

Measurement of Ultrasonic Velocity in Binary Liquid Mixture of N,N-Dimethyl Acetamide (NNDA) + Diethyl Amine (DEA)

Sravanti Vysyaraju¹, P. Paul Diwakar², K. Samatha³

Research Scholar, Department of Physics, College of Science & Technology, Andhra University, AP, India¹

Professor, Department of Physics, College of Science & Technology, Andhra University, AP, India³

Associate Professor, Department of Physics, Sir C.R.Reddy Autonomous College, Eluru, AP, India²

ABSTRACT: Ultrasonic velocity, viscosity and density of binary mixtures of N,N-dimethyl Acetamide with (NNDA) with Diethyl Amine (DEA) at 303.15K, 308.15K, 313.15K and 318.15K over the entire composition range of NNDA at a fixed frequency of 10MHz using Ultrasonic Interferometer was measured. Experimental data have been used to calculate excess thermodynamic parameters such as excess molar volume (V_m^E), excess ultrasonic velocities (U^E), excess acoustic impedance (Z^E), excess adiabatic compressibility (β_{ad}^E), excess viscosity (η^E), excess free length (L_f^E) and excess Gibbs free energy of activation of viscous flow (ΔG^E). The values of β_{ad}^E and L_f^E exhibits positive deviations and η^E exhibits negative deviation over the wide range of composition for all the binary mixture which suggest that dispersive forces are operative in the system in addition to dipole-dipole, dipole induced dipole interactions. The excess/deviations were fitted by a Redlich-Kister equation and the results were analysed in terms of specific interactions present in the mixture.

KEYWORDS: Ultrasonic Velocity, Viscosity, Density, acoustic impedance, adiabatic compressibility, intermolecular free length, molar volume.

I. INTRODUCTION

The measurement of ultrasonic velocities and parameters derived from it have been used in understanding the nature of inter molecular and intra-molecular interactions in binary liquid mixtures [1-6]. From the theoretical viewpoint, the properties of these mixtures are important sources of information for the characterization of the interactions between the components and they are also useful for understanding the liquid state theory. Amines are widely used in a variety of industrial and consumer applications and hence, the knowledge of their physical properties is of great importance from a practical point of view. The liquids chosen in the present investigation were on the basis of their industrial importance. NNDA is used as a solvent for fibres in production of pharmaceuticals, plasticizers and adhesive industry.

In the binary liquid mixture system NNDA + DEA, the excess molar volume (V_m^E), excess ultrasonic velocities (U^E), excess acoustic impedance (Z^E), excess adiabatic compressibility (β_{ad}^E), excess viscosity (η^E), excess free length (L_f^E) and excess Gibbs free energy of activation of viscous flow (ΔG^E) were reported. These results have been used to discuss the nature of interaction between unlike molecules. A survey of the literature reveals that these parameters are not reported for the selected system.

II. RELATED WORK

Rohini B et.al [7] reported the ultrasonic parameters of CuO: Diethylamine-Isopropanol binary nanofluids at six different concentrations at three different temperatures 298K, 308K and 318K. The acoustical parameters such as ultrasonic velocity, compressibility, inter molecular free length, acoustic impedance were calculated. Anil Kumar Nain [8] measured the densities, ultrasonic speeds and viscosities of binary mixtures of methyl methacrylate (MMA) with

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N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA), including those of pure liquids, over the entire composition range. The excess molar volume, excess isentropic compressibility, excess isobaric coefficient of thermal expansion, and excess molar isobaric expansion over the whole composition range have been calculated. The variations of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. The excess molar volume, excess isentropic compressibility, excess isobaric coefficient of thermal expansion, and excess molar isobaric expansion, were calculated. The variations of these parameters with composition and temperature of the mixtures were discussed in terms of molecular interaction in these mixtures.

SaharMrad et al [9] [10] [11] studied the thermophysical behaviour of the binary mixtures N,N-dimethylacetamide + methanol and N,N-dimethylacetamide + ethanol through the measurement of density, speed of sound, refractive index, and kinematic viscosity, over the entire mole fraction range at the temperatures of 283.15, 298.15 and 313.15 K. Excess volumes, excess isentropic compressibility, refractive index deviations and viscosity deviations were also calculated and correlated with the Redlich-Kister equation. The experimental results were interpreted based on strength of specific interactions, size, and shape of molecules.

