Acoustic Study of binary liquid mixtures of 2-methyl-2,4-pentanediol with triacetin at 308.15K and 318.15K

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Abstract

Ultrasonic velocity of binary liquid mixture of 2-methyl-2,4-pentanediol with triacetin have been measured at 308.15K and 318.15 K. Measurement of density, viscosity are used to determine the excess volume (V^E), deviation in isentropic compressibility(ΔK_S), Deviation in viscosity ($\Delta\eta$) Intermolecular free length(ΔL_f) , Intermolecular Free Volume(ΔV_f) and Deviation in acoustic impedance(ΔZ) were calculated. These results have been correlated with the Redlich and Kister type polynomial equation to derive the coefficients and standard errors. Significance of the calculated excess quantities were analyzed for mixtures of 2-methyl-2,4-pentanediol with triacetin , through which intermolecular interactions have been interpreted.

Key words: Density, Viscosity, Ultrasonic velocity, Excess properties, binary mixture, Molecular interaction.

Introduction

Study of acoustic properties is very helpful to determine thermodynamic properties for the liquid mixtures. This is most considerable method that can represent the types of intermolecular interactions between the liquids. The experimentally obtained values of thermodynamic parameters can be described to predict in terms of specific and nonspecific interactions proceeding between the molecules of the mixtures. The result of the experiment can suggest the appropriate solvent for the particular solute and its molecular behavior in the mixture. 2-methyl-2,4-pentanediol is important for the protein crystallography because of their amphiphilic nature. This is also used in cosmetics and pharmaceutical industry as lubricating agent. Since the 2-methyl-2,4-pentanediol have two alcohol groups it stabilized by intramolecular hydrogen bond. The investigation of G.Fytas and Th.Dorfmuller[1], 2-methyl 2, 4 -pentanediol has revealed that approximately 60% intermolecular hydrogen bond between like molecules. D.W.Davidson[2] observed that in 2- methyl 2, 4 pentanediol almost 40% of the OH groups are formed intramolecular hydrogen bonds in very dilution condition. Triacetin is a high viscous liquid and has high boiling point. Triacetin is used as the antifungal agent in pharmaceutical industry and used as plasticizer. Triacetin is stabilized by dipole-dipole self associated molecules. The investigation of Cornelio Delesma[3] et.al., reported that the triacetin transesterification is achieved by a van der Waals-driven attraction. Frank S. Parker[4] et.al,. revealed the evidence of formation of 1:1 hydrogen-bonded complex in the mixed solutions
of cholesterol and triglycerides. Study of the Effects of Temperature and Pressure on the Acoustic and Thermodynamic Properties of 2-Methyl-2,4-pentanediol was done by Edward Zorebski[5] et.al.

Experimental Section

Materials

2-methyl-2,4-pentanediol (SRL chemicals, Mumbai. purity >99%) was used after distillation. triacetin (SRL chemicals, Mumbai) with purity of >99% was purified by distillation.

The purity of the solvents is established by comparing experimental values of densities, viscosities, and ultrasonic velocities with reported in the literature values. Our Experimental values of densities, viscosities and ultrasonic velocities match very well with those reported in the literature and are presented in Table 1.

Table: 1 Comparison of Experimental Density(ρ), Viscosity(η), Ultrasonic velocity(*U*) of pure liquids with literature values at 308.15K and 318.15K.

Liquid	*T*/K	Density (ρ) g.cm^{-3}		Viscosity (η) mPa.s^{-1}		Ultrasonic Velocity (*U*)m.s^{-1}	
		expt.	lit.	expt.	lit.	expt.	lit
Hexylene	308	0.9110[a]	0.9109[5]	20.3740[a]		1285[a]	1269[5]
glycol	318	0.9041[b]	0.9038[5]	19.6916[b]		1257[b]	1239[5]
Triacetin	308	1.1427[a]	1.1415[6]	10.0335[a]	10.03[6]	1336[a]	
	318	1.1338[b]		7.3653[b]		1304[b]	

a – Measured at 308.15K and presented in Table 2
b – Measured at 318.15K and presented in Table 2

