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Study of Molecular Interaction in Ternary Liquid Mixtures by Ultrasonic Velocity Measurements

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Abstract: The ultrasonic velocity, density and viscosity have been measured for the mixtures of alkanols, namely, 1-propanol, 1-butanol and 1-pentanol with chlorobenzene in toluene at 303 K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i). The excess values of some of the above parameters are also evaluated and discussed in the light of molecular interaction present in the mixtures. Existence of strong molecular association is observed in the present study. Such a molecular association is found to be by hydrogen bonding through dipole-dipole interactions. Also, donor-acceptor complexation is observed in the present investigation. It is interesting to note that the hetro and homo association of molecules decreases with increasing chain length of the carbon atom in alkanols.

Key words: Primary alkanols, adiabatic compressibility, intermolecular free length, internal pressure, hydrogen bonding, dipole-dipole interactions

INTRODUCTION

The variation of ultrasonic velocity and other acoustic parameters along with their excess values in binary or ternary liquid mixtures with changing mole fractions of one of the components has been investigated by Oswal and Patel (1995), Arul and Palaniappan (2005), Thirumaran and Jayakumar (2009) and Thirumaran and Sabu (2009). The study of liquid mixtures containing of polar or non-polar components find applications in industrial and technological processes, as such liquid mixtures provide a wide range of solutions with appropriate properties. As a part of investigations on intermolecular interactions between the components of non-aqueous binary or ternary liquid mixtures by ultrasonic speed (Ali *et al.*, 1997). In the present study, the molecules of toluene are non-polar whereas that of alkanols and chlorobenzene are highly polar.

Chlorine atom in chlorobenzene is an electron-withdrawing atom, tends to attract to π -electrons of the benzene ring, thereby and decreases the electron density of ring. As a result, the benzene ring in chlorobenzene becomes relatively poor electron-donor towards the electron-seeking proton of any groups. Chlorobenzene has low dielectric constant $\epsilon' = 5.649$ and dipole moment $\mu = 1.69$ D. Its boiling point and melting points are 132°C and -45°C , respectively. Chlorobenzene is neither acidic nor basic colourless liquid with a pleasant smell. Chlorobenzene is insoluble in water and soluble in alcohol, benzene and ether. Chlorobenzene is more reactive because the chlorine atom is bonded with SP^3 hybridized

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carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is described by Paikray and Mohanty (2003). The study of molecular association in organic ternary mixtures having alcohol as one of the components is of particular interest, since, alcohols are strongly self-associated liquid having a three dimensional network of hydrogen bond (Kincaid and Eyring, 1938) and can be associated with any other group having some degree of polar attractions (Ali *et al.*, 2004). In toluene on account of the electronegativity of chlorine atom which acts as an electron acceptor towards the π -electrons of toluene ring. This is due to the fact that $-\text{CH}_3$ group of toluene is an electron-donating group through induction, enhances the π -electron density of the toluene ring. This makes the donation of π -electron of toluene for chlorine atom easier, thus forming donor-acceptor complex between toluene and neighbouring molecules (Ali and Nain, 2000).

In view of the above salient features, an attempt has been made to elucidate the molecular interaction studies in the ternary liquid mixtures of 1-propanol, 1-butanol and 1-pentanol with chlorobenzene in toluene at 303 K.

The following systems were taken up study at 303 K:

- **System-I:** 1-propanol+toluene+chlorobenzene
- **System-II:** 1-butanol+toluene+chlorobenzene
- **System-III:** 1-pentanol+toluene+chlorobenzene

MATERIALS AND METHODS

The chemicals used in the present work were Analytical Reagent (AR) and Spectroscopic Reagent (SR) grades with minimum assay of 99.9% were obtained from Sd fine chemicals India and E-merck, Germany. In all systems, the various concentrations of the ternary liquid mixtures were prepared in terms of mole fraction, out of which the mole fraction of the second component toluene ($X_2 = 0.4$) was kept fixed while the mole fractions of the remaining two (X_1 and X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the second component at 0.4. The density of pure liquids and liquid mixtures are determined using a specific gravity bottle by relative measurement method with a reproducibility of $\pm 0.01 \text{ kg m}^{-3}$ (Model: SHIMADZU AX-200). An Ostwald's viscometer of 10 mL capacity is used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ± 0.01 sec. An ultrasonic interferometer (Model: F81) supplied by Ms. Mittal Enterprises, New Delhi, having the frequency 3 MHz with an overall accuracy of $\pm 2 \text{ m sec}^{-1}$ has been used for velocity measurement. An electronically digital constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

Theory

Using the measured data, the following acoustical parameters have been calculated.

$$\text{Adiabatic compressibility: } \beta = \frac{1}{U^2 \rho} \quad (1)$$

Intermolecular free length (L_f) has been calculated from relation:

$$L_f = K_T \sqrt{\beta} \quad (2)$$

where, K_T is a temperature dependent constant.

