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Molecular Interaction study on N, N-dimethyle acetamide and benzonitrile at 308 K

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ABSTRACT

The measurements of ultrasonic velocity (υ), density (ρ) and viscosity (η) of the binary liquid mixture of N, N-Dimethyle acetamide and Benzonitrile of pure and binary mixture for the entire range of compositions at temperature 308 K have been carried out. The experimental data of these mixtures is used to evaluate other thermo dynamical parameters with their excess values such as compressibility (β_α), molecular free length (L_f), acoustic impedance (Z), free volume (V_f), internal pressure (π_i) and the excess values as excess compressibility β_α^E, free length L_f^E, acoustical impedance Z^E, free volume V_f^E and internal pressure π_i^E. From the nature of these excess parameters the nature and strength of the interactions in these binary systems are discussed in view of molecular interaction. The non linearity observed in the plots of these ultrasonic parameters and their excess values with the composition range indicates presence of the intermolecular interaction between the components molecules of the mixture. The nature of excess values of the β_α^E, L_f^E, Z^E, V_f^E and π_i^E conforms about the existence of the molecular association between the components of the mixture.

Keywords: Ultrasonic velocity, molecular interaction, free length, compressibility, Impedance, Internal Pressure, binary mixtures, Excess Values

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INTRODUCTION

The ultrasonic study of liquid mixtures consisting of polar and non-polar component have of greater importance in understanding the nature of intermolecular interaction in pure liquid and liquid mixtures and they find many applications in industrial and technological processes [1, 2] further, such studies are useful in gaining insight into the structure and bonding of associated molecular processes. The variation of ultrasonic velocity and other thermodynamic parameters along with their excess values of binary mixtures with changing mole fraction of one of the component has been investigated by many researchers [3-5].

In the present study the ultrasonic velocity, density and viscosity measurements have been carried out for pure N, N-Dimethyle acetamide (NNDMA) and Benzonitrile and their binary mixtures for various concentrations at 308.15 K. The variations of different ultrasonic parameters and their excess values with concentration of binary liquid mixtures are studied to understand molecular interaction between unlike molecules of the mixtures.

EXPERIMENTAL SECTION

Experimental details:
The chemicals N, N-dimethyle acetamide (NNDMA) is from Qualigens having excel grade (99.5%) purity and Benzonitrile is from Merck specialities Pvt. Limited having GR grade (99%) purity, used without further

purification the binary mixtures of various concentrations in mole fraction of the liquids NNDMA and Benzonitrile were prepared at room temperature and kept in a special airtight glass bottles to avoid air contact for different range of composition. The mixtures prepared were used within 24 hours of its preparation. Here the measurements of ultrasonic velocities were carried out on single crystal multi frequency ultrasonic interferometer operating at 1MHz (M-81). The ultrasonic interferometer (Mittal enterprises, New Delhi, India) is a single and direct device to determine ultrasonic velocity in liquids with a high degree of accuracy [6].The constant temperature of the liquid inside the interferometer cell was maintained by circulating water through the outer jacket by electronically controlled thermostat. Accuracy of measurement of ultrasonic velocity was within ±0.01m/s and the temperature of the test liquids during measurement were maintained within an accuracy of $\pm 0.1^0$C. The densities of the binary mixtures & pure liquids were measured using 25ml specific gravity bottle and a sensitive mono pan balance (K-Roy, K-12 classic) within ±0.1mg accuracy. The viscosity of the liquids and their mixtures were measured using the suspended level viscometer.

