

Study of Molecular Interactions in Liquidmixture Using Ultrasonic Technique

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Abstract: The ultrasonic velocity, density and viscosity of the mixtures namely, methylmethacrylate with methanol, p-dioxane and cyclohexane at 303K have been measured. From the measured data, some of the acoustical parameters such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ), acoustic impedance (Z_a) and Gibb's free energy (ΔG) values have been calculated for all the mixtures. The behavior of these parameters with composition of the mixture at the temperature 303K has been discussed in terms of molecular interaction between the components of liquids.

Keywords: Adiabatic compressibility, free length, frees volume, internal pressure, molecular interactions and binary systems.

I. Introduction:

The study of inter molecular interactions plays an important role in the development of molecular sciences. In recent years ultrasonic technique has become powerful tool in providing information regarding the behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium. The study of miscibility and molecular interaction present in polymer like methylmethacrylate and solvent in a polymer solution is of great significance for engineering applications of polymers [1]. They also provide substantial information on the process involving polymer production and their uses [2, 3]. Further, polymer dissolution also plays a key role in many industrial applications in a variety of areas and an understanding of the dissolution process allows for the optimization of design and processing conditions as well as selection of suitable solvent [4,5]. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements [6-11]. However, there are very few studies on the quantitative study of the interactions in a polymer solution system [12, 13].

Methylmethacrylate (MM) is a versatile fluid and has been used on a wide range of fields and applications [14, 15]. In view of growing interest, in this paper, the results of an ultrasonic velocity, density and viscosity to study the related acoustical parameters, for the binary systems of methylmethacrylate + methanol, methylmethacrylate + p-dioxane and methylmethacrylate + cyclohexane at the temperature 303K have been reported. The results are discussed in terms of molecular interactions.

II. Theory:

2.1 Adiabatic compressibility (β_a):

The adiabatic compressibility (β_a) has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta_a = 1 / (U^2 * \rho) \quad \text{----- (1)}$$

2.2 Intermolecular free length (L_f):

Intermolecular free length has been determined as:

$$L_f = K_J (\beta_a)^{1/2} \quad \text{----- (2)}$$

Where K_J is the temperature dependent Jacobson's constant [16,17] but independent of the nature of liquid.

2.3 Free volume (V_f):

The free volume [15, 17] has been calculated in terms of ultrasonic velocity (U) and viscosity (η) of the liquid as:

$$V_f = [(M_{eff} U) / (K \eta)]^{3/2} \quad \text{----- (3)}$$

Where, M_{eff} (Effective mass) = $\sum m_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively. K is the temperature independent constant, which is equal to $4.28 * 10^9$ for all liquids and η be the viscosity.

2.4 Internal pressure (π_i):

On the basis of statistical thermodynamics, Suryanarayana [18], derived an expression for the determination of internal pressure (π_i) by the use of free volume concept as:

$$\pi_i = (b RT) \left[\left(\frac{K \eta}{U} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \right] \text{-----(4)}$$

Where, b is the cubic packing which is assumed to be 2 for all liquids and solutions, K is the temperature independent constant, T is the absolute temperature, R is universal gas constant, η be the viscosity and M_{eff} the effective molecular weight .

2.5 Relaxation time (τ):

Relaxation time (τ) is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation as;

$$\tau = (4/3) \beta a \eta \text{----- (5)}$$

Where β and a are adiabatic compressibility and viscosity of the liquid and liquid mixtures.

2.6 Acoustic impedance (Z_a):

The specific acoustic impedance is given by

$$Z_a = U \rho \text{----- (6)}$$

Where U and ρ are the ultrasonic velocity and density of the liquid respectively.

2.7 Gibb's free energy (ΔG):

The relaxation time for a given transition is related to the activation energy. The variation of relaxation time (τ) with temperature (T) can be expressed in the form of Eyring self process theory.

$$1/\tau = (K_B T / h) \exp(-\Delta G / K_B T) \text{----- (7)}$$

The above equation can be rearranged as,

$$\Delta G = (-K_B T) \log [h / (K_B T \tau)] \text{----- (8)}$$

or,
$$\Delta G = (K_B T) \log [(K_B T \tau) / h] \text{----- (9)}$$

Where K_B is the Boltzmann's constant ($1.3806 \times 10^{-23} \text{ Jk}^{-1}$), h is the plank's constant ($6.63 \times 10^{-34} \text{ JS}$), T be the absolute temperature and τ be the relaxation time.

