Viscosities, Densities and Ultrasonic velocities of Methylbenzoate with 1-pentanol and 1-hexanol at 303.15 K

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Abstract : Densities, viscosities and ultrasonic velocities of binary liquid mixtures of Methylbenzoate with 1-pentanol and 1-hexanol have been measured at 303.15 K. The experimental data have been used to calculate the various acoustical parameters namely adiabatic compressibility (β), free length (L_f), Internal pressure (π_i), acoustical impedance (Z) and the excess values of the above parameters have also been evaluated. The variation of these parameters with composition of the mixture helps us in understanding the nature and extent of interaction between unlike molecules in the mixtures.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Binary system, Excess parameters.

1. Introduction

Knowledge of thermo acoustic properties is of great significance in understanding the physicochemical behavior and molecular arrangement in various liquid mixtures and solution (Dhok *et al.*, 2012). The practical applications of mixed solvents, rather than single solvent in industrial and biological processes have been recognized all over the world, as they provide a wide choice of solutions with appropriate properties (Ali *et al.*, 2001),. In recent years, the measurement of ultrasonic velocity has been successfully employed in understanding the nature of molecular interaction in pure liquids and liquid mixtures. The study of pure liquids and their properties cannot be altered continuously within a reasonable range by varying the concentration till an optimum value of some desired parameter is attain. This is only possible by considering the liquid mixtures and solutions which find direct applications in many chemical industries and technological processes (Nithiyanantham and Palaniappan, 2013).

Methylbenzoate is a colorless liquid that is poorly soluble in water, but miscible with organic solvents. It has a pleasant smell strongly reminiscent of the fruit of the feijoa tree and it is used in perfumery. It is also used as a solvent and as a pesticide which attract insects. Alcohols are strongly self-associated liquids with a three dimensional network of hydrogen and can be associated with any other group having some degree of polar attractions (Anwar Ali *et al.*, 2004). The interaction of alcohol[s] with organic liquids is interesting due to its acidic nature. The O-H bonds in alcohols are polar and allow the release of the hydrogen atom as proton [H^+]. Pentanol is used as a solvent for coating CDs and DVDs, another use is a replacement for gasoline. Hexanol is the odour of freshly mowed grass and is used in perfume industry. Owing to these considerations, an attempt has been made to elucidate the molecular interactions in the mixtures of 1-pentanol and 1-hexanol with methylbenzoate at 303.15 K. Further, the excess values of some of the acoustical and interaction parameters have been calculated from the measurements of ultrasonic velocity, density and viscosity of the mixtures. The excess parameters are used to explain intermolecular interaction in these binary mixtures.

2. Experimental technique

All the chemicals used were of Analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9%. The speeds of sound waves were obtained by using ultrasonic interferometer (Model No, F-81, M/S. Mittal enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of ± 2 ms^{-1}. An electronically digital operated constant temperature bath (RAAGA Industries, Madras 61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a pycnometer by relative measurement method with an accuracy of ± 0.1 K (Model: SHIMADZU AX-200). The pycnometer was calibrated at 303.15K with double distilled water and gave an estimated reproducibility of ±0.0001 gcm^{-3}. An Ostwald's viscometer was calibrated with fresh conductivity water immersed in the water bath which was kept at the experimental temperature. The time of flow (t_w) of water and the time flow (t_s) of solution was measured with digital stop clock having an accuracy ± 3 x 10^{-6} Nsm^{-2}. The temperature around the viscometer was maintained with in ± 0.1 K in an electronically controlled thermostatic water bath. The various concentrations of the binary liquid mixtures were prepared in terms of mole fraction, such as 1-pentanol with methylbenzoate and 1-hexanol with methylbenzoate varied from 0.1 to 0.9.

2.1 Theory

From the measured values of density (ρ) and ultrasonic velocity (U), acoustic parameters like adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i) and acoustic impedance (Z) were calculated using the following relations (More *et al.*, 2005).

$$\beta = \frac{1}{\rho U^2} \qquad (1)$$

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

$$\pi_i = bRT\left[\frac{K_\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M^{7/6}}\right] \quad (3)$$

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

Where K_T is the temperature dependent constant, K the temperature independent constant (K=4.28 x 10^9), b a constant which is 2 for cubic packing, R the gas constant and T is the temperature in K. U and ρ are velocity and density of liquids.

The non-ideality of the liquid mixtures, the difference between the parameters of the real mixtures (A_{exp}) and those corresponding to an ideal mixture (A_{id}) values, namely excess parameters (A^E) of all the acoustic parameters were computed by the relation.

$$A^E = A_{exp} - A_{id} \quad (5)$$

Where $A_{id} = \sum_{i=1}^{n} A_i X_i$, A_i is any acoustical parameters and X_i the mole fractions of the liquid component i.