The experimentally measured density (ρ), ultrasonic velocity (υ) and viscosity are used to evaluate various thermodynamic parameters like molecular free length (L_f), compressibility (β_α) and acoustic impedance (Z), free volume (V_f) and internal pressure (π_i) by using following standard relations:

(1) Adiabatic compressibility
$\beta_\alpha = 1/\upsilon^2\rho$

(2) Intermolecular free length
$L_f = K\beta_\alpha^{1/2}$

(3) Acoustic impedance
$Z = \upsilon\,\rho$

(4) The free volume
$V_f = \left[\frac{M_{eff}}{k\eta}\upsilon\right]^{3/2}$

(5) The internal pressure
$\pi_i = bRT\left(\frac{k\eta}{\upsilon}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$

(6) The excess values are determined by using the relation
$A^E = A_{exp} - A_{id}$

A^E - excess parameters of all acoustic parameters, $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameter and X_i – the mole fraction of liquid component.

Where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i X_i$ in which m_i and X_i are the molecular weight and mole fraction of the individual constituents respectively), K is Jacobson's constant ($K=93.875 + 0.375\ T$) X 10^{-8} and T being the absolute temperature, k is temperature independent constant which is equal to 4.28 X 10^9 for all liquids, b stands for cubic packing which is assumed to be 2 for all liquids

RESULTS AND DISCUSSION

The ultrasonic velocity (υ), density (ρ) and viscosity (η) of the binary mixture along with thermodynamic parameters like adiabatic compressibility (β_α), free length (L_f), impedance (Z), free volume(V_f) and internal pressure (π_i) at 308K temperature for varying concentration of the two liquids is represented in the table (01). The excess values of different acoustical and thermo dynamical parameters have been calculated from the measurements of ultrasonic velocities, densities and viscosities for the system of NNDMA and Benzonitrile for varying mole fractions at 308 K temperature. The Table (02) presented here gives the excess values of different parameters and their corresponding plots are shown in Figure (2). The variations observed in the above parameters and their excess values with composition of the mixture at 308K temperature are used to understand the nature of molecular interactions between the components of NNDMA and Benzonitrie binary liquid mixtures.

It is observed form the table(01) and figure (01) the specific variations in the different parameters of binary mixture of NNDMA and Benzonitrile, The density values decreases for the increase in temperature of the mixture this is the

basic nature of liquids. The ultrasonic velocity is showing increasing nature with the increasing concentration of NNDMA in Benzonitrile. The viscosity values are decreasing with the increasing concentration of NNDMA in the mixture. The decrease in values of density & viscosity with increase in mole fraction of NNDMA suggests the decrease in magnitude of intermolecular interaction [7-9]. A plot of ultrasonic velocity against mole fraction of NNDMA with Benzonitrile for all temperatures as seen in Figure 01 is presenting the increase of velocity with increase of mole fraction of NNDMA. The increase in the velocity is due to slightly increasing value of the intermolecular free length. The free length in this system shows slightly increasing nature with the increasing concentration of NNDMA in the binary mixture. The free length increases due to expansion which indicates the looser packing of the molecules hence the intermolecular cohesion is weaker leading to weak molecular associations [10]. The slightly increase of free length results in the slight increase of compressibility for the increasing concentration of NNDMA. This increase in free length and adiabatic compressibility with the NNDMA concentration has been qualitatively ascribed to the effect of hydrogen bonding or dipole-dipole interactions [11]. The increase in adiabatic compressibility and intermolecular free length with increase in mole fraction of NNDMA indicates the significant interaction between NNDMA and Benzonitrile. The value of acoustical impedance decreases with the increase in concentration of the NNDMA. It means the impedance decreases with the increase in the temperature of the binary mixture. The corresponding plot of acoustical impedance vs mole fraction of the NNDMA in mixtures is given in Fig. 01 at temperature 308.15K.