III. Experimental Details:

The component fluid namely methylmethacrylate (solute) and the methanol, p-dioxane and cyclohexane (solvents) were obtained of Anal R grade, again they were purified and redistilled in accordance with the usual procedure [18, 19] before use. The binary mixture of various mole fractions of two component in the systems, namely methylmethacrylate + methanol, methylmethacrylate + cyclohexane and methylmethacrylate + p-dioxane (here after p-dioxane referred as dioxane only), were prepared immediately before use.

The ultrasonic velocity (U) of frequency 10MHz and density (ρ) in these binary mixtures were measured by employing ultrasonic time inter-velometer (UTI -101, Innovative instrument, Hyderabad) and hydrostatic sinker method in the temperature range 10 - 40°C, with an overall accuracy of $\pm 0.1 \text{ m/s}$, Ultra thermo state U-10 maintained temperature of the sample constant to $\pm 0.1^\circ\text{C}$. A specially designed and fabricated double walled metallic ultrasonic cell and glass cell along with 6-digit monopan balance permitted to achieve accuracy of 1 in 10^4 m/s in velocity and 1 in 10^4 gm in density measurement. The viscosity (η) was measured using Ostwald's viscometer with an accuracy of $\pm 0.0001 \text{ Nm}^{-2}\text{S}$. All the precautions were taken to minimize the possible experimental error. The setup is checked for standard liquids. The values obtained are compared with Literature [18-21] values and found that, they match very well with each other.

IV. TABLES

Table – 4.1: Comparison of experimental values of density (ρ), viscosity (η) and ultrasonic Velocity (U) of pure liquids at 303K with literature values:

Pure liquids	Density(ρ) (Kg m ⁻³)		Viscosity (η) (10 ⁻³ NSm ⁻²)		Velocity (U) (m/s)	
	Expt.	Literature	Expt.	Literature	Expt	literature
1. Methylmethacrylate	947.4	---	0.4797	---	1141.0	---
2. Methanol	776.1	777.7	0.5150	0.5030	1086.0	1087.6
3. Dioxane	1027.4	1028.1	0.8154	1.010	1324.0	1323.0
4. Cyclohexane	772.3	763.7	0.6887	0.68950	1240.0	1243.3

Table – 4.2: The experimental values of density (ρ), viscosity (η) and Ultrasonic Velocity (U) at 303K for the systems - I, II & III:

Mole Fraction		density(ρ) (kg m ⁻³)	viscosity (η) (10 ⁻³ Nsm ⁻²)	velocity(U) (ms ⁻¹)
X1	X2			
System –I: methylmethacrylate + methanol.				
0.1	0.9	790.00	0.5380	1095.00
0.2	0.8	807.20	0.5600	1101.00
0.3	0.7	827.60	0.5830	1103.00
0.4	0.6	835.10	0.6010	1112.00
0.5	0.5	851.30	0.6240	1118.00
0.6	0.4	867.30	0.6470	1123.00
0.7	0.3	891.20	0.6700	1125.00
0.8	0.2	899.30	0.6930	1133.00
0.9	0.1	914.10	0.7160	1137.00
System – II: methylmethacrylate + dioxane				
0.1	0.9	1010.90	0.8088	1286.00
0.2	0.8	999.90	0.8022	1254.00
0.3	0.7	991.80	0.7957	1230.00
0.4	0.6	980.90	0.7890	1215.00
0.5	0.5	970.00	0.7824	1210.00
0.6	0.4	962.00	0.7757	1184.00
0.7	0.3	952.00	0.7691	1170.00
0.8	0.2	941.00	0.7623	1152.00
0.9	0.1	940.80	0.7588	1140.00
System – III: methylmethacrylate + cyclohexane				
0.1	0.9	786.90	0.6947	1230.00
0.2	0.8	801.20	0.7007	1219.00
0.3	0.7	825.70	0.7068	1206.00
0.4	0.6	846.80	0.7130	1198.00
0.5	0.5	845.30	0.7193	1187.00
0.6	0.4	863.90	0.7253	1180.00
0.7	0.3	885.90	0.7314	1164.00
0.8	0.2	892.90	0.7376	1155.00
0.9	0.1	910.30	0.7437	1151.00

Table – 4.3: The values of adiabatic compressibility (β_a), free length (L_f). Free Volume (V_f), internal pressure (Π_i), Acoustic impedance (Z_a), Relaxation time (τ) and Gibb’s Free energy (ΔG) at 303 K for the systems: I, II & III respectively.