3. Results and Discussion

Experimentally measured the values of density (ρ), viscosity (η) and ultrasonic velocity (U) for pure liquids and liquid mixture at 303.15 K are presented in Tables 1&2. The binary liquid mixture were used to calculate the acoustical parameters such as adiabatic compressibility (β), free length (L_f), internal pressure (π_i) and acoustic impedance (Z) are presented in Table 3. In all the mixtures, the density and the ultrasonic velocity decreased with increasing mole fraction of 1-alkanol. The decrease in velocity and increase in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules (Nemaniwar *et al.*, 2013).

Table -1 Values of density (ρ), Viscosity (η), and velocity (U) of Pure liquids at 303.15K

Liquids	ρKgm^{-3}	η x 10^3 NSm^{-2}	U ms^{-1}
I-Pentanol	806.14	2.4198	1253.7
I-hexanol	812.51	2.3619	1281.7
Methyl Benzoate	1062.84	1.1864	1365.4

Table -2 Values of density (ρ), Viscosity (η), and velocity (U) of systems I and II at 303.15 K

Mole fractions		ρKgm^{-3}	η x 10^3 NSm^{-2}	U ms^{-1}
X_1	X_2			
System I: 1-pentanol + Methyl Benzoate				
0.1001	0.8999	971.43	1.4446	1372.6
0.2001	0.8000	950.15	1.4608	1356.6
0.3001	0.7001	929.60	1.4879	1348.1
0.4001	0.6001	888.56	1.4896	1334.8
0.5000	0.5001	878.53	1.4911	1329.8
0.6000	0.3999	832.57	1.5056	1309.3
0.7000	0.2998	827.41	1.5183	1298.5
0.7999	0.1998	822.11	1.5419	1281.5
0.8998	0.1001	815.44	1.5945	1258.6
System II: 1-Hexanol + Methyl Benzoate				
0.1001	0.9000	955.44	1.4844	1382.6
0.2000	0.8999	949.19	1.5335	1358.9
0.3002	0.7001	926.10	1.5991	1352.2
0.4000	0.6001	881.95	1.6032	1339.8
0.5001	0.5000	858.19	1.6721	1335.4
0.6004	0.3999	830.01	1.7669	1329.9
0.7000	0.2999	823.01	1.8396	1301.0
0.8001	0.2001	818.42	2.0337	1292.4
0.9002	0.0999	815.45	2.2139	1291.2

Adiabatic compressibility (β) increases by increase in mole fraction of 1-alkanol (Table 3). Loss of dipolar association and difference is size and shape of the component molecules, which leads to decrease in velocity and increasing compressibility (Rama Roa, 2004). The intermolecular free length is found to be a predominant factor in determining the nature of sound velocities variation in liquid mixtures and also in deciding the variations of ultrasonic parameters. Intermolecular free length depends on "β" and shows a similar behavior as that of compressibility (Table 3). Hence free length also increases but at a slower rate. On the basis of a model for sound propagation by Eyring and Kincaid, ultrasonic velocity should decrease if the intermolecular free length increases and vice versa (Eyring and Kincaid, 1938).

Table-3 Values of Adiabatic compressibility (β), Free length (L_f), Internal pressure (π_i), Acoustic impedance (Z), of system I and II at 303.15 K

Mole fraction		$\beta \times 10^{10}$ pa^{-1}	$L_f 10^{10}$m	$\pi_i \times 10^{-6}$ pa	Z x 10^{-6} kgm^{-2}S^{-1}
X_1	X_2				
System I: 1- pentanol + Methyl Benzoate					
0.1001	0.8999	5.464	0.4664	335.6	1.333
0.2001	0.8000	5.724	0.4774	368.5	1.328
0.3001	0.7001	5.919	0.4854	384.5	1.253
0.4001	0.6001	6.317	0.5015	393.2	1.186
0.5000	0.5001	6.437	0.5062	410.8	1.126
0.6000	0.3999	7.006	0.5282	422.5	1.090
0.7000	0.2998	7.168	0.5342	447.7	1.071
0.7999	0.1998	7.631	0.5526	478.2	1.041
0.8998	0.1001	8.016	0.5687	517.4	1.011
System II: 1- Hexanol + Methyl Benzoate					
0.1001	0.9000	5.475	0.4669	313.4	1.321
0.2000	0.8999	5.765	0.4867	327.0	1.290
0.3002	0.7001	5.941	0.4892	381.6	1.252
0.4000	0.6001	6.373	0.5028	383.6	1.182
0.5001	0.5000	6.534	0.5100	398.2	1.120
0.6004	0.3999	7.095	0.5319	414.9	1.085
0.7000	0.2999	7.174	0.5344	441.0	1.031
0.8001	0.2001	7.851	0.5543	462.8	1.036
0.9002	0.0999	8.109	0.5706	511.2	1.007

