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Ultrasonic Studies on Molecular Interactions in Binary Mixtures at 308k and Different Concentrations

G. R. Bedare[1], V. D. Bhandakkar[2], B. M. Suryavanshi[3]

[1]Department of Physics, N. S. Sci. & Arts College, Bhadrawati Dist– Chandrapur (MS), India 442902

[2]Department of Electronics, Anand Niketan College, Warora Dist– Chandrapur (MS), India 442907

[3]Department of Physics, Institute of Science, Nagpur (MS), India 40001

Abstract: ***The ultrasonic velocity, density and viscosity at 308K temperature have been measured in the binary systems of acrylonitrile with 1, 4-Dioxane. From the experimental data of ultrasonic velocity, density and viscosity, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free volume (V_f), Specific acoustical impedance (Z), Relaxation time (τ), excess values of adiabatic compressibility (βa^E), free length (L_f^E) and free volume (V_f^E) were calculated. It has been observed that, weak dispersive type intermolecular interactions are confirmed in the systems investigated. Dipole inducement is found to be more predominant in the system. The results are interpreted in terms of molecular interaction between the components of the mixture.***

Keywords: Acoustical properties, Acrylonitrile, binary liquid mixture, Molecular interactions, 1, 4-Dioxane and Ultrasonic velocity.

1. Introduction

The variation of ultrasonic velocity, density, viscosity and other acoustic parameters such as adiabatic compressibility, intermolecular free length and free volume along with their excess values in binary liquid mixtures with changing mole fractions of one of the components are of immense importance. The ultrasonic study of liquid mixtures containing polar and non-polar components find applications in various industrial and technological processes, as such liquid mixtures provide a wide range of solutions with appropriate properties [1-5].

Ultrasonic velocity measurements are used to determine the structure-function relationship of biomolecules. The ultrasonic velocity gives information about the bonding between the molecule and formation of complexes at various temperatures through molecular interactions. Knowledge of ultrasonic velocity, density and viscosity of different mole fractions of solute-solvent mixtures can be used to compute important thermodynamic parameters [6- 9]. Ultrasonic velocity and viscosity measurements have been widely used in the field of interactions and structural aspect evaluations studies. In the present work, an attempt has been made to investigate the behavior of binary solutions of 1, 4-Dioxane in acrylonitrile with regard to adiabatic compressibility, intermolecular free length, free volume, Specific acoustical impedance (Z), Relaxation time (τ) and excess values of adiabatic compressibility (βa^E), free volume (V_f^E) and free length (L_f^E) from ultrasonic measurements at 308K temperature. The results are interpreted in terms of molecular interaction between the components of the mixtures.

2. Materials and Methods

The chemicals used in the present work were of AR grade. Solutions of different concentrations were prepared for each binary system. The ultrasonic velocity (U) in liquid mixtures prepared by taking purified AR grade samples, have been measured at 308K temperature using an ultrasonic interferometer (Mittal type, Model F-81) working at 2 MHz frequency. The accuracy of sound velocity was ±0.1m/s. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density of pure liquids and liquid mixtures was determined using pycknometer by relative measurement method with an accuracy of ±0.1Kgm^{-3}. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ±0.0001NSm^{-2}. The temperature around the viscometer and pycknometer was maintained within ±0.1K in an electronically operated constant temperature water bath. All the precautions were taken to minimize the possible experimental error.

3. Results and Discussion

Using the experimental data of ultrasonic sound velocity, density and viscosity, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), free volume (V_f), Specific acoustical impedance (Z), Relaxation time (τ) were calculated by the following equations (1-5).

$$\beta_a = (U^2 \rho)^{-1} \quad \ldots\ldots (1)$$

$$L_f = K_T \beta a^{1/2} \quad \ldots.. (2)$$

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

$$Z = U \rho \quad \ldots\ldots (4)$$

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

Where, K_T *is* the temperature dependent constant having a value $209.5906*10^{-8}$ in MKS system at 308K, K is constant equal to $4.28*10^9$ in MKS system, b is a cubical packing fraction taken as 2 for all the liquids, R is the Universal gas constant, T is the experimental temperature, $M_{eff} = \Sigma x_i m_i$, where x_i is the mole fraction and m_i is the molecular weight of the component. The excess values like V_f^E, β^E, L_f^E have been calculated using the following standard relation: $A^E = A_{exp} - A_{id}$. Where, $A_{id} = \Sigma A_i X_i$, where, A_i is any acoustical parameter and X_i is the mole fraction of liquid component.