Table 01. Ultrasonic Velocity, density, viscosity, adiabatic compressibility, free length, impedance free volume and internal pressure, for N, N- Dimethylacetamide + Benzonitrile mixtures at 308K temperature

mole fraction of NNDMA	density ρ kgm^{-3}	velocity υ ms^{-1}	Viscosity η μ Pas	compress β $x10^{-10}$ m^2N^{-1}	Free Length L_f $x\ 10^{-11}$ m	Impedance $Z\ x\ 10^6$ $Kgm^{-2}s^{-1}$	free volume V_f $X\ 10^{-7}$ m^3/mole	intrenal pressure π_i $X\ 10^6$ Pa
0	993.36	1384	1094.74	5.2555	4.8045	1.3748	1.6772	4.2066
0.1365	985.60	1388.6	1082.34	5.2618	4.8027	1.3686	1.6673	4.2532
0.2695	978.98	1394.72	1070.25	5.2510	4.7978	1.3654	1.6526	4.3074
0.3991	971.77	1398.88	1031.85	5.2586	4.8013	1.3593	1.6943	4.3115
0.5253	962.53	1402.8	1020.52	5.2795	4.8108	1.3502	1.6851	4.3527
0.6485	955.08	1406.28	985.700	5.2943	4.8176	1.3431	1.7237	4.3582
0.7685	947.03	1411.04	934.285	5.3033	4.8217	1.3363	1.8180	4.3173
0.8857	937.64	1416.36	879.265	5.3163	4.8276	1.3280	1.9392	4.2561
1	929.05	1421.44	832.954	5.3272	4.8325	1.3205	2.0472	4.2122

Table:-02 Excess adiabatic compressibility(β^E), Excess free length (L_f^E), Excess impedance (Z^E) Excess free volume (V_f^E), Excess internal pressure (π_i^E), of NNDMA +Benzonitrile mixture at 308 K

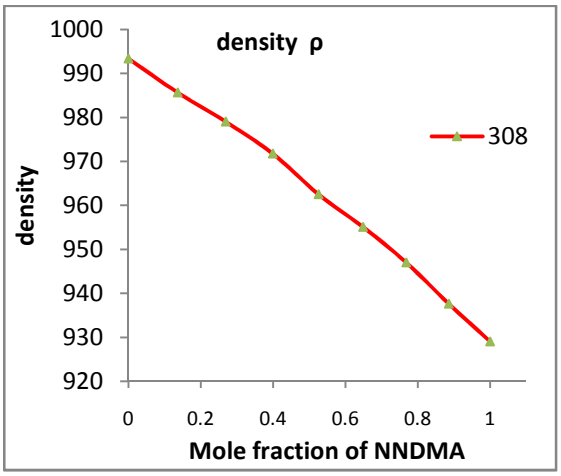
Mole fraction NNDMA	Excess adiabatic compress β^E	Excess free length L_f^E	Excess impedance Z^E	Excess free volume V_f^E	Excess Internal Pressure π_i^E
0	0.00000	0.00000	0.00000	0.0000	0.00000
0.13655	0.00412	0.00575	0.00020	-0.0685	0.05256
0.26954	-0.02379	-0.00757	0.00521	-0.1296	0.10370
0.39912	-0.02557	-0.00897	0.00623	-0.1312	0.10315
0.52539	-0.03372	-0.00404	0.00388	-0.1959	0.15113
0.64851	-0.00003	0.00161	0.00255	-0.2016	0.15485
0.76857	-0.00723	-0.00224	0.00316	-0.1483	0.11010
0.88570	0.01998	0.00963	-0.00159	-0.0745	0.05096
1	0.00000	0.00000	0.00000	0.0000	0.00000

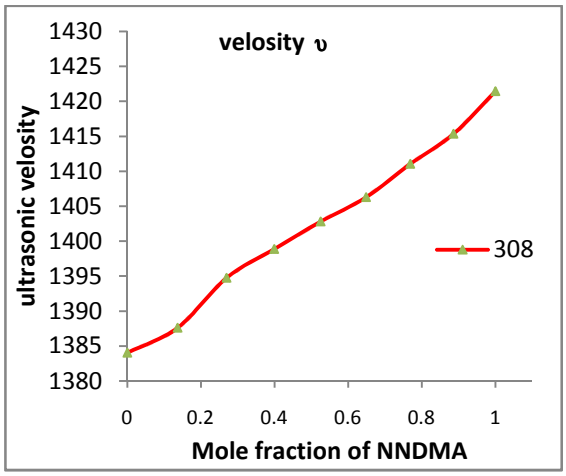
Table (01) shows that internal pressure of the liquid mixtures in the present study decreases with rise in temperature [12]. There is a rise in the internal pressure in the initial state for the increase in molar concentration of NNDMA up to 0.6 of the mole concentration of the NNDMA in the mixture. After that as the concentration of the NNDMA increases beyond the 0.6 mole fraction the internal pressure shows decreasing nature. This non linear variation in the internal pressure can be attributed as there is definite interaction presents between the unlike components of the mixture.