It is observed that internal pressure increases with increasing concentration of 1-ols (Table 3). The internal pressure increases due to the various degree of dispersive interaction and the coloumbic interaction existing between the component molecules (Sumathi and Umamaheswari, 2009). The magnitude of the adhesion increases with increasing mole fraction of 1-ol (Tabhane *et al.*, 1999). The acoustic impedance (Z) (Table 3) decreases with increasing mole fraction of 1-pentanol and 1-hexanol. When an acoustical wave travel in a medium, there is a variation of pressure from particle to particle. The decrease in acoustic impedance with increase in mole fraction indicates significant interactions between the component molecules. This is an agreement with the results of Anwar Ali (Anwar Ali *et al.*, 2001).

In order to highlight the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a physical property of the liquid mixtures from the ideal behavior is a measure of the interaction between the molecules, which may be due to either adhesive or cohesive force. The values of excess adiabatic compressibility (β^E) (Fig.1) and excess free length (L_f^E) (Fig.2) changes from negative to positive as the mole fraction of 1-ols increases. It is evident that the β^E and L_f^E value are almost negative for lower 1-ols but the magnitude of negative values diminishes and the positive values increases with the increasing chain length of the alcohols. The values of β^E and L_f^E in terms of negative are enhanced by the following order; 1-pentanol > 1-hexanol. These results can be explained in terms of molecular interaction and structural effects. Positive β^E and L_f^E are due to the breaking of interactions and the corresponding disruption order in the pure components (Mousumi Das and Mahedra Nath Roy, 2006, Nikam *et al.*, 2000, Ali and Nain, 2002).

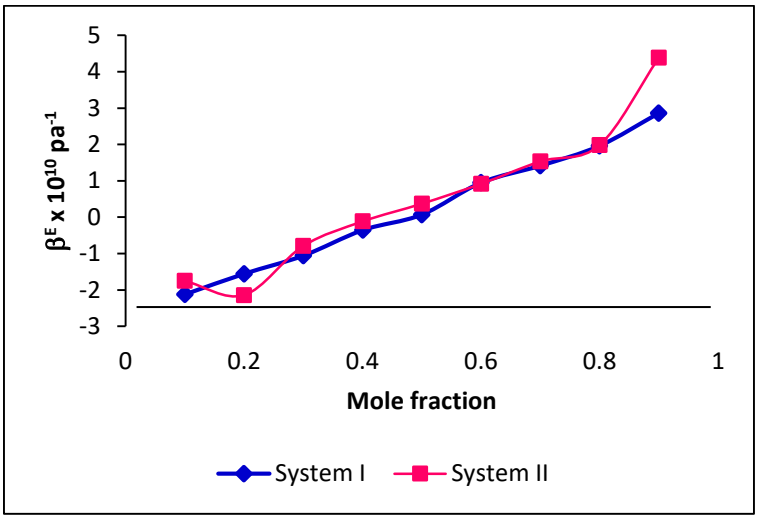

Figure.1: Excess adiabatic compressibility Vs. Mole fraction for the system I & II at 303.15 K