Methods

A set of nine compositions was prepared for each mixture, and their physical properties were measured at the respective compositions in the mole fraction scale from 0.1 to 0.9 in steps of 0.1. Binary liquid mixtures of various compositions were prepared by mixing fixed amount of pure liquids in air tight stoppered bottles of 50ml capacity. Densities of pure liquids and liquid mixtures were measured by relative density method[7-10] using 10ml relative density bottle and weighed with an accuracy of ± 0.001kgm^{-3}. Viscosities were determined using an Oswald viscometer[7-11] of 10ml capacity with an accuracy of ±0.001mPa. From the measured values of density and flow time *t*, the viscosity *η* was calculated using the relation[14-17]

$$\eta = (A \times t - B/t) \times \rho \quad (1)$$

Where A and B are viscometer constant. The values of constants were obtained by measuring the flow time with distilled water and pure nitrobenzene as standard liquids. The flow time were measured with electronic stop clock. Ultrasonic velocities of pure and liquid mixtures were measured by a single crystal variable path interferometer (Pico Chennai, Model BL-02)[10] at a frequency of 2MHz with an accuracy of ±0.02%. All the measurements were made at both 308.15K and 318.15K with the help of a digital thermostat with a temperature accuracy of ± 0.01K.

The excess volume V^E was calculated by the relation[7-11]

$$V^E = [\,[X_A M_A + X_B M_B] / \rho_{AB}\,] - [\,[\,X_A M_A / \rho_A\,] + [X_B M_B / \rho_B]\,] \quad (2)$$

Where X_A, X_B are mole fraction of components A & B, M_A, M_B are the molecular mass of components A & B . ρ_A, ρ_B, are the density of component A , B respectively and ρ_{AB} is the density of mixture.

Values of ultrasonic velocity u, and density of mixture ρ_{AB} were used to calculate isentropic compressibility K_S by using this relation[12-16] recommended by Benson and Kiyohara.

$$K_S = 1 / U^2\rho \quad (3)$$

Were the U is the ultrasonic velocity of pure and mixture, and ρ is the density of pure and mixture

The deviation in isentropic compressibility was obtained from the relation

$$\Delta K_S = K_S - (\phi_1 K_{S1} + \phi_2 K_{S2}) \quad (4)$$

Where ϕ_1 and ϕ_2 are the volume fraction of component 1 and 2, K_{S1} and K_{S2} are the isentropic compressibility of component 1 and 2. K_S is the experimental value of isentropic compressibility of the mixture.

Intermolecular free length(L_f) has been calculated from the following relation[16,17]

$$L_f = k / U\rho^{1/2} \quad (5)$$

Were the U is the ultrasonic velocity of pure and mixture, and ρ is the density of pure and mixture
k is the Jacobson's constant which is temperature dependent but independent of the nature of the liquids, whose value is (91.368 + 0.3565 T) 9 x 10^{-8} and is obtained from the literature[18] .

$$V_f = [M_{eff} U /k\eta]^{3/2} \quad (6)$$

Where *k* is a constant equal to 4.28_109 in MKS system[19] , independent of temperature for all liquids, M_{eff} is the effective molecular weight. $M_{eff} = \Sigma x_i m_i$ where, x is the mole fraction and m is the molecular weight of *i* th component.

$$\Delta Y = Y_{mix} - x_1 Y_1 + x_2 Y_2 \quad (7)$$

where ΔY is Δη or ΔV_f or ΔL_f and x represent mole fraction of the component and subscript 1 and 2 for the components 1 and 2.

Table 2. Physical and Thermodynamic properties of 2-methyl-2,4-pentanediol with triacetin at 308.15K and 318.15K

X_1	P g.cm^{-3}	V^E cm^3.mol^{-1}	η mPa.s	U m.s^{-1}	ΔK_s Tpa^{-1}	Δ η mPa.s	ΔL_f 10^{-11} m	ΔV_f $_{10}^{-17}$ m^3.mol^{-1}
308.15K								
0.0000	1.1427	0.0000	10.0335	1336.00	0.0000	0.0000	0.0000	0.0000
0.1755	1.1121	0.2154	11.5771	1322.50	1.7862	-0.2555	-4.0464	-5.2646
0.3249	1.0827	0.4523	12.4478	1310.50	4.4907	-0.9162	-6.0306	-5.8817

