

Ultrasonic Behaviour of Binary Mixture of N-Propyl Alcohol in Ethylene Diamine at 3 MHz Frequency

U.B. Tumberphale^a, R.S.Kawale^b, N.P. Pawar^a, and G.M. Kalamse^a

¹Department of Physics, N.E.S. Science College, NANDED-431605, Maharashtra. India

²Department of Electronics, D.S.M. College, Jintur, Dist: Parbhani-431509, Maharashtra. India

Abstract: Ultrasonic velocity (U) and density (ρ) for the binary liquid mixtures of n-propyl alcohol (nPA) with Ethylene diamine (EDA), have been measured for 2MHz ultrasonic frequency at 30°C. The experimental data have been used to calculate acoustic parameters such as Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A), relaxation time (τ). The results are interpreted in terms of molecular interaction between the components of the mixture

Keywords: ultrasonic velocity, adiabatic compressibility, intermolecular free length, ethylene diamine

1. Introduction

Mixed solvents, rather than pure solvents find practical applications in most chemical processes, their properties are less known. Derived parameters from Ultrasonic velocity measurements and the corresponding excess functions provide qualitative information regarding the nature and strength of molecular interactions in liquid mixtures.¹

In recent years, Ultrasonic technique has become powerful and reliable tools for studying the molecular interactions in pure liquids as well as liquid mixtures.^{2,3} Study of molecular interactions between solute and solvent media has got great importance in many field of science including medicinal chemistry, industrial processes, biochemistry etc.

Speed of sound itself is highly sensitive to the structure and interactions present in the liquid mixtures as it is fundamentally related to the binding process between the constituents of the medium. For the qualitative estimation of the molecular interactions in solutions, the ultrasonic velocity approach was first studied by Jageman⁵. The measurement of ultrasonic velocity has been employed in understanding the molecular interactions in the liquid mixtures⁴.

Alcohols have found various applications and commercial use in medical and other fields, for example n-propyl alcohol (nPA) is very effective against a broad spectrum of microorganisms including bacteria, fungi and viruses such as HIV, hepatitis – B, are respirator syncytial viruses. Also n-propyl alcohol is in use as the safest antiseptic compound for topical use and is feedstock in the manufacture of insecticides⁶.

Ethylene diamine (EDA) is used primarily as an intermediate in the production of bleach activators, fungicides, chelating agents, plastic lubricants, textile resins, polyamides and fuel additives. Therefore it seemed important to examine the ultrasonic study of n-propyl alcohol (nPA) with ethylene diamine (EDA).

2. Experimental

n-propyl Alcohol (nPA) and ethylene diamine (EDA) used were of AR grade with minimum assay of 99.9% procured from S.D. fine chemicals and Spectrochem Pvt. Ltd. Mumbai. These chemicals are used without further purification. Samples of solution with different mole fraction EDA were prepared. The density (ρ) and viscosity (η) of pure liquids and liquid mixtures were determined by using Pycnometer and Ostwald's viscometer respectively. The Ultrasonic velocity (U) in the liquid and liquids mixtures have been measured using an Ultrasonic Fixed-frequency interferometer (Mittal type Model F-05.)

3. Theory

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), free length (L_f), Acoustical impedance (Z), Relative association (R_A), relaxation time (τ) by the following relations⁷.

$$\beta_{ad} = \frac{1}{\rho U^2} \quad \dots (1)$$

$$L_f = K (\beta_{ad})^{1/2} \quad \dots (2)$$

$$Z = U\rho \quad \dots (3)$$

$$R_A = \frac{\rho_s}{\rho_0} \left(\frac{U_0}{U_s} \right)^{1/3} \quad \dots (4)$$

$$\text{And } \tau = 4/3 \eta \beta_{ad} \quad \dots (5)$$

Where, K is temperature dependent constant, ρ_0 and U_0 are the density and ultrasonic velocity of the solute EDA.

The strength of interaction between the component molecules is well reflected in the deviations, in excess viscosity ($\Delta\eta$) Excess Adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f), Excess Acoustic impedance (ΔZ) etc. These parameters were calculated using the relation.

$$\Delta Y = Y_m - (X_1 Y_1 + X_2 Y_2) \quad \dots (6)$$

Where, Δy is any excess parameter, and y refers to above mentioned parameter. The subscripts m , 1 and 2 used in the above equation are respectively for the mixture, component (1) and component (2). X_1 and X_2 are the mole fractions of two components in the liquid mixture.

4. Results and Discussion

The experimental values of density (ρ), ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z), and relative association (R_A), Relaxation time (τ) of the binary liquid mixture of EDA + nPA with mole fraction of EDA at 303 K are listed in table (1) and the values of excess viscosity ($\Delta\eta$), excess ultrasonic velocity (ΔU), Excess adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f) are reported in table (2).

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. From fig. (1), it is observed that ultrasonic velocity (U) increases with mole fraction of EDA. The velocity increases non-linearly with concentration indicates that there is intermolecular interaction exists with mixture⁷. The maximum deviation from the linearity at a point of mole fraction, where change in the slope maximum indicating the complex formation⁸. In present system the formation of the complex is occur at 0.4 mole fraction of EDA.