Mole Frac.		$\beta_a \times 10^{-10}$ (m ² N ⁻¹)	$L_f \times 10^{-10}$ (m)	$V_f \times 10^{-7}$ (m ³ .mole ⁻¹)	$\Pi_i \times 10^6$ (Pa.S)	$\tau \times 10^{-12}$ (S)	$Z_a \times 10^6$ (kgm ⁻² S ⁻²)	$\Delta G \times 10^{-20}$ (KJmole ⁻¹)
X ₁	X ₂							
System- I: Methylmethacrylate + Methanol								
0.1	0.9	10.5371	0.6482	0.7941	873.331	0.7573	0.8651	0.2841
0.2	0.8	10.2192	0.6377	0.9606	846.642	0.7630	0.8887	0.2855
0.3	0.7	09.9313	0.6287	1.1167	658.112	0.7719	0.9128	0.2876
0.4	0.6	09.6794	0.6207	1.2970	980.623	0.7756	0.9286	0.2885
0.5	0.5	09.2971	0.6083	1.4549	526.514	0.7734	0.9518	0.2880
0.6	0.4	09.1422	0.6032	1.6071	482.992	0.7886	0.9740	0.2915
0.7	0.3	08.8641	0.5940	1.7418	451.878	0.7918	1.0026	0.2922
0.8	0.2	08.6623	0.5872	1.8993	417.522	0.8003	1.0189	0.2942
0.9	0.1	08.4624	0.5803	2.2029	368.888	0.8078	1.0393	0.2959

System-II: Methylmethacrylate + dioxane								
0.1	0.9	05.9185	0.4854	1.9075	440.952	0.6382	1.3000	0.2531
0.2	0.8	06.3591	0.5031	1.9006	434.666	0.6801	1.2539	0.2646
0.3	0.7	06.6645	0.5150	1.9063	428.111	0.7070	1.2199	0.2717
0.4	0.6	06.9059	0.5243	1.9328	419.371	0.7264	1.1918	0.2766
0.5	0.5	07.0413	0.5294	1.9833	409.146	0.7345	1.1737	0.2786
0.6	0.4	07.4105	0.5431	1.9820	403.730	0.7664	1.1397	0.2863
0.7	0.3	07.6735	0.5527	2.0094	395.616	0.7868	1.1138	0.2911
0.8	0.2	08.0051	0.5645	2.0267	388.311	0.8136	1.0844	0.2972
0.9	0.1	08.1782	0.5708	2.0461	383.093	0.8273	1.0725	0.3002
System III: methylmethacrylate + Cyclohexane								
0.1	0.9	8.3998	0.5782	2.1131	370.744	0.7780	0.9679	0.2890
0.2	0.8	8.3995	0.5582	2.1156	370.502	0.7847	0.9767	0.2906
0.3	0.7	8.3269	0.5757	2.1157	371.0	0.7847	0.9958	0.2903
0.4	0.6	8.2282	0.5723	2.1191	375.141	0.7822	1.0145	0.2900
0.5	0.5	8.3963	0.5781	2.1175	370.441	0.8052	1.0034	0.2953
0.6	0.4	8.3133	0.5752	2.1270	371.009	0.8039	1.0194	0.2950
0.7	0.3	8.3312	0.5758	2.1119	394.186	0.8124	1.0312	0.2969
0.8	0.2	8.3952	0.5780	2.1264	371.787	0.8256	1.0313	0.2998
0.9	0.1	8.2588	0.5733	2.1243	371.687	0.8189	1.0478	0.2984