III. EXPERIMENTATION

The velocity of ultrasonic waves in the liquid mixture have been measured using a singlecrystal variable path ultrasonic interferometer (Model-F81, Mittal Enterprises, New Delhi) at different temperatures, namely 303.15K, 308.15K, 313.15K and 318.15K at 10MHz with accuracy of ± 0.1 m/s. Density was calculated using 10 ml specific gravity bottle by the standard procedure with accuracy of ± 0.1 kg m⁻³. The viscosity was measured using Ostwald's viscometer of capillary type. The time of flow was measured with an accuracy of ± 0.01 sec. The constant temperature was maintained by using a thermostat throughout the experiment. The chemicals used in the present work are AR grade of minimum of 99.9% purity and hence used without for further purification. The liquid mixture was prepared by mixing calculated amount of pure liquids.

IV. THEORETICAL ASPECTS

Various Physical and thermodynamical parameters are calculated using the measured parameters, viz., the ultrasonic velocity (U), density (ρ) and viscosity (η) of pure liquids and their mixtures as a function of mole fraction of NNDA. The derived parameters are Acoustical Impedance (Z), Adiabatic Compressibility (β), Free length (L_f), Molar volume (V_m) and Gibb's free energy (ΔG)

Acoustical Impedance	$Z = \rho U \text{ kg-m}^2/\text{sec}$	(1)
Adiabatic Compressibility	$\beta = 1/(\rho U^2) \text{ m}^2/\text{N}$	(2)
Intermolecular free length	$L_f = k (\beta)^{1/2} \text{ m}$	(3)
Gibbs Free Energy	$\Delta G = RT \ln(\eta V_m)$	J/mole (4)
Molar Volume	$V_m = M_{\text{mix}}/\rho$	m ³ /mole (5)

Here the K values [12] are a temperature dependent constant and they are taken as.

Temperature (°K)	303.15	308.15	313.15	318.15
Value of K	627	631.5	636	640.5

Here M_{mix} is the molecular weight of the mixture in which $M_{\text{mix}} = \sum m_i x_i$, here m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively.

The excess values of all parameters are calculated using the general formula, $P^E = P_{\text{exp}} - P_{\text{id}}$ where, $P_{\text{id}} = \sum P_i x_i$ where P_i is any acoustical parameter and x_i is the mole fraction of liquid component. The variation of all these excess values

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with mole fraction were fitted to the Redlich-Kister equation [13] with coefficients A_0, A_1, \dots, A_7 and Y^E (any one of excess parameter) of the type

$$Y^E = x_1(1-x_1)[A_0 + A_1(1-2x_1) + A_2(1-2x_1)^2 + \dots + A_7(1-2x_1)^7] \quad (6)$$

The standard deviations are estimated by using the equation

$$\sigma(Y^E) = [\sum(Y_{obs}^E - Y_{cal}^E)^2 / (n-7)]^{1/2} \quad (7)$$

Here, n is number of observations. The estimated values are given in the Table 1.

V. EXPERIMENTAL RESULTS

The excess velocity (U^E) values are negative in magnitude over the whole mole fraction range as seen Figure 1. The values become more negative as temperature increases. Negative deviations from linear dependence on composition in U^E suggest weak interactions between unlike molecules and the importance of interstitial accommodation of component molecules into each other's cavities. Negative values of U^E indicate the predominance of long-range dispersive forces. Hence the results for U^E , suggest weak interactions between the solute and solvent molecules in the mixture under investigation.