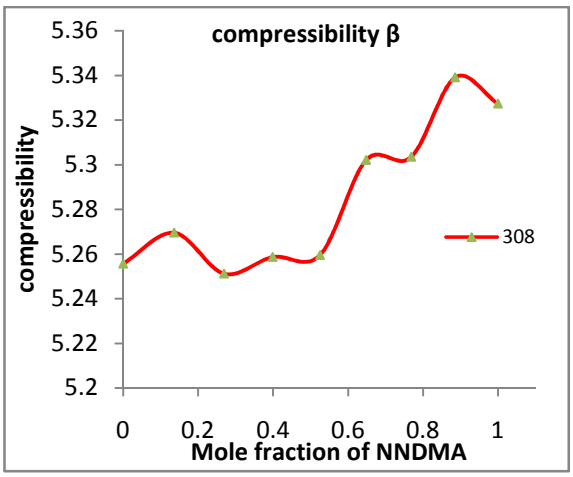
As seen in the figure (01) the free volume of the system is showing non linearity in its behaviour the free volume values are almost remaining uniform for the increase in the concentration of the NNDMA up to 50% in the mixture but beyond that the free volume is increasing with the increasing concentration of NNDMA and which can be concluded that there must be the formation of some complexes beyond 0.5 of the mole fraction of NNDMA in the binary mixture [13].

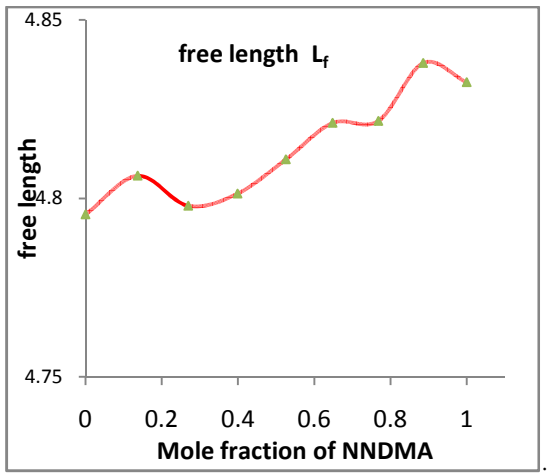
There is increase in the values of ultrasonic velocity for the concentration of NNDMA in the solution as seen from the table (02). Whereas the excess values of ultrasonic velocity (υ^E) is not purely positive or negative therefore it suggests the there is some kind of molecular interaction which is responsible for the association as well as dissociation of the different components of the mixture.

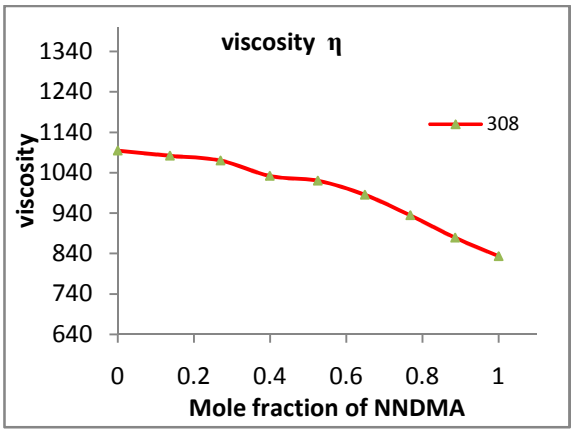
Figure -01: Graph of ultrasonic velocity (υ), density (ρ), compressibility (β_α), free length (L_f), impedance (Z) and viscosity(η) of NNDMA+Benzonitrile mixture with respect to concentration of NNDMA in Benzonitrile mixture at 308K

