Acoustical Studies on Binary Liquid Mixture of Methylmethacrylate in 1, 4-Dioxane at 303 K Temperature

G. R. Bedare

Department of Physics, N. S. Science & Arts College, Bhadrawati Dist– Chandrapur (MS), India gr.bedare@gmail.com

B. M. Suryavanshi

Department of Physics, Institute of Science, Nagpur (MS), India bm_suryavanshi@yahoo.co.in

V. D. Bhandakkar

Department of Electronics, Anand Niketan College, Warora Dist– Chandrapur (MS), India vivekbhandakkar@gmail.com

Abstract: Molecular interaction studies using ultrasonic technique in the binary liquid mixture of Methylmethacrylate in 1, 4-dioxane has been carried out at 303 K and at 2 MHz frequency. Using measured values of Density (ρ), Ultrasonic velocity (U) and Viscosity (η) acoustical parameters such as Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z), Internal pressure (π_i) and Relaxation time (τ) are evaluated. From the properties of these parameters, the nature and the strength of molecular interactions in this binary system are discussed.

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

1. INTRODUCTION

The ultrasonic velocity determined by interferometer method is considered as more reliable and precise as compared to other methods have been reported in the literature for computing ultrasonic velocity. In many industrial applications, rather than single component liquid system, liquid mixtures are used in processing and product formulations [1, 2]. Liquid mixtures consisting of polar and non-polar components are of considerable importance in industries such as petrochemical, pharmaceutical and dye. The ultrasonic study of liquids is of immense important in understanding the nature and strength of molecular interactions. The biological activity of drug molecules and the activation energy of the metabolic process [3, 4] basically depend on the type and strength of the intermolecular interactions. Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality [5, 6]. From the literature, the nature and degree of molecular interactions in different solutions changes, depending upon the nature of solvent, the structure of solute molecule and extent of solution taking place in the solution [7, 8].

In view of growing interest, the result of an ultrasonic velocity, density and viscosity to study the related acoustical parameters for the binary system of Methylmethacrylate +1, 4-dioxane at the temperature 303 K and at 2 MHz frequency have been reported in the present paper. The variations of these properties with composition at the temperature 303 K are studied in terms of molecular interactions between unlike molecules. Further, these properties have been widely used to study the intermolecular interactions between the various species present in the mixture.

In the present work, the measurement of ultrasonic velocity, density and viscosity and computation of related parameters at 303 K in non-ideal binary mixture of 1, 4-dioxane with Methylmethacrylate has been studied.

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Methyl methacrylate polymers and copolymers are used in waterborne, solvent and undissolved coatings. Exterior latex paint based on emulsions containing methyl methacrylate is used most widely. Solvent reducible polymers containing methyl methacrylate are used for industrial finishes, metal and foil coatings. Solvent and emulsion polymers containing methacrylates are also used in adhesives, sealants, leather coatings, paper coatings, inks, floor polishes and textile finishes. Special methacrylate polymers are used for dental prostheses, surgical bone cements. Polymer concretes based on methyl methacrylate and Portland cement are used to patch highways and bridges. Methyl methacrylate is also used in the production of polymers added to lubricating oils. 1, 4-Dioxane can be used as a stabilizer for 1, 1, 1-trichloroethane for storage and transport in Aluminium Containers.

2. EXPERIMENTAL DETAILS

All the chemicals used were of Analytical Reagent (AR) grade with minimum assay of 99.9%. The ultrasonic velocity (*U*) in liquid and liquids mixtures have been measured using an ultrasonic interferometer (Mittal type, Model F-81) working at 2 MHz frequency with an accuracy of ± 0.1 ms⁻¹. 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 ± 0.1 Kgm⁻³. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with an accuracy of ± 0.0001 NSm⁻². The temperature around the viscometer and pycknometer was maintained within ± 0.1 K in an electronically operated constant temperature water bath. All the precautions were taken to minimize the possible experimental error.

The various acoustical parameters such as adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z), Internal pressure (π_i) and Relaxation time (τ) have been calculated from the measured data using the following standard expressions:

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

$$L_{\rm f} = K_{\rm T} \beta_{\rm a}^{1/2} \tag{2}$$

$$Z = U \rho \tag{3}$$

$$\pi_{\rm i} = b R T (K \eta / U)^{1/2} (\rho^{2/3} / M_{\rm eff}^{7/6})$$
(4)

$$\tau = 4/3 \ \eta \beta_a \tag{5}$$

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.

3. RESULTS AND DISCUSSION

The experimentally measured values of Density (ρ), Ultrasonic velocity (U) and Viscosity (η) and calculated thermodynamic parameters Adiabatic compressibility (β_a), Intermolecular free length (L_f), Acoustic impedance (Z), Internal pressure (π_i) and Relaxation time (τ) of binary liquid system - Methylmethacrylate in 1, 4 - Dioxane at temperatures 303 K at frequency 2 MHz are presented in Table-1

Table-1 clearly shows that, density decreases with concentration of Methylmethacrylate in 1, 4 - Dioxane at temperatures 303K. The ultrasonic velocity values also have the same trend in the system. Viscosity increases in this system, suggesting thereby more association between solute and solvent molecules [9-11].