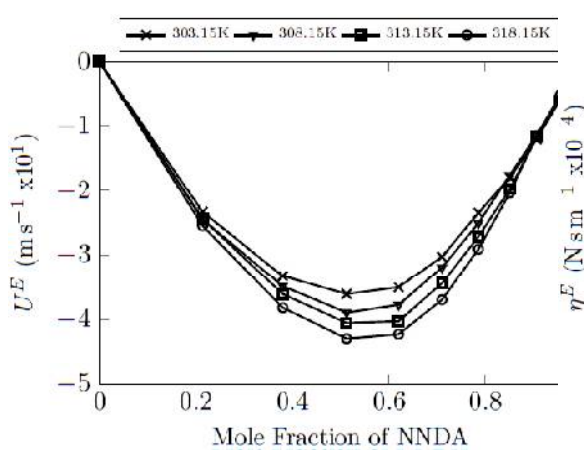


Fig 1: Variation of Excess Ultrasonic Velocity

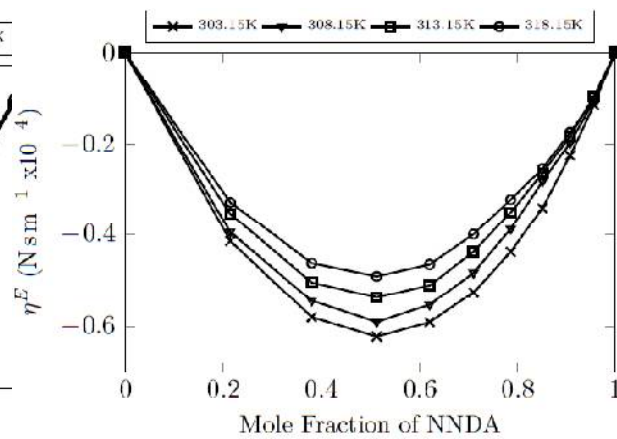


Fig 2: Variation of Excess Viscosity

The excess viscosity (η^E) (See Figure 2), from the linear dependence on mole fraction reveals that it is negative. It has been reported [14] that negative deviations in η^E occur in the mixtures where dispersion forces are primarily responsible for the interaction between the component molecules. Negative deviations in viscosity may also occur due to the difference in molecular size of the component molecules [15], as in the present case. This may be attributed to the presence of weak interaction between component molecules in the mixture. Similar behaviour in η^E was also

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Temp(K)	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	σ
U^E									
303.15	-14.3422	-2.426	-5.1466	16.2577	45.773	-58.379	-81.2513	88.2388	0.0635
308.15	-15.4994	-3.1778	1.6609	11.256	11.3153	-14.4101	-26.7394	22.274	0.0675
313.15	-15.8856	-11.8774	8.2723	153.6102	-301.582	-211.2531	863.0035	-506.5568	0.0923
318.15	-16.9679	-7.5627	5.129	71.9809	-150.65	-81.7124	434.6695	-270.3248	0.0617
η^E									
303.15	-2.4784	-0.3549	0.4648	4.4374	-12.6503	-5.1762	32.7825	-20.1412	0.0097
308.15	-2.3739	0.4137	-0.0163	-9.7966	18.7598	17.0859	-55.8427	29.0718	0.0084
313.15	-2.1415	-0.1885	-0.1676	2.4445	-0.42	-5.3018	4.2385	-1.0357	0.0002
318.15	-1.9412	-0.7206	0.7687	12.8819	-27.4926	-17.5743	77.1186	-46.8725	0.0134
V_m^E									
303.15	24.8764	11.3047	-5.3764	13.639	69.6904	-65.5096	-135.6727	132.9266	0.0924
308.15	28.3892	11.638	6.8147	18.0097	-7.8839	-6.8831	19.7019	-23.1348	0.0500
313.15	30.6049	1.2107	18.083	208.1226	-404.1361	-277.9486	1147.5715	-678.3833	0.1100
318.15	33.0555	8.4948	11.3556	104.5287	-151.6079	-151.6345	460.8058	-239.8668	0.1140
Z^E									
303.15	-0.4544	-0.2199	-0.0327	0.0811	-0.6931	0.0654	1.6257	-1.2241	0.0004
308.15	-0.4939	-0.2359	-0.1149	-0.0733	0.0539	-0.1763	-0.2347	0.3791	0.0001
313.15	-0.5171	-0.2074	-0.189	-0.852	1.6552	0.921	-4.7201	2.925	0.0004
318.15	-0.5455	-0.254	-0.1395	-0.4248	0.1401	0.7178	-0.7874	-0.0117	0.0007
ΔG^E									
303.15	10.4484	2.4871	0.1428	16.3571	-21.627	-28.9554	64.4863	-28.4781	0.0562
308.15	10.9069	6.9828	-4.6235	-58.6024	192.2181	47.9	-522.1089	353.6707	0.1292
313.15	11.7503	4.587	2.9901	3.7413	14.4996	-13.3624	-45.7356	43.3065	0.0073
318.15	12.608	0.1546	6.2473	95.8324	-180.5335	-136.0469	518.3974	-299.2251	0.0958
β^E									
303.15	6.6246	2.1253	-1.3398	-14.22	15.0863	25.164	-48.2748	22.1544	0.0033
308.15	7.3491	2.1576	-1.5519	-9.6274	4.9342	23.3927	-13.1502	-7.8321	0.0340
313.15	7.8935	3.8197	0.0961	-34.8433	59.2747	59.4047	-181.0809	95.9172	0.0177
318.15	8.5901	2.3241	-1.4319	-6.4976	50.5783	-13.4344	-136.0829	115.441	0.0151
L_m^E									
303.15	6.8236	2.0634	-0.0264	-5.0353	4.8692	9.1025	-16.1477	7.2443	0.0013
308.15	7.9291	2.3233	0.1301	-2.5148	-1.0886	7.9797	2.7919	-8.138	0.0139
313.15	8.8889	3.2442	0.6654	-12.482	21.9286	21.6495	-66.1726	34.9458	0.0070
318.15	9.9368	3.0687	0.069	-3.3741	22.8924	-4.2606	-60.5358	50.0289	0.0052