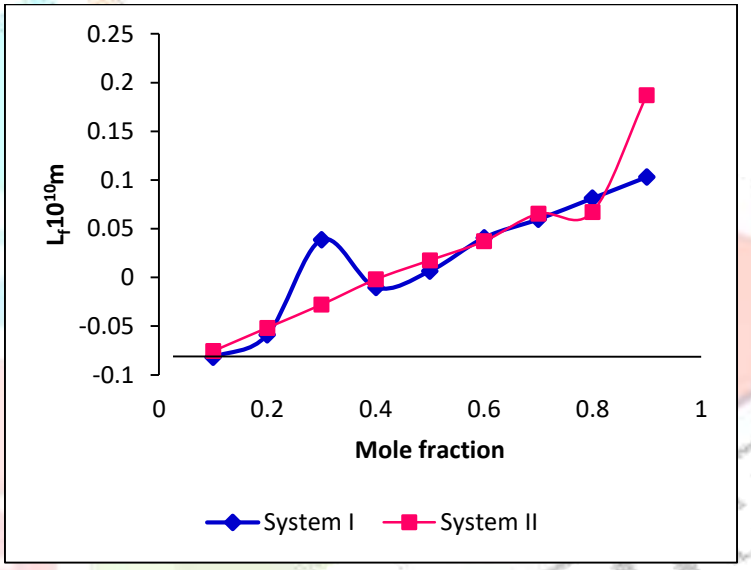

Figure.2: Excess free length Vs. Mole fraction for the system I & II at 303.15 K

In the study of liquid mixture the variations of the excess internal pressure (π_i^E) (Fig.3) may give some information regarding the nature and force existing between the molecules. According to Deshphande *et al.* (1968), the negative sign of excess internal pressure indicate the weak interaction, while the positive sign of excess internal pressure (π_i^E) indicates the strong bonding between the molecule (Subramanyan Naidu and Ravindra Prasad, 2002). The excess values of acoustic impedance (Z^E) changes from positive to negative as we increase the concentration of 1-ols (Fig.4). This may be indicative of the decreasing strength of interaction between the component molecules for 1-pentanol and for 1-hexanol, it exhibits positive values for all the mole fraction (Sumathi *et al.*, 2011).

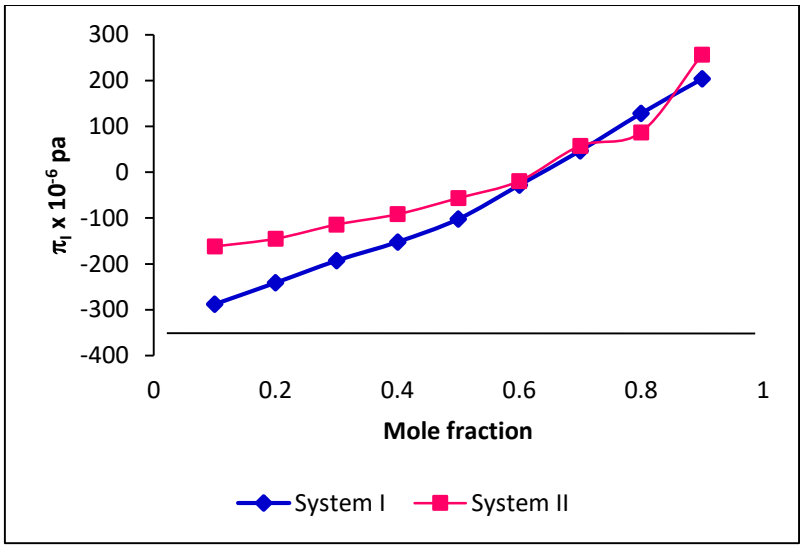

Figure.3: Excess internal pressure Vs. Mole fraction for the system I & II at 303.15 K

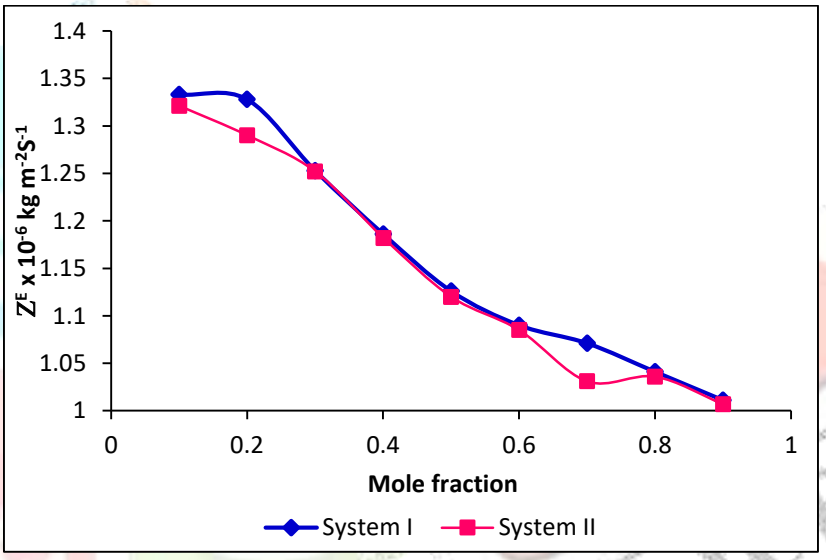

Figure.4: Excess acoustic impedance Vs. Mole fraction for the system I & II at 303.15 K

4. Conclusion

In the present investigation, the variation in the acoustic parameters and the sign and magnitude of the excess functions derived from the ultrasonic velocity, density and viscosity suggest the presence of molecular interaction in the binary mixture and is due to hydrogen bonding through polar oxygen atom of Methyl benzoate and hydrogen atom of alcohols. Perusal of the sign and magnitude of different parameters, it is concluded that the average strength of molecular interaction become weaker with rise in the chain length of the 1-alkanol and the order of the interaction is 1-pentanol > 1 – hexanol.

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