0.4456	1.0567	0.6485	12.9033	1302.00	6.3408	-1.6983	-6.8130	-5.3619
0.5551	1.0311	0.8018	13.6085	1295.50	7.5021	-2.1159	-6.8415	-4.7392
0.6531	1.0069	0.8538	14.5062	1290.50	8.0878	-2.2227	-6.2737	-3.9970
0.7335	0.9863	0.8009	15.6020	1288.50	6.7003	-1.9507	-5.7472	-3.2743
0.8110	0.9657	0.6498	16.8399	1287.50	4.4533	-1.5078	-4.9589	-2.4393
0.8818	0.9460	0.4543	17.9531	1286.50	2.6363	-1.1205	-3.6411	-1.5692
0.9457	0.9274	0.2398	19.3099	1285.50	1.3444	-0.4187	-1.8499	-0.7469
1.00000	0.9110	0.0000	20.2852	1285.00	0.0000	0.0000	0.0000	0.0000
318.15K								
0.0000	1.1338	0.0000	7.3653	1304.00	0.0000	0.0000	0.0000	0.0000
0.1755	1.1039	0.1421	8.0537	1292.50	0.6628	-1.1403	-4.5987	-9.0884
0.3249	1.0750	0.3514	8.7442	1282.50	2.1959	-2.0065	-7.0364	-12.0586
0.4456	1.0493	0.5359	9.5235	1274.50	4.0072	-2.4852	-7.8994	-12.5502
0.5551	1.0241	0.6796	10.1235	1268.00	5.5038	-3.0264	-7.8706	-11.1703
0.6531	1.0003	0.7018	11.0089	1262.50	6.7750	-3.1622	-7.1462	-9.5619
0.7335	0.9802	0.6073	12.2519	1261.00	4.8326	-2.7565	-6.7786	-7.9611
0.8110	0.9599	0.4392	13.6595	1259.00	3.6033	-2.1570	-5.6984	-5.9647
0.8818	0.9401	0.2887	15.1042	1258.50	1.5609	-1.4501	-4.3165	-3.8632
0.9457	0.9211	0.1461	16.7626	1258.50	-0.3444	-0.4576	-2.5056	-1.8380
1.0000	0.9042	0.0000	17.7859	1257.00	0.0000	0.0000	0.0000	0.0000

Results and Discussion

Experimental values of density (ρ), viscosity(η), and ultrasonic velocity(u) were measured from which, calculated values of Excess volume V^E, deviation in isentropic compressibility ΔK_S of the binary mixtures are presented in Tables 2.

The excess properties of V^E, ΔK_S , $\Delta\eta$, ΔL_f and ΔV_f were fitted to Redlich – Kister[20] type polynomial equation

$$\Delta A = x_1x_2 [a + b (x_1-x_2) + c (x_1-x_2)] \quad (8)$$

By the method of least squares to derive the adjustable parameters a, b & c

The standard deviations (σ) presented in this work were computed using

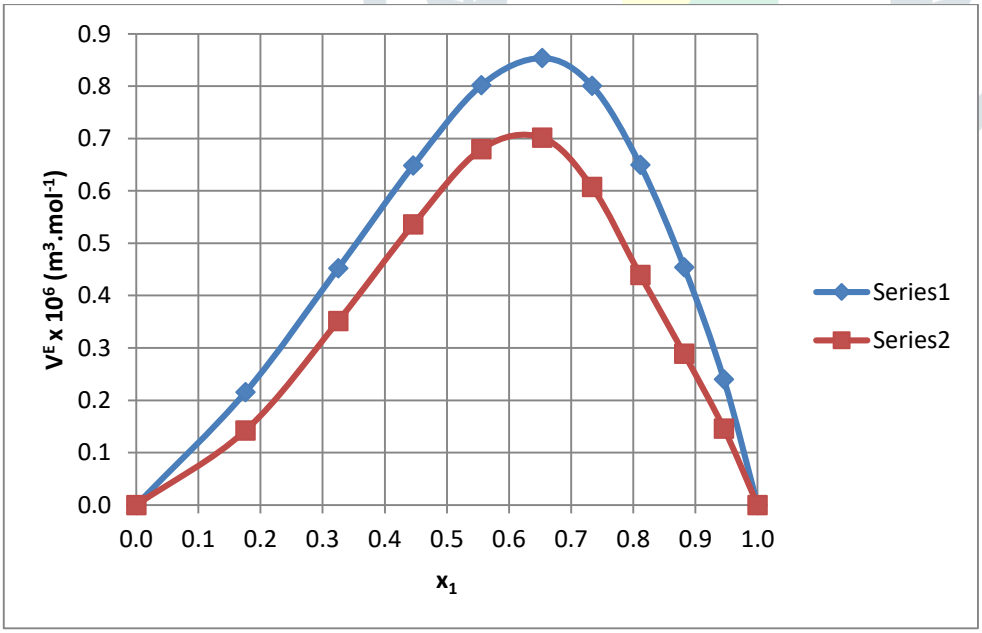
$$\sigma = \Sigma \left(\frac{X_{exp} - X_{cal}}{N - n} \right)^2]^{1/2} \quad (9)$$