Table. 1: Coefficients of Redlich-Kister equation and standard deviation values of Excess Ultrasonic Velocity, Excess Viscosity, Excess Molar Volume, Excess Acoustic Impedance, Excess Gibbs's Free Energy, Excess Adiabatic Compressibility and Excess Free Length of NNDA + DEA at 303.15K, 308.15K, 313.15K and 318.15K

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suggested by Casas et al. [16] that negative deviations in η^E reflect weak interaction, whereas positive deviations show significant interaction between unlike molecules in the mixture.

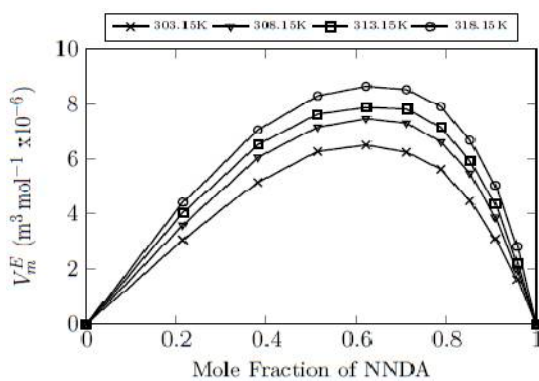


Fig 3: Variation of Excess Molar Volume

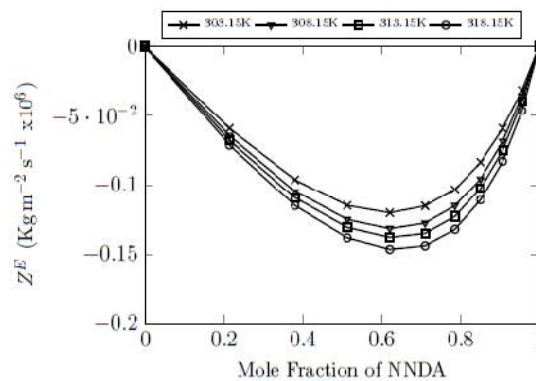


Fig4: Variation of Excess Acoustic Impedance

In the present study, the excess molar volume shows positive trend in the Figure 3 over the entire range of composition and reaches positive maximum at about 0.6 mole fraction of NNDA. The magnitude of V_m^E is the result of non-specific physical interactions and unfavourable interactions between dissimilar molecules [17]. It is observed that the excess acoustic impedance (Z^E) in this mixture is negative (Figure 4) suggest rupture of the hydrogen bonds. The trend of Z^E follows the trend of U^E , as expected. The G^E is positive over the whole mole fraction range for NNDA+DEA at the four studied temperatures, from the Figure 5. The G^E values also indicate weak molecular interactions occur between NNDA and DEA.