The measured parameters *viz*., density (ρ), ultrasonic velocity (U) and viscosity (η) and calculated parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f) and free volume (V_f) for the system: Acrylonitrile+ 1, 4-dioxane at temperature 308K are given in Table-1. Table-2 shows the calculated parameters such as Specific acoustical impedance (Z), Relaxation time (τ), excess values of adiabatic compressibility (βa^E), free volume (V_f^E) and free length (L_f^E) for the system: Acrylonitrile+ 1, 4-dioxane at temperature 308K. Table-1 shows that, in the system, density decreases with concentration of Acrylonitrile in 1, 4- Dioxane. This indicates that, the molecular interaction is observed in the system studied. The velocity values have the reverse trend within the system. It is observed that for a given concentration as the number of CH- group or chain length increases, the sound velocity increases. Viscosity decreases in system, suggesting thereby more association between solute and solvent molecules.

Also from the Table-1, it is observed that, the adiabatic compressibility and free length increases with increase of mole fraction of the solute in system. This may lead to 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 the liquid systems. Increase in intermolecular free length in system leads to positive deviation in sound velocity and in compressibility. This indicates that, the molecules are nearer in the system.

The free volume is the space available for the molecule to move in an imaginary unit cell. The increase in free volume in system shows that the strength of interaction increases gradually with the increase in solute concentration. It represents that there is weak interaction between the solute and solvent molecules. The observed increase values of V_f in system are due to close association between solute and solvent molecules. Thus, a progressive increase in free volume in Acrylonitrile + 1, 4-dioxane mixtures clearly indicates the existence of ion-solvent interaction, due to which the structural arrangement is considerably affected [10-12].

To understand the nature of molecular interactions between the components of the liquid mixtures, it is important to discuss the same parameters in term of excess parameters rather than actual values. Non-ideal mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures.
In Table-2, the acoustic impedance (Z) (which is the product of ultrasonic velocity and density of the solution) decreases with increase in concentration of Acrylonitrile, but relaxation time (τ) have completely same trend with that of the acoustic impedance for the system. This also indicates the significant interactions in the system. The increase in L_f and decrease of Z with the concentration of Acrylonitrile, suggest the presence of intermolecular interactions in the system.

In Table-2, to ascertain the exact type of interaction existing between the components, respective excess parameters have been calculated for the system, it indicates that βa^E and L_f^E are positive over the entire mole fraction range, except at 0.1 mole fraction. Thus, βa^E clearly suggests that weak dispersive interactions between the components of the mixture.

Table-2 shows that βa^E and L_f^E are non-linear as Acrylonitrile mole fraction is increased. Thus, strong dipolar interactions are restricted more and more whereas the weak dispersive interactions are predominating and are maximum around 0.9 mole fractions. As the molecular symmetry is retained to a greater extent, after 0.9 mole fraction, βa^E and L_f^E are found to decrease. However, V_f^E for the system is mostly negative, existing weak dispersive interactions [13-15].

The variations of Density (ρ), Velocity (U), Viscosity (η), Adiabatic compressibility (β_a), Intermolecular free length (L_f), free volume (V_f), Specific acoustical impedance (Z) and Relaxation time (τ) with respect to mole fraction (x) of Acrylonitrile + 1,4-dioxane binary systems are shown in Fig.: I, II, III, IV, V, VI, VII and VIII respectively.

4. Tables and Figures

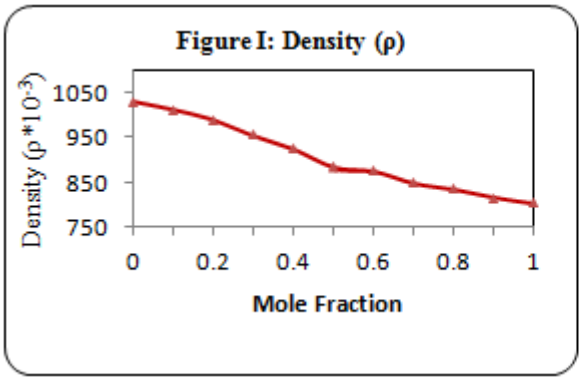
Table 1: Density (ρ), Velocity (U), Viscosity (η), adiabatic compressibility (β_a), Intermolecular free length (L_f) and free Volume (V_f) of Acrylonitrile + 1, 4-dioxane at 308K temperature and 2 MHz frequency.