Where N is the number of data points , and n is the number of co-efficients.

Table 3: Values of the co-efficient of the redlich - kister type polynomial equation (Eq. 8) and Standard deviation (Eq. 9) at the different temperature

Properties	a	b	c	σ
308.15K				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	2.9797	2.3303	-0.3168	0.0004
ΔK_S (TPa^{-1})	31.2063	1.1497	-26.3679	0.0868
$\Delta\eta$ (mPa.s)	12.6828	68.366	110.314	0.3670
$\Delta L_f \times 10^{-11}$ (m)	-271.5510	-24.8718	-77.9188	0.0220
$\Delta Vf \times 10^{-17}$ ($m^3\ mol^{-1}$)	-0.0050	-0.0039	0.0024	0.00117
318.15K				
$V^E \times 10^6$ ($m^3.mol^{-1}$)	2.5231	2.5231	-1.5172	0.0003
ΔK_S (TPa^{-1})	24.1184	4.7000	-35.6258	0.0605
$\Delta\eta$ (mPa.s)	7.7899	56.3186	98.7018	0.1190
$\Delta L_f \times 10^{11}$ (m)	11.1403	151.0280	-309.3330	0.1351
$\Delta Vf \times 10^{-17}$ ($m^3\ mol^{-1}$)	-0.0470	0.0032	0.0121	0.0032

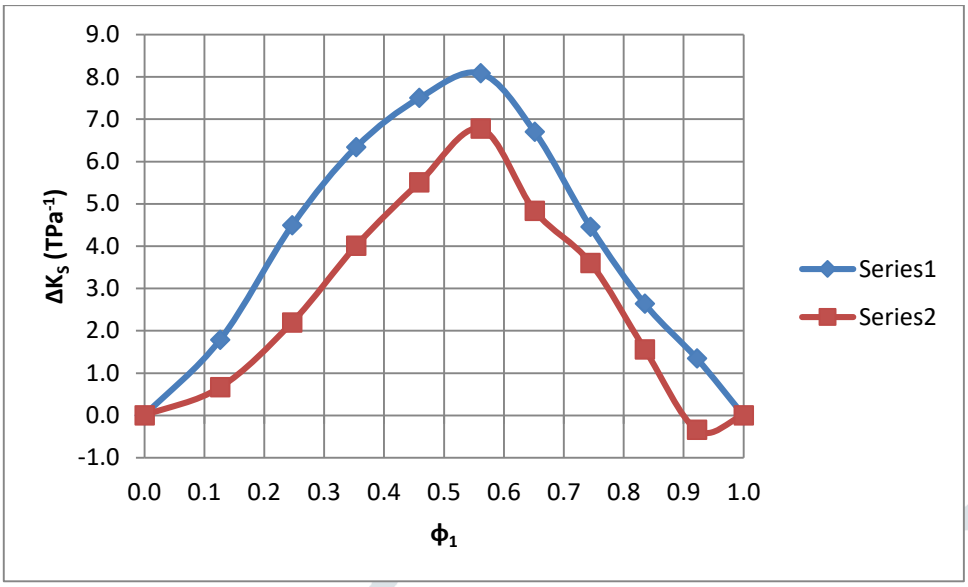
Figure 1: Excess volume, V^E for 2-methyl-2,4-pentanediol with triacetin at 308.15K and 318.15K