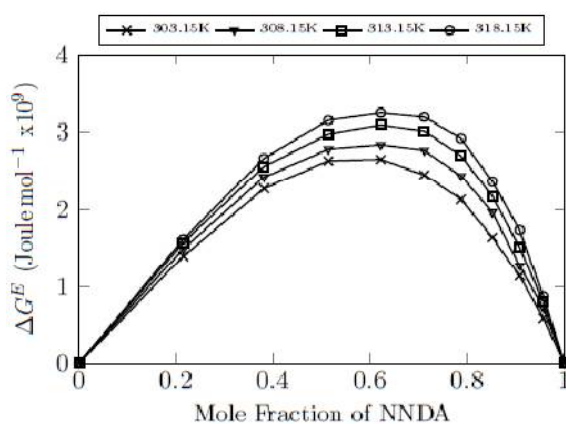


Figure 5: Variation of Excess Gibbs Free Energy

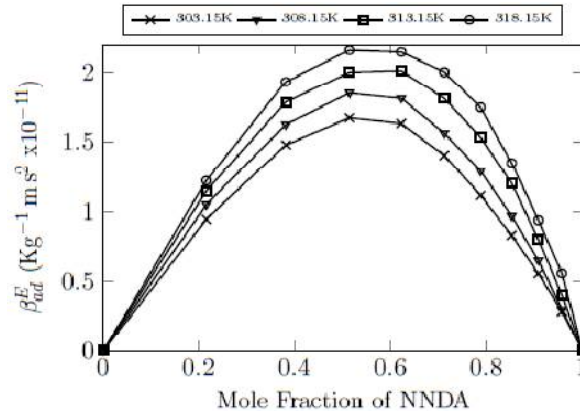


Figure 6: Variation of Excess Adiabatic Compressibility

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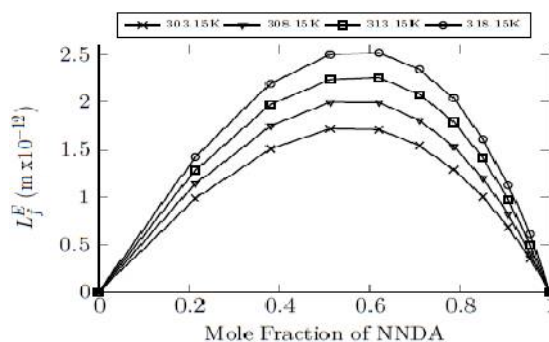


Fig 7: Variation of Excess Free Length

The β_{ad}^E and L_f^E (Figures 6 and 7) exhibit positive deviations over the entire composition range of NNDA. This suggests that in addition to dipole-dipole and dipole-induced dipole interactions, dispersive forces are also operative. It has been reported that dispersive forces tend to make a positive contribution to the excess functions. The positive values further attribute that apart from dispersion forces, weak dipolar forces are also operating with some specific interactions between molecules of the mixtures. So dispersive interactions [18] [19] [20] are dominant between NNDA and DEA.

V. CONCLUSION

The ultrasonic velocity, densities and viscosities at four different temperatures over the entire composition range of NNDA + DEA have been measured. From these measured physical property data, excess molar volumes, excess viscosity, excess ultrasonic velocity, excess Gibbs's free energy, excess free length and excess adiabatic compressibility have been calculated and correlated by a Redlich-Kister type polynomial equation to derive the coefficients and standard deviation.

From ultrasonic velocity, related excess acoustical parameters, it is concluded that there exists a weak molecular association between the component molecules in the mixtures. The values of U^E , β_{ad}^E and L_f^E exhibit positive deviations over the entire range of composition suggests that in addition to dipole-dipole and dipole-induced dipole interactions, dispersive forces are also operative in the system.

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