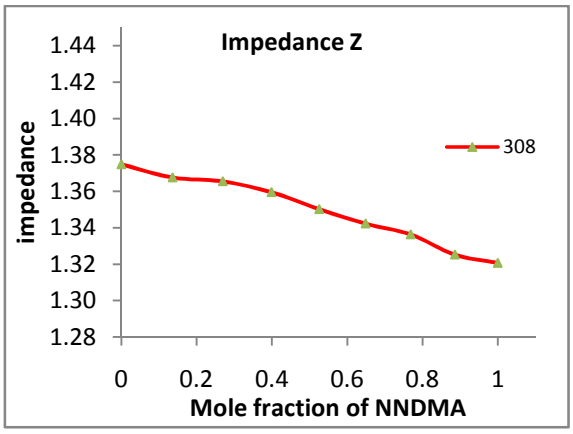


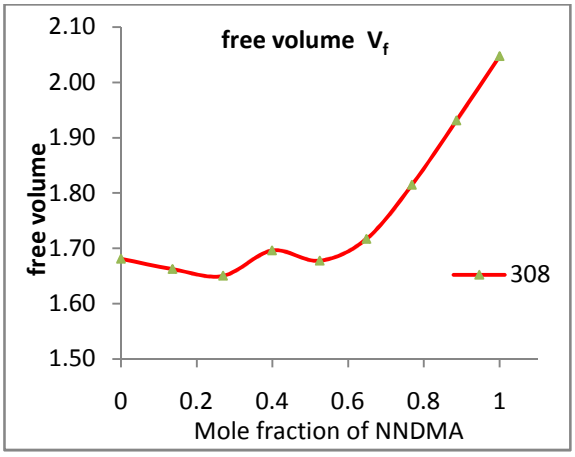


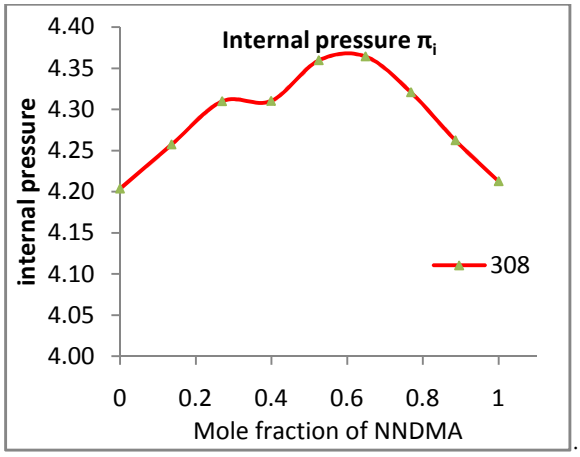






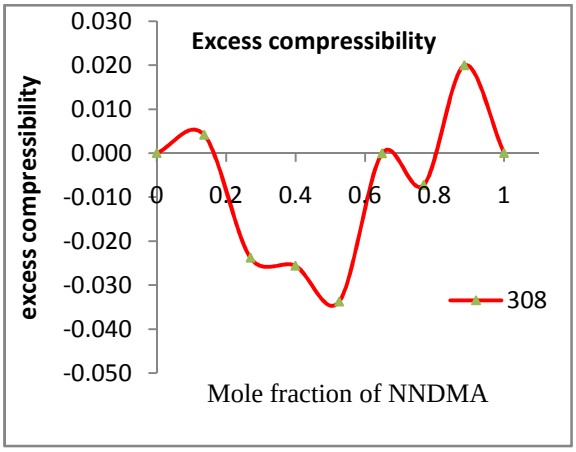


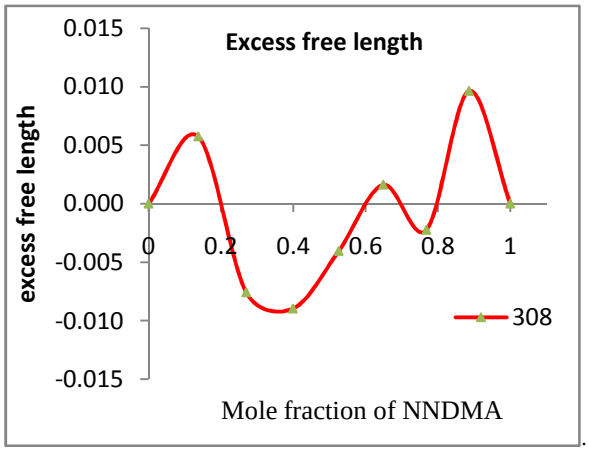


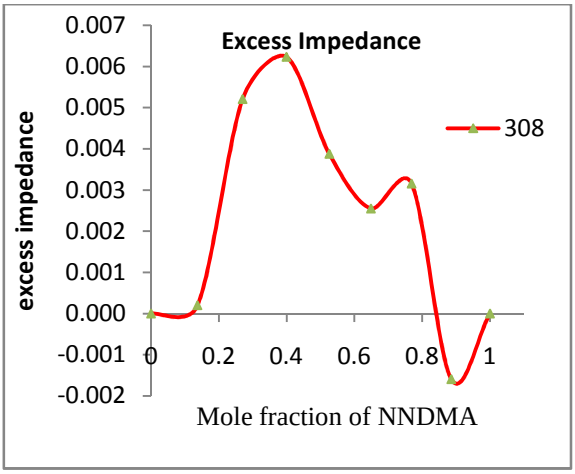


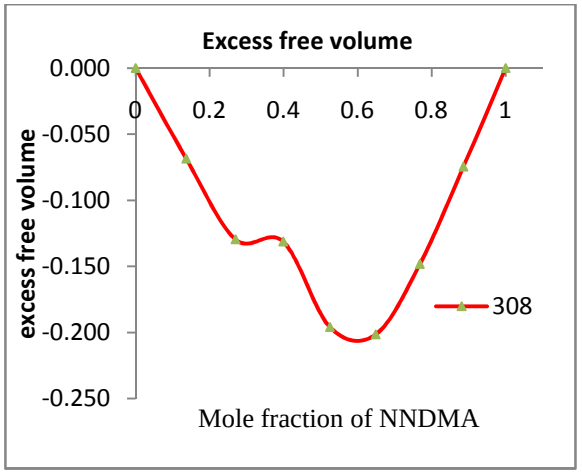
According to Fort and Moore [14], a negative excess compressibility is an indication of strong molecular interaction in the liquid mixtures while a positive value indicates a weak interaction attributable to dispersion