Free volume (V_f) has been calculated from relation:

$$V_f = \left(\frac{M_{\text{eff}} U}{K \eta} \right)^{3/2} \quad (3)$$

where, M_{eff} is the effective molecular weight ($M_{\text{eff}} = \sum m_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents, respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The internal pressure (π_i) can be find out as:

$$\pi_i = bRT \left(\frac{K \eta}{U} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right) \quad (4)$$

where, K is a constant, T is the absolute temperature, η is the viscosity in Nsec m^{-2} , U is the ultrasonic velocity in m sec^{-1} , ρ is the density in kg m^{-3} and M_{eff} is the effective molecular weight.

Excess parameter (A^E) has been calculated by using the relation:

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

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

RESULTS AND DISCUSSION

The experimentally determined values of the density (ρ), viscosity (η) and ultrasonic velocity (U) at 303 K of all the pure components are shown in Table 1 whereas Table 2 summarize the same for all the ternary systems (I-III). The values of adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f) and internal pressure (π_i) of the three liquid systems at 303 K are given in Table 3. The respective excess values of the some of the above parameters have been evaluated for the three liquid systems and are presented in the Table 4.

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids at 303 K

Liquids	Density $\rho/(\text{kg m}^{-3})$	Viscosity $\eta/(\times 10^{-3} \text{Nsec m}^{-2})$	Velocity $U/(\text{m sec}^{-1})$
Chlorobenzene	1056.36	0.7027	1236
Toluene	837.70	0.5944	1290
1-propanol	791.60	1.6580	1194
1-butanol	794.30	2.2384	1237
1-pentanol	803.87	2.6564	1272

Table 2: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303 K

Mole fraction		Density ρ /(kg m ⁻³)	Viscosity η /(x 10 ⁻³ Nsec m ⁻²)	Velocity U/(m sec ⁻¹)
X ₁	X ₂			
System I: 1- propanol + toluene + chlorobenzene				
0.0000	0.6000	783.38	0.5399	1245.64
0.0999	0.5000	1048.77	0.7290	1256.86
0.2000	0.4000	1056.66	0.8450	1268.78
0.2999	0.3000	1072.74	0.9206	1280.96
0.3999	0.2000	1088.56	1.0463	1291.10
0.4999	0.0999	1099.72	1.1494	1305.24
0.6000	0.0000	1113.24	1.2369	1317.65
System II: 1- butanol+ toluene + chlorobenzene				
0.0000	0.6000	783.38	0.5399	1245.64
0.1000	0.4999	867.14	0.6065	1264.21
0.2000	0.3999	931.83	0.7497	1278.50
0.3000	0.2999	941.85	0.8577	1290.64
0.4000	0.2000	950.73	0.9872	1304.63
0.5000	0.999	962.06	1.0463	1319.42
0.6000	0.0000	975.84	1.2486	1331.56
System III: 1- pentanol + toluene + chlorobenzene				
0.0000	0.6000	783.38	0.5399	1245.64
0.0999	0.5000	981.87	0.7365	1251.20
0.1999	0.3999	992.16	0.8045	1262.64
0.3000	0.2999	1022.08	0.9564	1284.50
0.4000	0.2000	1043.69	1.2106	1296.70
0.5000	0.1000	1064.24	1.4128	1310.20
0.6000	0.0000	1080.40	1.6565	1322.80

