IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861, PP 36-39
www.iosrjournals.org

Study of molecular interactions in the binary liquid mixtures from acoustic and thermodynamic parameters at 303K

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ABSTRACT: *The ultrasonic velocity, density and viscosity at 303K have been measured in the binary systems of acrylonitrile with 1, 4-Dioxane. From the experimental data, various acoustical parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), specific acoustical impedance (Z), free volume (V_f), internal pressure (π_i) and relaxation time (τ) 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.*

I. INTRODUCTION

Among various spectroscopic techniques such as X-ray crystallography, chromatography, NMR, EPR, vibration and Raman spectroscopy, neutron & light scattering, circular dichroism (CD), IR and ultrasonic velocity measurements, ultrasonic velocity measurements have been found to be most powerful tool in the investigation of structure and thermodynamic properties and predict the intermolecular interactions in pure liquid [1], liquid mixtures [2-5] and ionic interactions in electrolytic solutions [6, 7]. 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 [8, 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 and internal pressure from ultrasonic measurements at 303K. The results are interpreted in terms of molecular interaction between the components of the mixtures.

II. MATERIALS AND METHODS

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 303K 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 $\pm 0.1 Kgm^{-3}$. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of $\pm 0.0001 NSm^{-2}$. 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.

III. 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), specific acoustical impedance (Z), free volume (V_f), internal pressure (π_i) and relaxation time (τ) were calculated by the following equations (1-6).

$\beta_a = (U^2 \rho)^{-1}$ …… (1)

$L_f = K_T \beta a^{1/2}$ ….. (2)

$Z = U \rho$ …… (3)

$V_f = (M_{eff}\, U/\eta K)^{3/2}$ ….. (4)

$\pi_i = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M_{eff}^{7/6})$ ….. (5)

$\tau = 4/3\ \eta\ \beta_a$ ….. (6)

Where, K_T is the temperature dependent constant having a value $207.7121*10^{-8}$ in MKS system at temperature 303K, 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 measured parameters *viz*., Density (ρ), Velocity (U), Adiabatic compressibility (β_a), Intermolecular free length (L_f) and specific acoustical impedance (Z) for the system: Acrylonitrile+ 1, 4-dioxane at temperature 303K are given in Table-1. Table-2 shows, Viscosity (η) and calculated parameters such as free Volume (V_f), Internal Pressure (π_i) and Relaxation time (τ) for the system: Acrylonitrile+ 1, 4-dioxane at temperature 303K. 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.

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. In Table-1, the acoustic impedance (Z) is observed to be decreased with increase in concentration of Acrylonitrile.

From the Table-2 it is observed that, Viscosity decreases in system, suggesting thereby more association between solute and solvent molecules. The internal pressure decreases with increasing mole fraction of the solute in system. The internal pressure may give information regarding the nature and strength of forces existing between the molecules. 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 free volume is the space available for the molecule to move in an imaginary unit cell. This reduces internal pressure. As stated above the internal pressure (π_i) decreases with increase in concentration of Acrylonitrile in the systems. 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 and decrease in internal pressure in Acrylonitrile + 1, 4-dioxane mixtures clearly indicates the existence of ion-solvent interaction, due to which the structural arrangement is considerably affected. The relaxation time (τ) have completely reverse trend with that of velocity, indicates the significant interactions in the system[10-13].

The variations of Velocity (U), Density (ρ), Viscosity (η), Adiabatic compressibility (β_a), Intermolecular free length (L_f), and free volume (V_f) with respect to compositions (x) of Acrylonitrile+ 1,4-dioxane binary systems are shown in Fig.: 1(A), 1(B), 1(C), 1(D), 1(E), and 1(F) respectively.

IV. TABLES AND FIGURES

TABLE-1: - Density (ρ), Velocity (U), adiabatic compressibility (β_a), Intermolecular free length (L_f) and specific