forces. Also, the magnitude of the excess function depends on the relative strength of interaction .The types of interactions between components of different mixtures are charge transfer, hydrogen bonding dipole induced-dipole and dipole-dipole interactions.

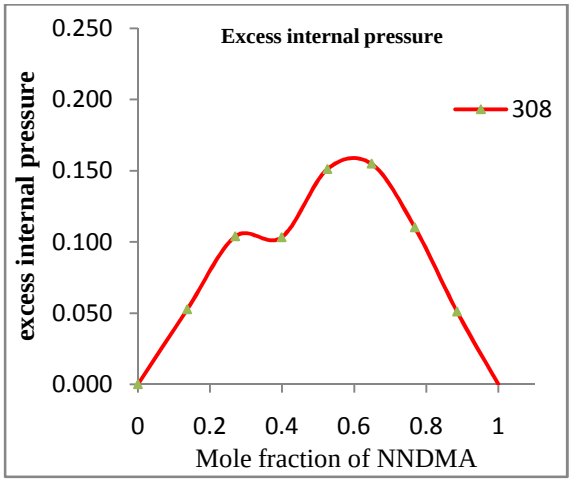
Figure 02:- Graph of Excess adiabatic compressibility (β^E), Excess free length (L_f^E), Excess impedance(Z^E), Excess free volume (V_f^E) and Excess internal pressure (π_i^E) of NNDMA+ Benzonitrile mixture at 308 K