V. Result discussion:

The experimentally measured and literature values [18-20] of density, velocity and viscosity for pure liquids at 303K are presented in **table -4.1**. Experimental density, viscosity and ultrasonic velocity values for the three binary systems namely, **system-I:** methylmethacrylate + methanol, **system-II:** methylmethacrylate +dioxane and **system-III :** methylmethacrylate+ cyclohexane respectively at 303K are given in the **table - 4.2**. The parameters, adiabatic compressibility(β_a), free length (L_f), free volume(V_f),acoustic impedance (Z_a), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG) at temperature 303K are listed in **table – 4.3**. The variation of β_a , L_f and V_f , V_s mole fraction(x) at 303K for the **system -I :** methylmethacrylate+methanol , **system- II :** methylmethacrylate+ dioxane & **system III –** methylmethacrylate+ cyclohexane are shown in the **fig. 1, 2 and 3** respectively. The variation of π_i , Z_a , τ & ΔG Vs mole fraction(x) at 303K for the **system - I:** methylmethacrylate + methanol, **system-II:** methylmethacrylate+ dioxane and **system –III** methylmethacrylate + cyclohexane are shown in the **fig. 4, 5, 6 & 7** respectively.

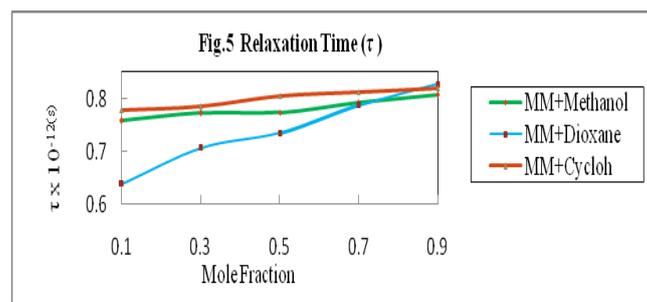
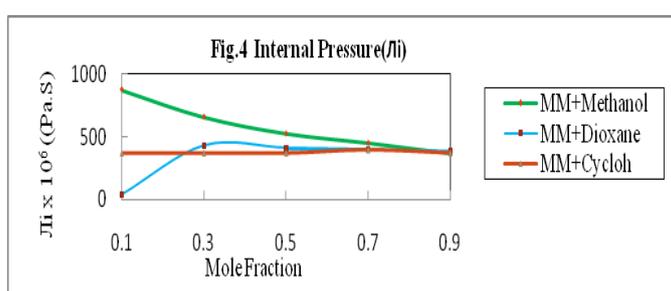
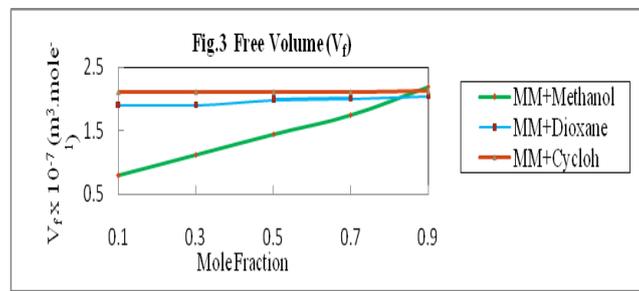
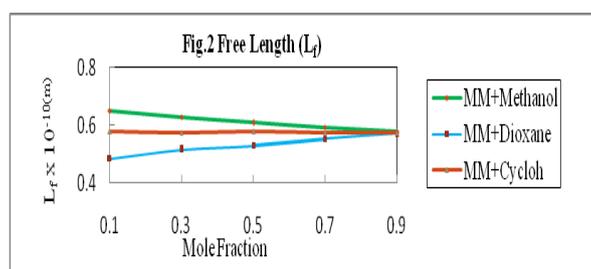
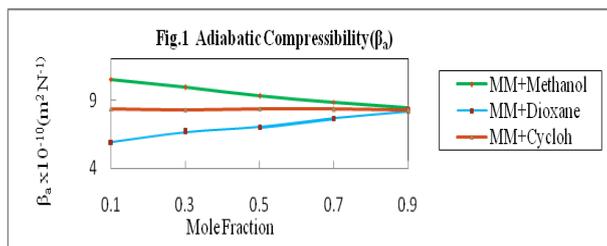
From **the table – 4.2**, it is noted that, the density (ρ) increases with increase in mole fraction for the systems-I & III i.e. for methylmethacrylate + methanol and methylmethacrylate + cyclohexane and the density decreases for the system –II i.e. for the system methylmethacrylate+ dioxane with increase in mole fraction. Ultrasonic velocity and viscosity increases with increase in mole fraction of the solute in case of the system - I (methylmethacrylate + methanol). In case of the system -II (methylmethacrylate +dioxane) ultrasonic velocity