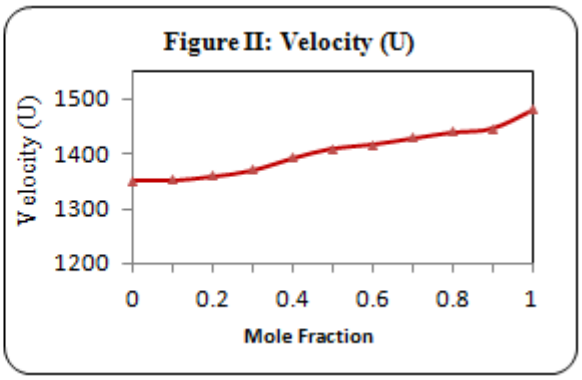
Mole fraction of Acrylonitrile in 1,4 - Dioxane	ρ (kg/m^3)	U (m/s)	$\eta*10^{-3}$ (CP)	β_a*10^{-10} (Pa^{-1})	L_f*10^{-10} (m)	$\mathbf{V_f}*10^{-7}$ (m^3mol^{-1} **)**
0.0	1014.9	1273.00	0.401	6.080	0.5075	1.997
0.1	978.21	1270.00	0.395	6.338	0.5182	2.315
0.2	951.56	1293.66	0.390	6.280	0.5158	2.740
0.3	922.63	1318.66	0.387	6.234	0.5139	3.191
0.4	894.75	1338.66	0.381	6.237	0.5140	3.706
0.5	878.45	1351.33	0.378	6.234	0.5139	4.180

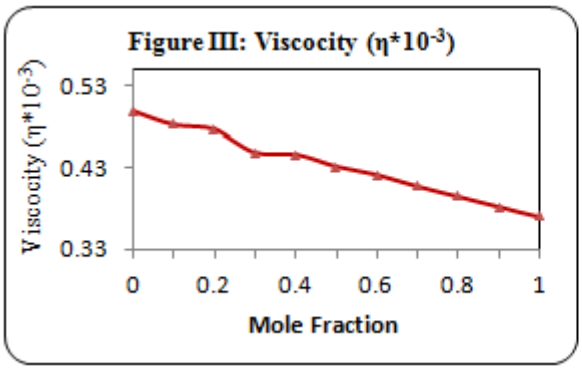
0.6	852.37	1366.00	0.373	6.287	0.5161	4.751
0.7	840.12	1387.66	0.370	6.187	0.5120	5.375
0.8	820.18	1403.00	0.367	6.194	0.5123	5.987
0.9	799.14	1416.33	0.366	6.241	0.5142	6.592
1.0	786.00	1430.00	0.365	6.222	0.5134	7.240

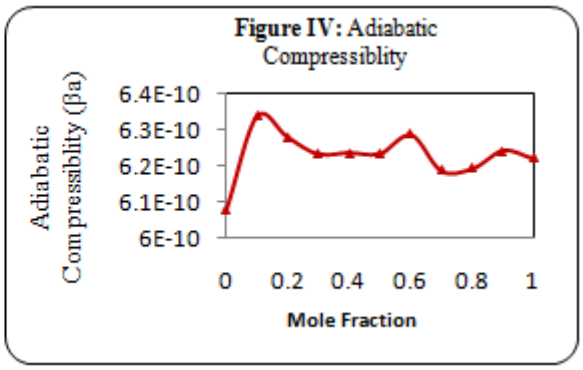
Table 2: Specific acoustical impedance (Z), Relaxation time (τ), Excess values of adiabatic compressibility (βa^E), free length (L_f^E) and free volume (V_f^E) of Acrylonitrile + 1, 4-dioxane at 308K and 2 MHz frequency.