Series 1- 308.15K

Series 2- 318.15K

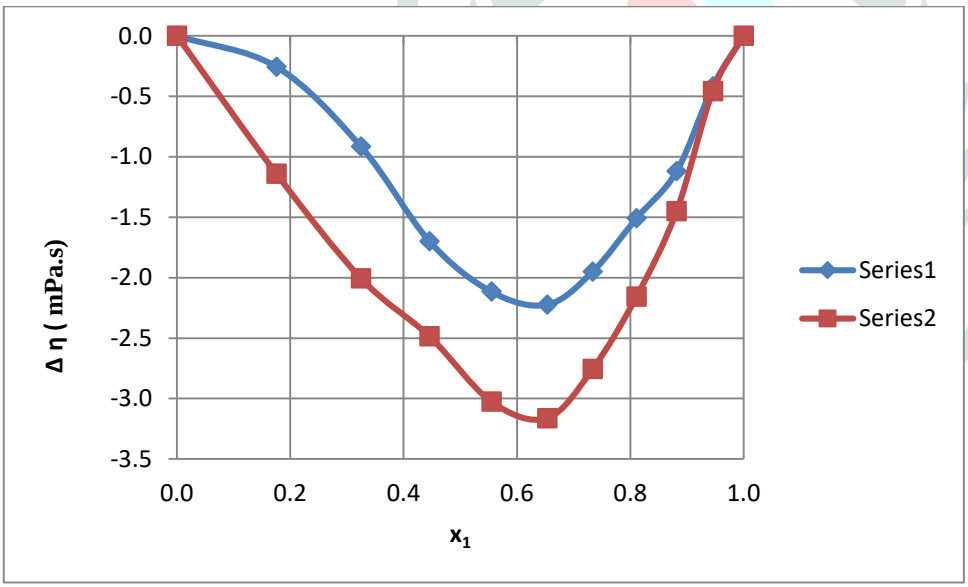
Figure 2: ΔK_S ,for 2-methyl-2,4-pentanediol with triacetin at 308.15K and 318.15K



Series 1- 308.15K

Series 2- 318.15K

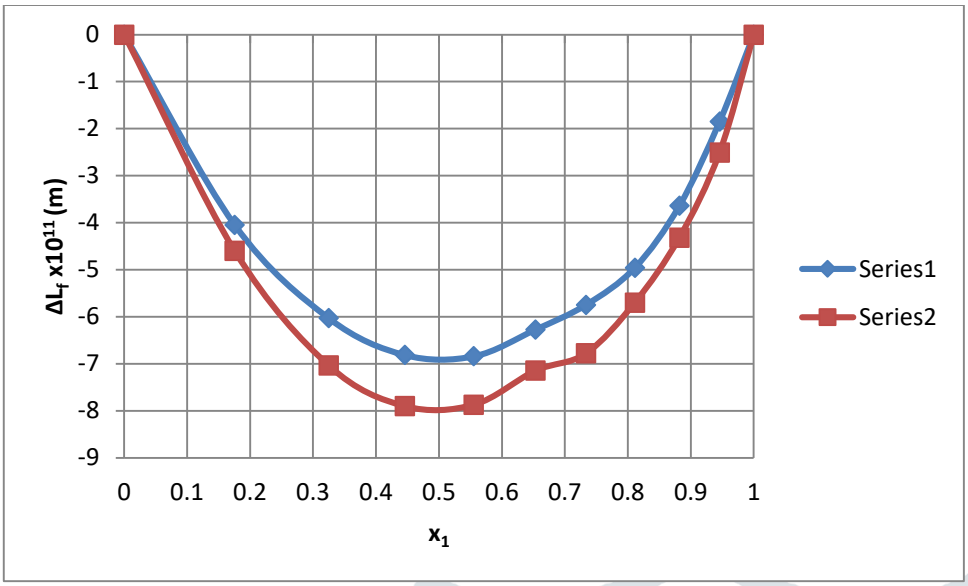
Figure 3: Δη for 2-methyl-2,4-pentanediol with triacetin at308.15 and 318.15K