Table 3: Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 303 K

Mole fraction		Adiabatic compressibility β /(x 10 ⁻¹⁰ m ² N ⁻¹)	Free length L _f /(x10 ⁻¹⁰ m)	Free volume V _f /(x10 ⁻⁷ m ³ mol ⁻¹)	Internal pressure π_i /(x10 ⁶ N m ⁻²)
X ₁	X ₂				
System I: 1- propanol + toluene + chlorobenzene					
0.0000	0.6000	783.38	0.5399	1245.64	256.15
0.0999	0.5000	981.87	0.7365	1251.20	383.07
0.1999	0.3999	992.16	0.8045	1262.64	438.73
0.3000	0.2999	1022.08	0.9564	1284.50	494.78
0.4000	0.2000	1043.69	1.2106	1296.70	566.74
0.5000	0.1000	1064.24	1.4128	1310.20	641.64
0.6000	0.0000	1080.40	1.6565	1322.80	724.26
System II: 1- butanol + toluene + chlorobenzene					
0.0000	0.6000	6.8525	0.5723	2.9972	256.24
0.1000	0.4999	6.7455	0.5397	2.7235	301.142
0.2000	0.3999	6.7155	0.5112	2.5844	365.29
0.3000	0.2999	6.5653	0.5037	1.8333	411.10
0.4001	0.2000	6.1797	0.4960	1.7475	463.67
0.5000	0.0999	6.1797	0.4875	1.7268	475.20
0.6000	0.0000	5.9707	0.4796	1.4290	583.00
System III: 1- pentanol + toluene + chlorobenzene					
0.0000	0.6000	6.6525	0.5723	4.2173	255.98
0.999	0.5000	6.5025	0.5088	2.5720	356.62
0.1999	0.3999	6.3224	0.5017	2.2015	384.15
0.3000	0.2999	5.9298	0.4858	1.6790	436.41
0.4000	0.2000	5.6983	0.4763	1.1512	510.33
0.5000	0.1000	5.4737	0.4668	0.8925	572.54
0.6000	0.0000	5.2896	0.45589	0.6850	642.90

It is observed from the Table 2 that the density (ρ), viscosity (η) and ultrasonic velocity (U) increases in all the three liquid systems with increasing molar concentration of primary alkanols. The variation of ultrasonic velocity in a mixture depends upon the increase or

Table 4: Excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), internal pressure (π_i^E) and acoustic impedance (Z^E)

Mole fraction		Excess adiabatic compressibility	Excess free length $L_f^E/$	Excess free volume $V_f^E/$	Excess internal pressure $\pi_i^E/$	Excess acoustic impedance
X_1	X_2	$\beta^E/(\times 10^{-10} \text{ m}^2 \text{ N}^{-1})$	$(\times 10^{-10} \text{ m})$	$(\times 10^{-7} \text{ m}^3 \text{ mol}^{-1})$	$(\times 10^6 \text{ N m}^{-2})$	$(Z^E)/\times w^6 \text{ kg Sm}^{-2}$
System I: 1- propanol + toluene + chlorobenzene						
0.0000	0.6000	-0.5520	-0.059	-0.167	-67.608	-0.2352
0.0999	0.5000	-0.8346	-0.031	-0.378	-41.320	0.1424
0.2000	0.4000	-1.2483	-0.047	-0.517	-44.530	0.2002
0.2999	0.3000	-1.7152	-0.065	-0.406	-53.580	0.2691
0.3999	0.2000	-2.1476	-0.082	-0.463	-22.105	0.3358
0.4999	0.0999	-2.5866	-0.099	-0.321	-41.770	0.4015
0.6000	0.0000	-3.0114	-0.1162	-0.324	-69.045	0.4687
System II: 1- butanol + toluene + chlorobenzene						
0.0000	0.6000	-0.555	-0.0598	-0.1674	-0.2352	1.2110
0.1000	0.4999	-0.0919	-0.0198	-0.1565	0.1424	1.1794
0.2000	0.3999	-0.4417	-0.016	-0.0103	0.2002	1.1478
0.3000	0.2999	-0.8318	-0.030	-0.4763	0.2691	1.1162
0.4001	0.2000	-1.2284	-0.045	-0.2781	0.3358	1.0850
0.5000	0.0999	-1.6294	-0.061	-0.0124	0.4015	1.0520
0.6000	0.0000	-2.0263	-0.077	-0.026	0.4687	1.0210
System III: 1- pentanol + toluene + chlorobenzene						
0.0000	0.6000	-0.5555	-0.0598	-1.0527	-67.78	1.2110
0.0999	0.5000	-0.250	-0.008	-0.0251	-40.70	1.1824
0.1999	0.3999	-0.576	-0.021	-0.3956	-13.54	1.1548
0.3000	0.2999	-1.114	-0.043	-0.6348	-16.50	1.1283
0.4000	0.2000	-1.492	-0.057	-0.8792	-38.54	1.1000
0.5000	0.1000	-1.861	-0.063	-0.8539	-63.78	1.0732
0.6000	0.0000	-2.191	-0.056	-0.7778	-97.14	1.04556

decrease of intermolecular free length after mixing the components. On the basis of a model for propagation proposed by Kincaid and Eyring (1938). Ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing of components and vice versa. This in fact observed in the present investigation.

