy (ΔS) and Gibb's Free energy ($\Delta G^0$) for N, N-DMF+1 Propanol+n Hexane**

| S.N. | CONC(M) X$10^{-3}$ | Delta S | | | Delta $G^0$ KJ$mol^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | Temperature (K) | | | Temperature (K) | | |
| | | 303 | 308 | 313 | 303 | 308 | 313 |
| 1 | 1 | -120.36 | -119.92 | -119.63 | -9864.9 | -9730.5 | -9644.2 |
| 2 | 2 | -113.85 | -113.40 | -113.09 | -7891.7 | -7756.0 | -7661.4 |
| 3 | 3 | -115.75 | -115.34 | -115.06 | -8469.5 | -8343.9 | -8259.7 |
| 4 | 4 | -114.10 | -113.70 | -113.40 | -7967.6 | -7847.3 | -7756.0 |
| 5 | 5 | -112.76 | -112.29 | -112.03 | -7563.0 | -7421.1 | -7340.3 |
| 6 | 6 | -112.03 | -111.61 | -111.32 | -7340.3 | -7213.9 | -7125.9 |
| 7 | 7 | -111.07 | -110.65 | -110.33 | -7050.2 | -6924.2 | -6825.3 |
| 8 | 8 | -110.49 | -110.10 | -109.81 | -6875.3 | -6757.2 | -6669.4 |
| 9 | 9 | -109.87 | -109.45 | -109.14 | -6687.2 | -6559.8 | -6464.7 |
| 10 | 10 | | | | | | |

**Table 9**
**Comparison between Theoretical value and Experimental Value for each pure component present in the N, N-DMF+1 Propanol+n Hexane system at 303 K**

| S.N. | Name of the component in the mixture | Theoretical value | | | Experimental Value | | |
|---|---|---|---|---|---|---|---|
| | | Density Kg$m^{-3}$ | Viscosity Ns$m^{-2}$ | Ultrasonic velocity $ms^{-1}$ | Density Kg$m^{-3}$ | Viscosity Ns$m^{-2}$ | Ultrasonic velocity $ms^{-1}$ |
| 1. | NNDMF | 0.944 | 0.920 | 1456.0 | 0.968 | 0.965 | 1550.8 |
| 2. | 1 Propanol | 0.803 | 0.196 | 1186.6 | 0.801 | 0.138 | 1182.5 |
| 3. | n hexane | 0.661 | 0.297 | 1057.0 | 0.651 | 0.243 | 1076.1 |

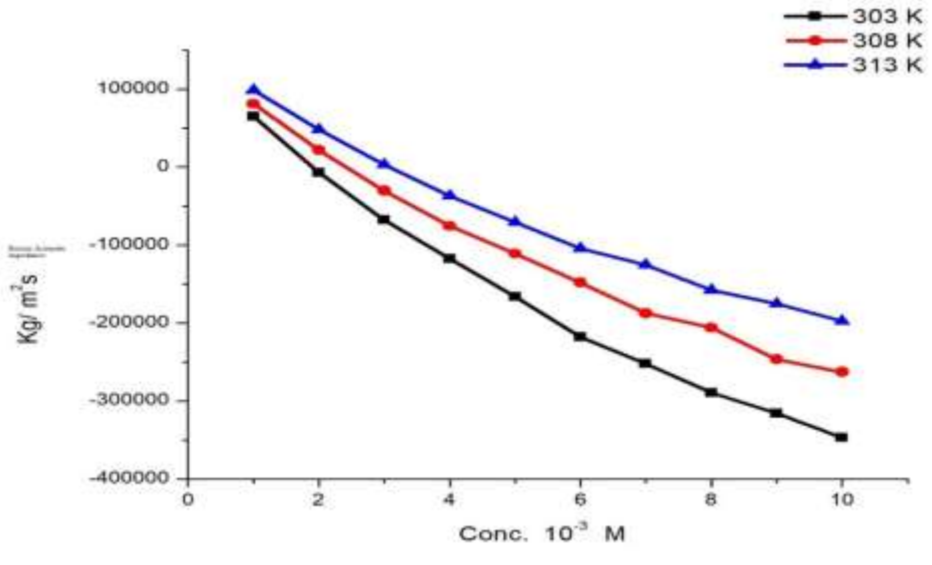

**Fig. 1: Plot between Conc. Vs Excess acoustic impedance of N, N-DMF+1 propanol+n hexane at different temperatures.**

This decrease in acoustic impedance is due to the thermal agitation at higher temperature which causes less interactions. Acoustic impedance is also used for assessing the absorption of sound in medium [4]. The corresponding plot is given in fig. 1.