On the basis of the model for the sound propagation proposed by Eyring and Kincaid ultrasonic velocity (U), increases on decrease of intermolecular free length (L_f) and vice-versa⁷ as shown in fig (2). Also the maximum deviation from linearity in the intermolecular free length curve occurs at 0.4 mole fraction of EDA which supports to our earlier conclusion.

Adiabatic compressibility (β_{ad}) decreases with increases in concentration of EDA as shown in Fig. (3). indicates that the free dipoles of nPA molecules would induced moments in the neighbouring molecules of the EDA resulting in dipolar induced dipolar interaction leading to contraction in the volume. This leads to subsequent decrease in the adiabatic compressibility (β_{ad}) as well as intermolecular free length (L_f)⁷ as shown in fig. (3) & (2) respectively. Also the maximum deviation occurs at 0.4 mole fraction of EDA supports to our earlier conclusion drawn in ultrasonic velocity curve.

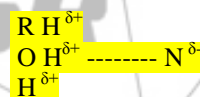
Specific acoustic impedance (Z) of the medium is governed by the inertial & elastic properties of the medium⁹. In the present system the acoustic impedance (Z) increases with increase in concentration of EDA. Increasing trend of acoustic impedance supports the possibility of the molecular interaction between solute and solvent molecules. Also, relaxation time (τ) have completely reverse trend with that of ultrasonic velocity. This indicates significant molecular interactions¹².

Fig. (5) Represents the graphical variations in Excess free length (ΔL_f) with mole fraction of EDA. As observed ΔL_f values are negative over entire range indicates presence of intermolecular reactions in the system¹⁰. The maximum negative value of Excess free length (ΔL_f) at the 0.4 mole fraction of EDA indicates the formation of complex.

Fig. (6) Shows the variation of excess adiabatic compressibility ($\Delta\beta_{ad}$) with mole fraction of EDA. The values of ($\Delta\beta_{ad}$) are negative over entire concentration range, suggests the strong molecular interaction between the unlike molecules of the component liquids¹¹. The maximum negative value of ($\Delta\beta_{ad}$) exists at 0.4 mole fraction of EDA indicates the formation of complex with supports to our earlier conclusion.

The excess viscosity ($\Delta\eta$) values are positive over entire range indicating the strong interaction between unlike molecules of the system.

In the present system the complex formation may be favoured by the linkage between $N^{\delta-}$ of EDA with $H^{\delta+}$ of nPA as represent below.



Conclusions

1. The acoustical parameters in the nPA + EDA system suggests the strong molecular interactions in the unlike molecules of the system.
2. Non linear behavior of Acoustic parameters suggests the formation of complex in the mixture.

EDA+ Propanol {Table No. 1}

The values of density (ρ), ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z) and relative association (R_A) of the binary liquid mixture of EDA+ nPA with mole fraction of EDA

Mole fraction of EDA (X)	ρ (Kg m ⁻³)	Viscosity	Sq. of R.I.	U (ms ⁻¹)	β_{ad} (10 ⁻¹⁰ m ² N ⁻¹)	L_f (10 ⁻¹¹ m)	Z (10 ⁶ kgm ⁻² s ⁻¹)	R_A	$\tau \times 10^{-13}$
0.0000	803.00	1.9380	1.9237	1206.6	8.55377	6.02485	0.968899	1.0000	22.1029
0.1378	825.13	2.2050	1.9386	1299.3	7.17891	5.51946	1.072091	1.0025	21.106
0.2717	835.67	2.2493	1.9695	1359.3	6.47641	5.24245	1.135926	1.0001	19.4231
0.4018	842.72	2.2245	2.0007	1428.6	5.81427	4.96724	1.203910	0.9920	17.24512
0.5282	854.72	2.1390	2.0206	1473.3	5.39132	4.78316	1.258964	0.9956	15.37604
0.6510	854.902	2.0064	2.0464	1530.6	4.99298	4.60307	1.308513	0.9834	13.3572
0.7705	854.905	1.8592	2.0695	1579.5	4.68860	4.46055	1.350322	0.9732	11.6227
0.8868	855.001	1.7501	2.0868	1626.6	4.42050	4.33115	1.390745	0.9638	10.31509
1.0000	899.00	1.7000	2.1228	1658.84	4.0423	4.1417	1.491297	---	9.16254

EDA+ Propanol {Table No. 2}

The values of Excess viscosity ($\Delta\eta$), Excess ultrasonic velocity (ΔU), Excess adiabatic compressibility ($\Delta\beta_{ad}$), Excess intermolecular free length (ΔL_f) of the binary liquid mixture of EDA+ nPA with mole fraction of EDA