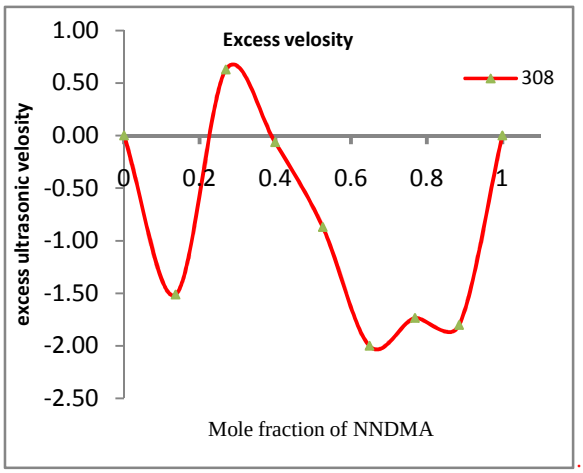












The excess adiabatic compressibility (β_α^E) is mostly negative excepting some small variations for the concentration of NNDMA in the binary mixture. Again the non linear nature of the excess compressibility is the indication of molecular interaction. Here from the close perusal of the table (02) and the figure (02) the excess compressibility is negative for the concentration of NNDMA at 0.2 to 0.6mole at temperature. As should be expected from the excess free length (L_f^E) the nature is similar to the nature of compressibility. β^E and L_f^E behave similarly at all concentrations.[15,16]

The excess impedance (Z^E) is behaving exactly opposite to the nature of the free length and thus it is mostly positive for all the concentrations excepting 0.2 and 0.9 mole at temperature 308 K. The opposing tendencies (in various excess parameters) may be due to the fact that strong dipolar interactions and highly directional interaction bonding act simultaneously between the constituent molecules and the relationship between the excess functions is not simple and reflects the properties of the interaction molecules [17]

Free volume being increasing with concentration of NNDMA in the mixture there is a negative nature of the excess free volume (V_f^E). The internal pressure is the property of the liquid depends on the density and viscosity as there is increase in the viscosity the internal pressure should show increase because of the closeness of the molecules. The excess internal pressure (π_i^E) here as seen from figure (02) is positive at 308K temperature. The respective graphs between thermodynamic parameters with compositions in figure 01 show a non linear nature indicating intermolecular interactions.

CONCLUSION

Ultrasonic velocity (υ), density (ρ) and viscosity (η) have been measured for NNDMA and Benzonitrile mixtures at 308 K. The variations of different thermodynamic parameters indicate the presence of specific interactions, namely hydrogen bonding and dipole-dipole forces between unlike molecules.

The internal pressure of the liquid mixtures in the present study decreases with rise in temperature and free volume of the system is showing non linearity in its behaviour the free volume is increasing with the increasing concentration of NNDMA and which can be attributed as there is definite interaction presents between the unlike components of the mixture.

The excess viscosity (η^E) obtained here is positive, the positive values of excess parameters are the indications of weak interactions between the components. The excess adiabatic compressibility (β_α^E) is mostly negative excepting some small variations for the concentration of NNDMA in the binary mixture. The excess free length (L_f^E) is similar to the nature of excess compressibility β^E at all concentrations. This non linear nature of the excess compressibility and free length is the indication of molecular interaction. There is a negative nature of the excess free volume (V_f^E). The excess internal pressure (π_i^E) here as observed is positive. According to the excess internal pressure the interactions should be strong but the other parameters which are positive are suggesting the weak molecular interactions and the dispersive type of forces are exists between the components of the mixture. From the positive values of η^E mostly endothermic type of reaction is suggested in the mixture.

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