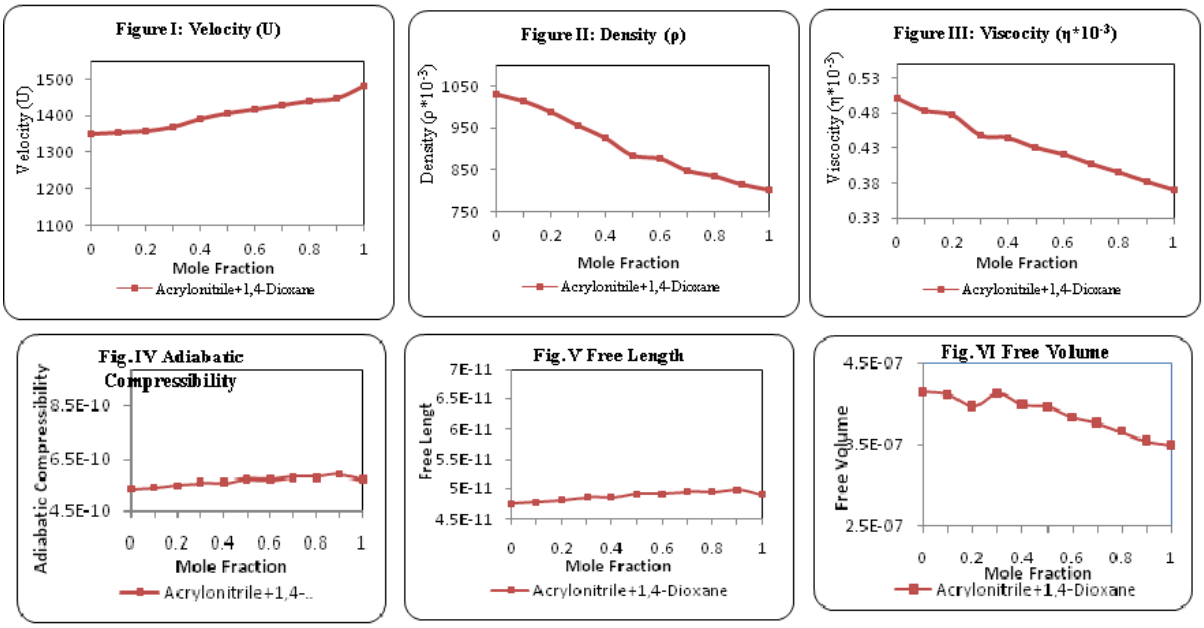
Acoustical impedance (Z) of the binary system: Acrylonitrile+ 1, 4-dioxane at 303K.

Mole fraction of Acrylonitrile in 1,4 - Dioxane	ρ (kg/m^3)	U (m/s)	β_a*10^{-10} (Pa^{-1})	L_f*10^{-10} (m)	$Z*10^6$ (kg/m^2s)
0.0	1023.9	1286.41	5.902	0.5000	1.3172
0.1	1003.1	1298.66	5.911	0.5004	1.3027
0.2	982.10	1314.00	5.897	0.4999	1.2904
0.3	938.89	1323.42	6.081	0.5076	1.2425
0.4	916.59	1341.66	6.061	0.5067	1.2297
0.5	889.14	1358.00	6.099	0.5083	1.2074
0.6	866.23	1373.14	6.123	0.5093	1.1894
0.7	843.00	1392.00	6.122	0.5093	1.1734
0.8	828.36	1408.66	6.084	0.5077	1.1668
0.9	804.36	1426.66	6.108	0.5087	1.1475
1.0	795.00	1454.00	6.950	0.6021	1.1559

TABLE-2: Viscosity (η), free Volume (V_f), Internal Pressure (π_i) and Relaxation time (τ) of the binary System: Acrylonitrile + 1, 4-dioxane at 303K.

Mole fraction of Acrylonitrile in 1,4 - Dioxane	$\eta*10^{-3}$ (CP)	V_f*10^{-7} (m^3mol^{-1})	π_i*10^{8} (P_a)	$\tau*10^{-13}$ (s)
0.0	0.448	1.718	7.047	3.525
0.1	0.435	2.070	6.163	3.435
0.2	0.419	2.519	5.395	3.297
0.3	0.406	2.980	4.711	3.298
0.4	0.398	3.475	4.206	3.223
0.5	0.390	4.027	3.758	3.174
0.6	0.384	4.586	3.396	3.140
0.7	0.376	5.267	3.065	3.073
0.8	0.370	5.960	2.804	3.005
0.9	0.369	6.588	2.570	3.008
1.0	0.367	7.351	2.379	2.915

FIG. I-VI: The variations of Velocity (U), Density (ρ), Viscosity (η), adiabatic compressibility (β_a), free length (L_f), and free Volume (V_f) w. r. to mole fraction (x) of the system: Acrylonitrile + 1, 4-dioxane at 303K are shown in Fig.: I, II, III, IV, V and VI respectively.



V. 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, Z, V_f, π_i and τ data. The variation in ultrasonic velocity (U), density (ρ) and viscosity (η) and other related thermodynamic parameters is non-linear. Ultrasonic velocities 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.

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