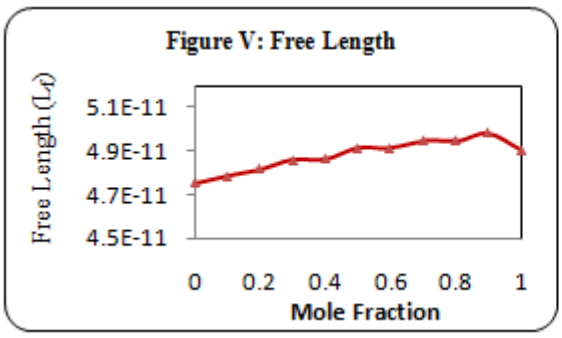
Mole fraction of Acrylonitrile in 1, 4-dioxane	$Z*10^6$ (kg/m^2s)	$\tau*10^{-13}$ (s)	$\beta_a^E*10^{-10}$ (Pa^{-1})	$L_f^E*10^{-10}$ (m)	$V_f^E*10^{-7}$ (m^3mol^{-1})
0.0	1.2920	3.251	0.0000	0.00000	0.0000
0.1	1.2423	3.343	0.2441	0.01008	-0.2062
0.2	1.2309	3.268	0.1719	0.00711	-0.3060
0.3	1.2165	3.217	0.1113	0.00461	-0.3787
0.4	1.1977	3.170	0.1002	0.00415	-0.3885
0.5	1.1870	3.149	0.8318	0.00344	-0.4391
0.6	1.1643	3.133	0.1225	0.00506	-0.3921
0.7	1.1652	3.053	0.8269	0.00034	-0.2927
0.8	1.1507	3.038	0.7814	0.00003	-0.2049
0.9	1.1315	3.050	0.3349	0.00138	-0.1242
1.0	1.1239	3.029	0.0000	0.00000	0.0000

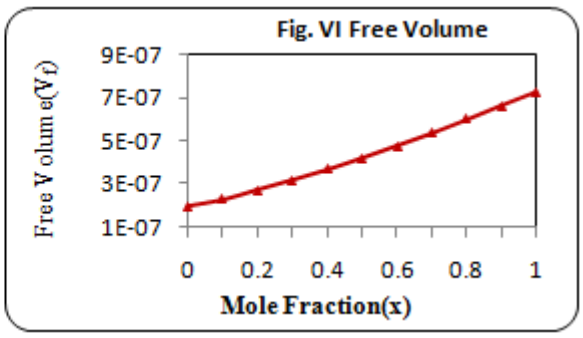


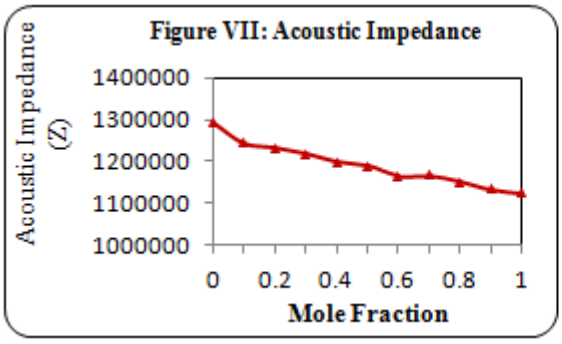












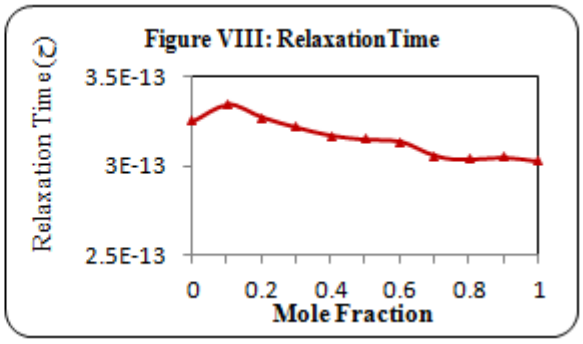


Figure I-VIII: The variations of Density (ρ), Velocity (U), Viscosity (η), adiabatic compressibility (β_a), free length (L_f), free Volume (V_f), Specific acoustical impedance (Z) and Relaxation time (τ) w. r. to mole fraction (x) of the system: Acrylonitrile + 1, 4-dioxane at 308K are shown in Fig.: I, II, III, IV, V, VI, VII and VIII respectively.

5. Conclusion

The observed increase of ultrasonic velocity indicates the solute-solvent interaction. The existence of solute-solvent type molecular interaction is favored in system studied, confirmed from the U, ρ, η, βa, L_f, V_f, Z and τ data. The variation in ultrasonic velocity (U), density (ρ) and viscosity (η) and other related thermodynamic parameters is non-linear. Ultrasonic velocity of the system increases, depending on the concentration of Acrylonitrile. The non linear behavior confirms the presence of solute-solvent, solvent-solvent, and dipole-dipole interactions. For the observed molecular interaction, hydrogen bond formations are responsible for the heteromolecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of the mixture as existing in the liquid systems. Parameters like acoustic impedance, relaxation time also indicate a weak dipole-induced dipole interaction between the components, which is also confirmed by the nature of their excess values.

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