The excess adiabatic compressibility increases (considering the magnitude alone) with increase in concentration at particular temperature and the negative excess values are due to strong interaction between the molecules, the negative excess compressibility values have been due to closed packed molecules. Similar conclusions were also arrived by Islam and Quadri[9]. Similarly, when the temperature increases, at particular concentration the excess compressibility values increases, this shows that stronger interaction exists due to thermal agitation. The corresponding plot is given in fig. 2.

Excess free length decreases with increase of concentration that predicts the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in liquid systems. The values of excess inter molecular free length follow the same trend as that of $\beta^E$. The values of excess inter molecular free length ($Lf^E$) are negative. The negative deviation of excess free length is an indication of the existence of strong interaction between the components. And at the same time for a particular concentration, the free length increases with increase in temperature. This also supports the existence of strong interaction between the components. The corresponding plot is given in fig. 4.

From the table 3, an uneven trend is observed for free volume irrespective of temperatures while the concentration of the mixture increases and at particular concentration, increase in temperatures shows decrease in free volume. The decrease in free volume shows that the strength of interaction increases gradually with the increase in concentration. This indicates that the attractive forces between the molecules of components are stronger than the intermolecular attractions. The corresponding plot is given in fig. 3.

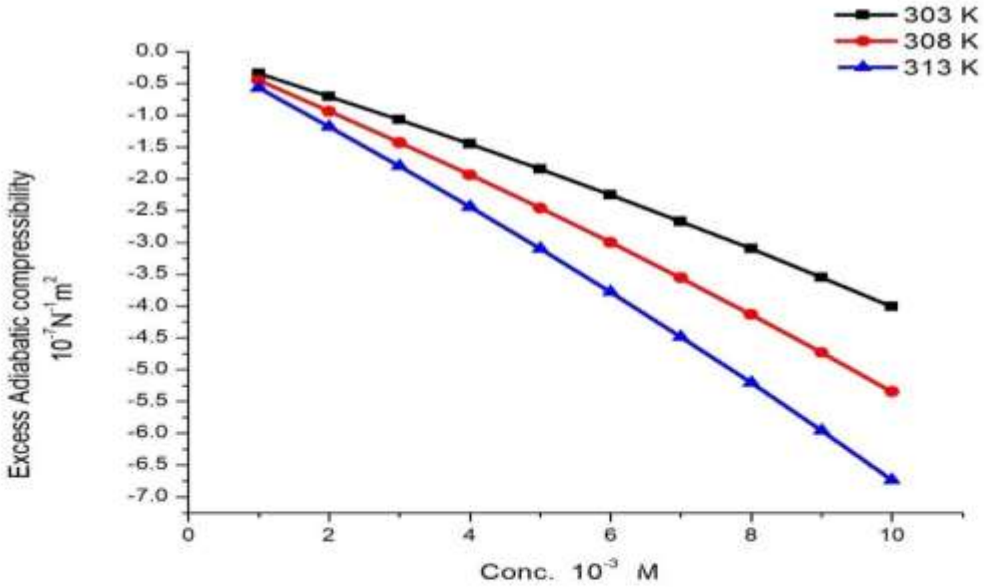

**Fig. 2: Plot between Conc. Vs Excess adiabatic compressibility of N, N-DMF+1 propanol+n hexane at different temperatures.**