Mole fraction of EDA (X)	($\Delta\eta$)	(ΔU) ms^{-1}	$\Delta\beta_{ad}$ ($10^{-10}m^2N^{-1}$)	ΔL_f ($10^{-11}m$)	ΔZ ($10^6kgm^{-2}s^{-1}$)
0.0000	0.0000	0.0000	0.0000	0.0000	0.00000
0.1378	0.2997	30.3868	-0.7531	-0.2459	0.0312
0.2717	0.3759	29.8372	-0.8516	-0.2707	0.0250
0.4018	0.3821	40.3060	-0.9268	-0.3009	0.0251
0.5282	0.3267	27.8479	-0.7795	-0.2470	0.0141
0.6510	0.2233	29.6178	-0.6238	-0.1958	-0.0005
0.7705	0.1046	24.4799	-0.3891	-0.1133	-0.0211
0.8868	0.0232	18.9890	-0.1325	-0.0237	-0.0414
1.0000	0.0000	0.0000	0.0000	0.0000	0.00000

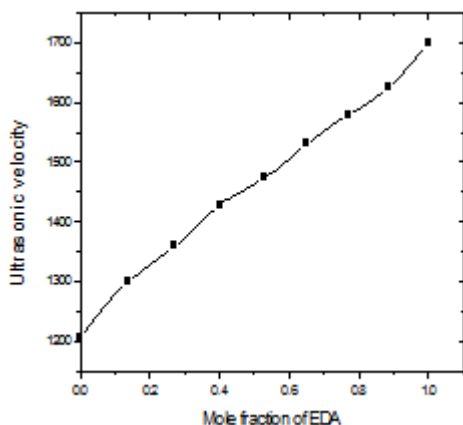


Figure 1: Variation of ultrasonic velocity with mole fraction of EDA

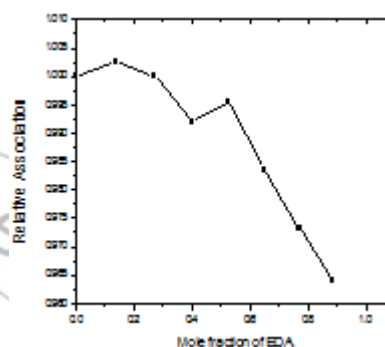


Figure 4: Variation of Relative Association with mole fraction of EDA

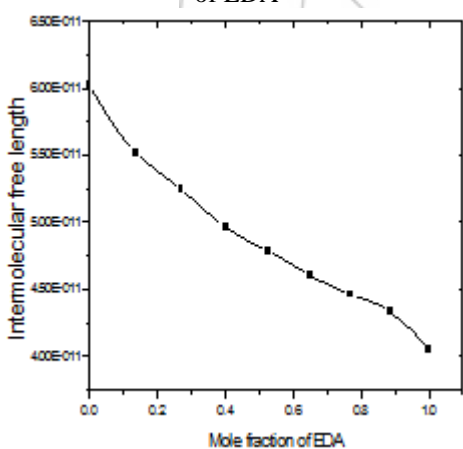


Figure 2: Variation of Intermolecular free length with mole fraction of EDA

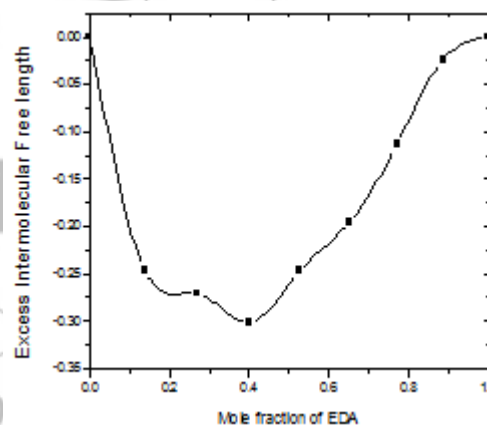


Figure 5: Variation of Excess intermolecular Free length with mole fraction of EDA

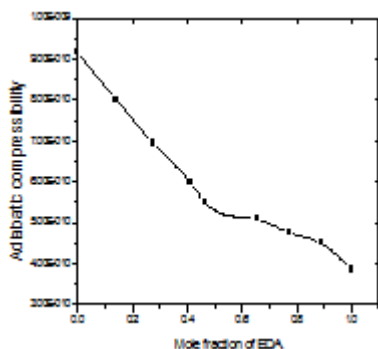


Figure 3: Variation of adiabatic compressibility with mole fraction of EDA

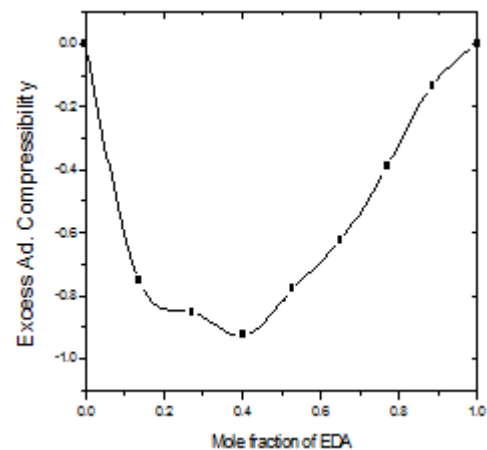


Figure 6: Variation of Excess Ad. Compressibility with mole fraction of EDA

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