Series 1- 308.15K

Series 2- 318.15K

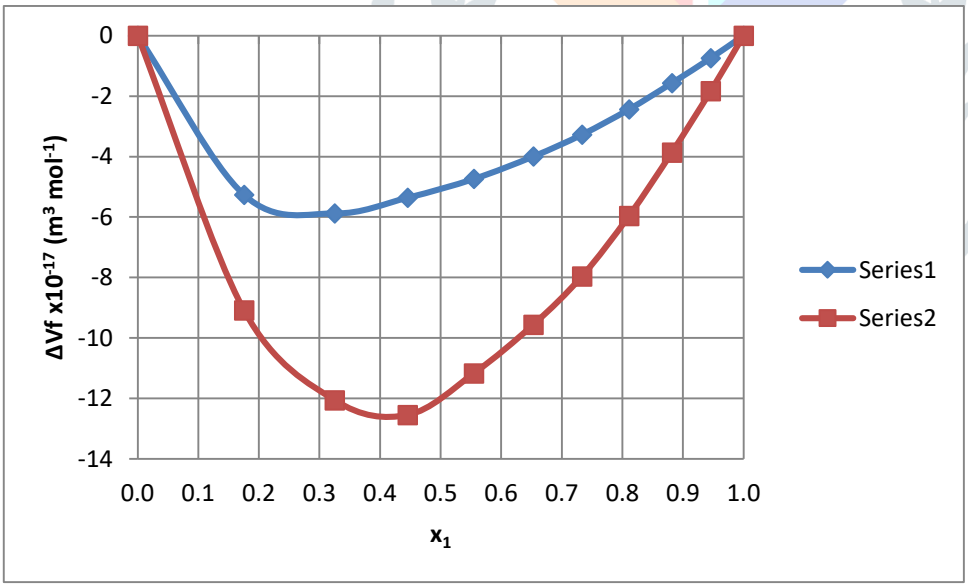
Figure 4: ΔL_f, for 2-methyl-2,4-pentanediol with triacetin at308.15 and 318.15K



Series 1- 308.15K

Series 2- 318.15K

Figure 5: ΔV_f, for 2-methyl-2,4-pentanediol with triacetin at308.15 and 318.15K



Series 1- 308.15K

Series 2- 318.15K

The positive values of Excess volume and deviation in isentropic compressibility are obviously reveal that the volume expanding after mixing liquids. The factors that are responsible for expansion in volume are as Follows i. Loss of dipolar association, ii. The geometry of molecular structure, which does not allow fitting of one component into other component, iii. Steric hindrance, which opposes the proximity of the

constituent molecules[21]. In our case due to large size of the MPD and triacetin molecules both have steric hinderence, hence it repul each other resulting expansion in volume. The positive values are very high at 0.5 mole fraction of MPD, so it implies that mixtures show more repulsion at equimolar ratio than the other mole fraction. The positive values of excess volume and deviation in isentropic compressibility values decreases with increasing temperature, this suggests that the molecules move closer to each other because of the thermal energy. According to Rastagi et.al[22] as temperature increases, the thermal energy activates the molecules and increases the rate of association between unlike molecules. This shows the intermolecular forces is greater than the kinetic energy of the liquid. The sign and magnitude of deviation in viscosity may depend on the combined effect of factors such as molecular size, shape and intermolecular forces[23]. In general for the systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative[24-26]. In this work $\Delta\eta$ values are high negative shows repulsion, these two liquids are high viscous liquids and shows also negative values suggests repulsion between two molecules. deviation in intermolecular free length values are negative and the deviation in intermolecular free volume values are also negative because of the big size of both MPD and triacetin molecule create more voids between them and negative values become more negative when increasing temperature this supports above suggestion. This confirms the above idea.

Conclusion

This work has determined V^E, ΔK_S, ΔL_f, $\Delta\eta$ and ΔV_f for mixtures of 2-methyl-2,4-pentanediol with triacetin. The importances of V^E and ΔK_S , ΔL_f , $\Delta\eta$ and ΔV_f have been interpreted in terms of different molecular interaction between those molecules. The magnitudes of excess properties have shown that 2-methyl-2,4-pentanediol + triacetin gets repulsion due to steric hindrance. Interaction increases with increasing temperature because of intermolecular force greater than kinetic energy .

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