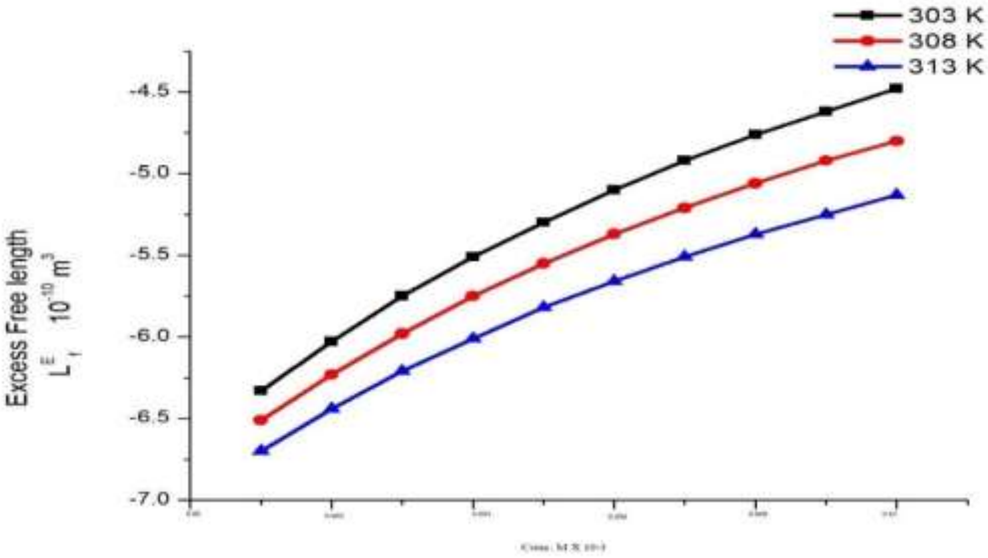

**Fig. 3: Plot between Conc. Vs Excess free length of N, N-DMF+1 propanol+n hexane at different temperatures**

It is noticed that the values of excess ultrasonic velocity decrease (considering the magnitude alone) with increase in temperatures under which investigation is done irrespective of the concentration of the mixture. Similarly, the velocity increases with increase in concentration at all the temperatures of the mixtures. It predicts the linear behavior of the system and moderate to strong interactions exhibits by the system which may be attributed to the negative values. The corresponding plot is given in fig. 5. The internal pressure is important factor in deciding the thermodynamic properties of liquids.

The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules. Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent (n hexane) arise through hydrogen bonding, charge transfer, Columbic (or) Van der waals forces.

The internal pressure is the single factor which varies due to all type of interactions. In the present study, the negative excess internal pressure $\pi_i^E$ over the entire range of concentration of the system with respect to 303 K, 308 K and 313 K also supports the presence of stronger interaction. The corresponding plot is given in fig. 6. This statement is strongly complemented by the values of cohesive energy and absorption coefficient or attenuation coefficient. When concentration of N,N-DMF increases, the attenuation coefficient increases and the wave is more and more attenuated.