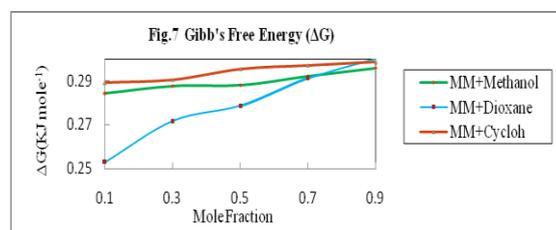
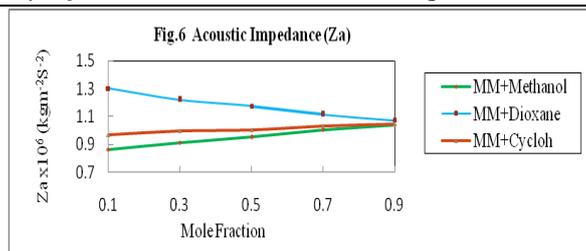
and viscosity decreases with increase in mole fraction of the solute. While in case of the system- III (methylmethacrylate + cyclohexane), ultrasonic velocity decreases, and viscosity increase with increase in mole fraction of the solute. The increase in the velocity, in the system- I (methylmethacrylate +methanol) is due to decrease in adiabatic compressibility and free length (**fig-1 & fig-2**). In the system –II (methylmethacrylate+dioxane), velocity decreases, due the increase in adiabatic compressibility and the free length (**fig- 1 & fig- 2**).

It has been observed that for a given concentration, as the number of CH-group or Chain length changes, the sound velocity changes. 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. The internal pressure decrease (**fig-4**) and free volume increase (**fig-3**) with increasing mole fraction of the salute in all the three systems. The internal pressure may gives information regarding the nature and strength of forces existing between the molecules. It represents the presence of weak interaction between the solute and solvent molecules.

Acoustic impedance (Z_a) increases with increase in the mole fraction of the solute in the systems- I & III and decrease in the system- II (**fig-6**). The relaxation time (τ) also increases with increasing the mole concentration of the solute in all the systems (**fig-5**). The dispersion of the ultrasonic velocity in the system may contain information about the characteristic time (τ) of the relaxation process that causes dispersion. The relaxation time which is in the order of 10^{-12} sec., is due to structural relaxation process [22] and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process [23].

The Gibb's free energy (ΔG) increases with increasing mole fraction the solute of all the systems (**fig-7**). This may be due to the intermediate compound formation between the binary liquids. It is observed that, generally, the increase in Gibb's free energy favors the formation of product from reaction. This observation confirms the formation of hydrogen bonding in the binary mixture.





VI. Conclusion:

The molecular interactions present in methylmethacrylate with methanol, dioxane & cyclohexane as a solvent have been studied by viscosity, density and ultrasonic velocity study. Polymer solvent interaction parameters for the systems have been estimated based on Gibb's free energy calculations using data on viscosity and ultrasonic velocity of the solutions, at 303K temperature. The result indicates the existence of molecular interaction between the polymer and the solvent in their solutions. The result is also shows the presence of higher degree of molecular interaction between methylmethacrylate and methanol in solution compared to methylmethacrylate with dioxane and cyclohexane in solutions.

The computed acoustical parameters and their values show the presence of specific molecular interaction in the mixtures. Hence it is concluded that, the association in this mixture is the result of Hydrogen bonding in the binary liquid mixtures. The dependence of ultrasonic velocity and other derived parameters on composition of the mixtures is indication of the presence of molecular interactions. The interaction primarily of dipole-dipole and dipole -induce dipole type and becomes stronger with mole-fraction in methylmethacrylate + methanol system.

VII. Acknowledgement:

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