Adiabatic compressibility is a measure of intermolecular association or dissociation or repulsion. The structural change of the molecules in the mixture takes place due to the existence of electrostatic field between the interacting molecules. The structural arrangement of the molecule affects the adiabatic compressibility. From the Table-1, the adiabatic compressibility and free length increases with increase of mole fraction of the Methylmethacrylate in the solution. This indicates the presence of specific molecular interaction between the molecules of the liquid mixture. Generally, when the ultrasonic velocity decreases; the value of free length increases.

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Increase in intermolecular free length in system leads to negative deviation in ultrasonic velocity and positive deviation in adiabatic compressibility.

The specific acoustic impedance (Z) is related to density and velocity. In Table-1, the acoustic impedance (Z) decreases with increase in concentration of Methylmethacrylate The increase in L_f and decrease in Z with the concentration of Methylmethacrylate in the solution., suggest the presence of intermolecular interactions in the system. 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 decrease in free volume in system show that the strength of interaction decreases gradually with the increase in Methylmethacrylate and 1, 4 - Dioxane molecules.

The free volume is the space available for the molecule to move in an imaginary unit cell. This reduces internal pressure. Internal pressure (π_i) decreases with increase in concentration of Methylmethacrylate in the system. Thus, a progressive decrease in internal pressure in Methylmethacrylate + 1, 4 - Dioxane mixtures clearly indicates the existence of intermolecular interaction, due to which the structural arrangement is considerably affected. But, relaxation time (τ) have completely same trend with that of velocity and the acoustic impedance for the system. This also indicates the significant interactions in the system [12, 13].

Table 1. The experimentally measured values of Density (ρ), Ultrasonic velocity (U), Viscosity (η) and calculated values of Adiabatic compressibility (β_a), Intermolecular free length (L_f), specific acoustical impedance (Z), Internal Pressure (π_i) and Relaxation time (τ) w. r. to concentrations of Methylmethacrylate in 1,4-Dioxane at .303K and 2MHz frequency.

Mole fraction of	ρ	U	β _a	L_{f}	Z*10 ⁶	η*10 ⁻³	$\pi_{i}^{*}10^{8}$	τ *10 ⁻¹³
Methylmethacrylate in 1,4 - Dioxane	(kg/m ³)	(m/s)	*10 ⁻¹⁰ (Pa ⁻¹)	*10 ⁻¹⁰ (m)	(kg/m²s)	(CP)	(P _a)	(s)
0.0	1023.9	1286.41	5.902	0.5000	1.3172	0.448	7.047	3.525
0.1	1013.1	1283.66	5.990	0.5038	1.3004	0.4631	6.432	3.699
0.2	994.32	1268.00	6.255	0.5148	1260	0.4751	5.894	3.962
0.3	982.56	1236.66	6.655	0.5311	1.2150	0.4806	5.461	4.264
0.4	969.83	1212.00	7.019	0.5453	17543	0.4898	5.092	4.584
0.5	961.07	1188.66	7.372	0.5589	1.1417	0.5013	4.796	4.928
0.6	954.85	1173.33	7.607	0.5677	1.1203	0.5205	4.560	5.279
0.7	945.31	1153.33	7.953	0.5805	1.0902	0.5289	4.308	5.608
0.8	939.41	1146.75	8.095	0.5856	1.0772	0.5436	4.094	5.867
0.9	935.88	1136.25	8.276	0.5922	1.0633	0.5622	3.930	6.204
1.0	927.00	1130.00	8.448	0.5983	1.0475	0.5761	3.744	6.489



Figure 1-6. The variations of Density (ρ), Ultrasonic Velocity (U), Viscosity (η), adiabatic compressibility (β_a), free length (L_f) and free Volume (V_f) w. r. to mole fraction of the Methylmethacrylate in 1,4-Dioxane at 303K are shown in the Figures: 1, 2, 3, 4, 5 and 6 respectively.

4. CONCLUSION

The ultrasonic velocity, density, viscosity and other related parameters were calculated. The existence of type of molecular interaction in solute-solvent is favored in the system, confirmed from the U, ρ , η , β_a , L_f , Z, η , π_i and τ data. The variation in ultrasonic velocity (U), density (ρ) and viscosity (η) and other related thermodynamic parameters such as β_a , L_f , Z, η , π_i and τ at various concentrations and at 303K temperature in the binary solution of Methylmethacrylate in 1,4 - Dioxane shows the variation to be non-linear. Weak dispersive type intermolecular interactions are confirmed in the systems investigated. Components maintain their individuality in the system investigated. All the experimental determinations of acoustic parameters are strongly correlated with each other. 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 system.

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AUTHOR'S BIOGRAPHY



Gajendra R. Bedare

Date of Birth: 21st MARCH, 1976 Asstt. Professor in Physics Degrees: B. Sc., 1996 (Nagpur University, India) M. Sc. (Physics), 1998 (Nagpur University, India) M. Phil. (Physics), 2009 (Alagappa University, India) Area of Research Work: Ultrasonics