Further, it is observed that the adiabatic compressibility (β) and intermolecular free length (L_f) which are given in the Table 3 are found to be decreased with increasing molar concentration of primary alkanols in all the three liquid systems. Such a decrease in β as well as L_f with increasing molar concentration of primary alkanols in the present study indicate significant interactions between chlorobenzene and alkanol molecules forming hydrogen bonding through dipole-dipole interactions ($\text{O}-\text{H}^+-\text{Cl}^-$). Further, alkanols are liquids, associated through hydrogen bonding and in the pure state, they exhibit an equilibrium between multimer and monomer species. In the pure state, halogenated compounds present weak dipole-dipole interactions. When chlorobenzene is mixed with alkanols, the halogenated solvents can interact with the -OH groups (Letcher *et al.*, 1993; Letcher and Nevines, 1994). The aromatic derivatives set up an interaction between the π -electron cloud and the hydroxyl group (Stokes and Robinson, 1982). Though, the interaction is of minor intensity compared with the hydrogen bonding but they can lead to the formation of intermolecular complexes (Prigogine, 1957). Finally, the contribution due to structural effects which must be taken into account which may result in decrease of adiabatic compressibility (β) and intermolecular free length (L_f)

The values of free volume (V_f) which are furnished in the Table 3 show decreasing trend in all the three liquid systems with increasing concentration of primary alkanols. It may be interpreted that by taking into account the electronegativity of chlorine atom which acts as an electron acceptor towards the π -electron of toluene ring. This is due to the fact that $-\text{CH}_3$ group of toluene is an electron-donating group through induction (Ali and Nain, 2000) enhances the π -electron density of the toluene ring. This results in formation of donor-

acceptor complex between toluene and chlorobenzene molecules. As a result, there is contraction in volume, which makes the free volume (V_f) to decrease in all the systems. The increasing values of internal pressure (π_i) in all the three liquid systems which are shown in Table 3 clearly supporting this. Further, the decrease in free volume and increasing trend of internal pressure with rise in concentration of primary alkanols in all the systems clearly show the increasing magnitude of interactions (Anbanantham, 1979).

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures.

It is learnt that the dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values (Fort and Moore, 1965). In the present investigation, the values of excess adiabatic compressibility (β^E), excess free length (L_f^E) and excess free volume (V_f^E) are shown in Table 4. These excess values exhibit negative values over the entire range of composition in all the three liquid systems. The negative values of β^E almost increases with increasing concentration of primary alkanols which reflect the existence of strong molecular interactions in the liquid mixtures. As mentioned earlier, as $-CH_3$ group of toluene which is an electron donating group through induction, enhances the π -electrons of toluene for chlorine atom easier forming donor-acceptor complex between toluene and chlorobenzene molecules (Ali and Nain, 2000) resulting in the negative values of excess compressibility.

In the present study, the negative values of β^E is an indication of strong interaction in the liquid mixtures (Rai *et al.*, 1989) as well as interstitial accommodation of chlorobenzene molecules into the aggregates of alcohols. Also, in the present investigation, it is seen that from the magnitude of negative values excess adiabatic compressibility as well as excess free length, the molecular interaction which follows the order: 1-propanol > 1-butanol > 1-pentanol. This trend suggests that hetero and homo association of molecules decrease with increasing chain length of carbon atoms in alkanols (Ali and Nain, 2000), . Probably this may be due to less proton donating tendency of higher alkanols (Norton, 1939; Mecke, 1950). The negative values of excess internal pressure (π_i^E) in all the three liquid systems clearly confirms the existence of molecular association between unlike molecules. It is further supported by the excess values of acoustic impedance Z^E , which are shown in the Table 4. The excess values of acoustic impedance exhibit positive values over the entire range of composition in all the three liquid mixtures. Such a positive values of Z^E suggest the strong molecular interactions among the component molecules in the mixture (Tiwari *et al.*, 1995).

CONCLUSION

Hence, it is very obvious that there exists a strong molecular association between the component molecules in the mixtures. The molecules of chlorobenzene and primary alkanols form hydrogen bonding through dipole-dipole interactions. The donor-acceptor complexation is observed between toluene and chlorobenzene molecules. The hetero and homo association of molecules decrease with increasing chain length of carbon atoms in alkanols. The molecular interactions existing in the present systems of mixtures are of the order: 1-propanol > 1-butanol > 1-pentanol.

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