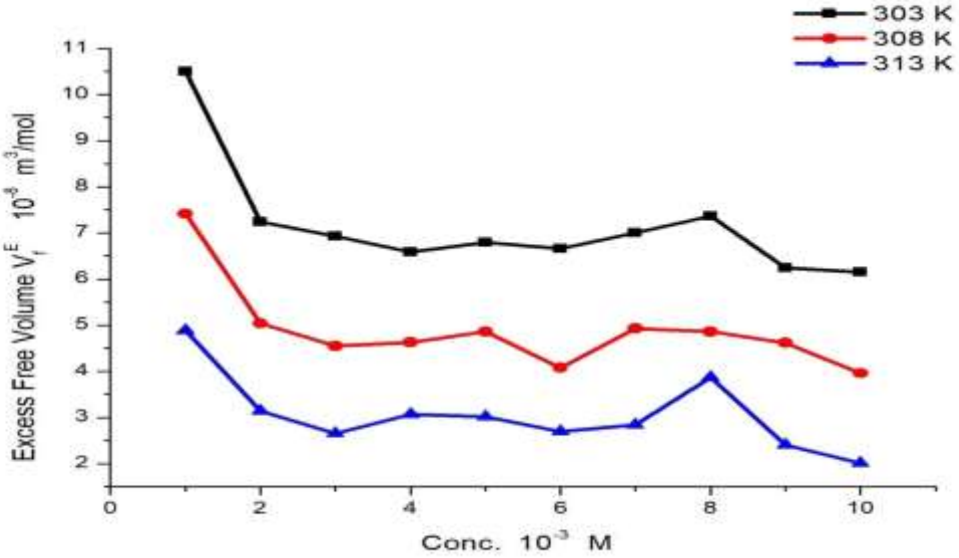

**Fig. 4: Plot between Conc. Vs Excess free volume of N, N-DMF+1 propanol+n hexane at different temperatures.**

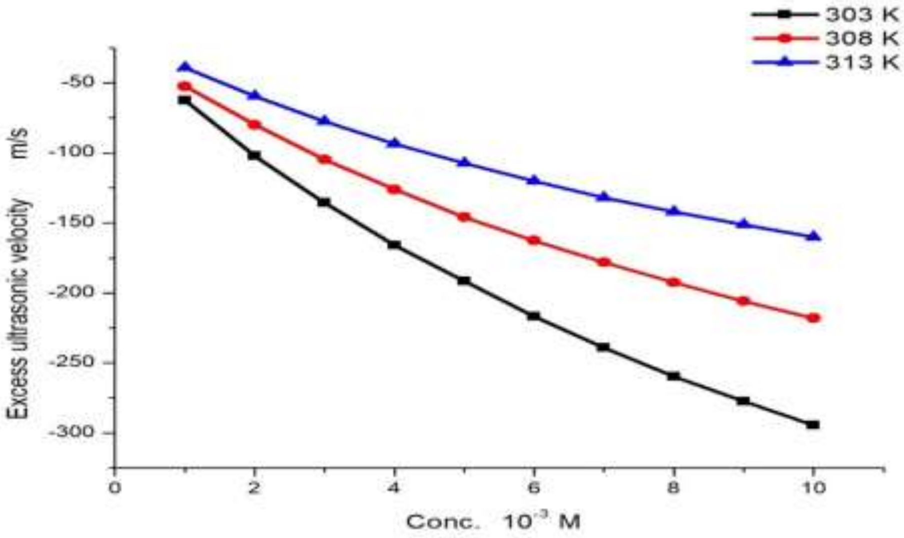

**Fig. 5: Plot between Conc. Vs Excess ultrasonic velocity of N, N-DMF+1 Propanol+n Hexane at different temperatures.**

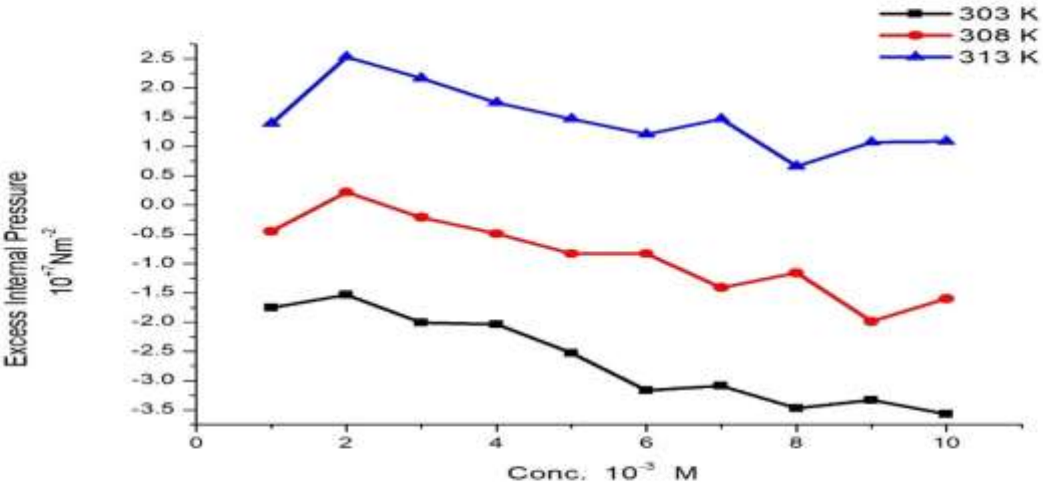

**Fig. 6: Plot between Conc. Vs Excess internal pressure of N, N-DMF+1 propanol+n hexane at different**

The relaxation time (τ) increases (table 7) with increasing temperature irrespective of concentrations. The dispersion of the ultrasonic velocity in the system should contain information about the characteristic time τ of the relaxation process that causes dispersion. The relaxation time which is in the order of $10^{-13}$ sec is due to structural relaxation process and in such a situation the molecules might have got rearranged due to co-operative process[17].

The increase in polarizability of donor molecule N,N-DMF, increases the ease of complexation. In the present study, formation constant or stability constant K decreases with increase in temperature. The mean 'K' value is greater for the system at 303 K which confirms the formation of the charge transfer complex which is mainly due to the existence of inter molecular hydrogen bonding in between donor NNDMF and acceptor 1-propanol and its stability at the same temperature comparing with the system at other two temperatures 308 and 313 K (table 5).

The negative deviations of $G^0$ (table 8) over the whole concentration range at 303, 308 and 313 K implies that the charge transfer complexes are thermodynamically stable. The same is reported by Kannappan et al.[11] There is a certain degree of association in the pure N,N-DMF due to hydrogen bond formation, even though these associations are broken down on formation of mixture. This statement is strongly supported by Mehra et al.[15] Generally, in ternary systems fewer interactions are reported because the addition of third component decreases the energy of interaction and the system behaves as ideal one[6,8]. These results are also found to be in good agreement with the results reported by Gulwade et al[5] in the ternary mixture.

## Conclusion

The computed excess acoustical parameters and their values point to the presence of certain molecular interaction in the liquid mixtures of N,N-DMF+1 propanol +n hexane. The increase in temperature causes an agitation in thermal energy which results in increase in molecular separation of the mixture. Hence it is concluded that the association in these mixtures is the result of strong hydrogen bonding between the molecules and strong dipole-dipole, dipole- induced dipole interactions, weak van der waals forces of attraction and to some extent, formation of the charge transfer complex.

Further it is also concluded that the presence of dispersive forces, steric hindrance, unfavourable configuration and repulsive forces decide the molecular interactions in the ternary system of N,N-DMF+1 propanol +n hexane at various temperatures.

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