Molecular Interaction Studies on *N*-Alkanols with DMA in Toluene at 303K

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Abstract: The ultrasonic study of velocity, density and viscosity has been measured for the mixtures of *n*-alkanols, namely; 1-propoanol, 1-butanol and 1-pentanol in toluene with *N-N* dimethyl acetamide (DMA) at 303K. The experimental data have been used to calculate the acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), and acoustic impedance (Z). The excess values of the above parameters have also been evaluated and presented. From the present investigation, it is obvious that a weak molecular association was identified. Mixing of DMA with *n*-alkanols causes dissociation of hydrogen bonded structures of *n*-alkanols. Also, further addition of DMA with the mixture not only causes dissociation of hydrogen bonded structures of *n*-alkanols but also a decrease in molecular association between toluene and *n*-alkanols is observed. The evaluated excess values predict weak molecular interactions existing between DMA-*n*-alkanols as well as toluene-*n*-alkanols.

Keywords: Adiabatic compressibility, Free length, Hydrogen bonding, Dipole-dipole interactions, Viscous relaxation time

Introduction

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures¹⁻³. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids⁴⁻⁷, binary and ternary mixture. The variation of ultrasonic velocity and related parameters throw much light upon

the structural changes associated with the liquid mixtures having weakly interacting components^{8,9} as well as strongly interacting components. 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 bond¹⁰ and can be associated with any other group having some degree of polar attractions¹¹.

An exhaustive survey of literature has shown that a few attempts have been made for the ultrasonic velocity data of ternary mixtures¹²⁻¹⁴. However, no effort appears to have been made to collect the ultrasonic velocity data for the ternary mixtures of *N,N*-dimethylacetamide, in toluene with 1-alkanols. Hence, experimental study were carried out by the author and reported *N,N*-dimethylacetamide + toluene + 1-propanol + 1-butanol, and 1-pentanol at 303K. The main purpose of this study is to characterize the molecular interactions in these systems and to subsequently evaluate the effect of chain length of 1-alcohols on the ultrasonic velocity values of these mixtures.

The present ternary liquid systems taken for study at 303K are

System-I	1-Propanol	+ Toluene	+ Dimethylacetamide (DMA)
System-II	1-Butanol	+ Toluene	+ Dimethylacetamide (DMA)
System-III	1-Pentanol	+ Toluene	+ Dimethylacetamide (DMA)

Experimental

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay were obtained from Sd fine chemicals India and E-merck, Germany as such without further purification. 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 components 1-alkanols (X_1) and DMA (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 were determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An Ostwald's viscometer which is 10 mL capacity was used for the viscosity measurement of pure liquids and liquid mixtures. The 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 of 0.01s (Model: RACER HS-10 W) An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 3MHz with an overall accuracy of ± 2 ms⁻¹ has been used for velocity measurement.

Theory

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

Adiabatic Compressibility

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

Intermolecular free length (L_f) has been calculated from the following 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,

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

Where, M_{eff} is the effective molecular weight ($M_{eff} = \sum m_i x_i$, 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 found out as

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

K is a constant, T the absolute temperature, η the viscosity in Nsm^{-2} , U the ultrasonic velocity in ms^{-1} , ρ the density in Kgm^{-3} , M_{eff} the effective molecular weight. Excess parameter (A^E) has been calculated by using 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 fraction of the liquid component.

Results and Discussion

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

Table 1. Density (ρ), viscosity (η) and Ultrasonic velocity (U) of pure liquids.

Liquids	Density $\rho/\text{kg/m}^3$	Viscosity $\eta/\times 10^{-3} \text{ NSm}^{-2}$	Velocity $U/\text{m/s}$
1-Propanol	793.25	1.6075	1184.9
1-Butanol	799.62	2.1025	1218.7
1-Pentanol	805.60	2.6875	1251.6
Toluene	851.65	0.5729	1276.2
<i>N-N</i> Dimethylacetamide (DMA)	930.25	0.8991	1432.0

In all the three ternary liquid systems, the ultrasonic velocity decreases with increasing concentration of 1-alkanols. This behaviour at such concentrations is different from the ideal mixtures behaviour can be attributed to intermolecular interactions in the systems studied¹⁵⁻¹⁶. The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components.

On the basis of a model, for sound propagation proposed by Eyring and Kincaid¹⁷, ultrasonic velocity should decrease, if the intermolecular free length increase and *vice-versa*. This is observed in the present investigation for all the three liquid systems. Such a decrease in ultrasonic velocity (U) in all the three liquid systems with increasing molar concentration of alcohols which is attributed to, as the number of hydrocarbon group or chain-length of alcohol increases, a gradual decrease in sound velocity is noticed. This behaviour at such

concentrations is different from the ideal mixtures behaviour can be attributed to intermolecular interactions in the systems studied^{15,16}. The value of adiabatic compressibility (β) however, shows an inverse behaviour as compared to the ultrasonic velocity (U) *i.e.* the adiabatic compressibility (β) increases with increase of concentration of alcohols in all the three liquid systems, which are tabulated in Table 3. It is primarily the compressibility that increases due to structural changes of molecules in the mixture leading to a decrease in ultrasonic velocity^{18,19}. Such a continuous increase in adiabatic compressibility with respect to the concentration of alkanols has been qualitatively ascribed to the effect of hydrogen bonding or dipole-dipole interactions²⁰.

Table 2. Density (ρ), viscosity (η) and Ultrasonic velocity (U).

Mole Fraction		Density	Viscosity	Velocity
X_1	X_3	$\rho/\text{kg/m}^3$	$\eta/\times 10^{-3} \text{ NSm}^{-2}$	U/m/s
System-I - 1-Propanol + toluene + dimethylacetamide (DMA)				
0.0000	0.6001	819.6	0.6706	1269.6
0.0998	0.5002	814.3	0.6958	1263.7
0.2000	0.4000	809.8	0.7154	1257.6
0.3000	0.3000	807.4	0.7390	1250.8
0.3999	0.2000	804.2	0.7524	1244.7
0.5000	0.1000	800.91	0.7732	1239.6
0.6001	0.0000	787.87	0.7995	1230.3
System-II- 1-Butanol + toluene + dimethylacetamide (DMA)				
0.0000	0.5999	827.6	0.7944	1279.8
0.0998	0.5000	822.9	0.8842	1272.4
0.1998	0.4004	820.7	0.9242	1265.7
0.3035	0.2918	816.8	0.9676	1259.4
0.4000	0.2000	810.7	0.9776	1256.4
0.5000	0.0998	806.3	1.0101	1249.6
0.6001	0.0000	800.22	1.1010	1241.4
System-III - 1-Pentanol + toluene + dimethylacetamide (DMA)				
0.0000	0.5999	827.6	0.7944	1279.8
0.0998	0.5000	822.9	0.8842	1272.4
0.1998	0.4004	820.7	0.9242	1265.7
0.3035	0.2918	816.8	0.9676	1259.4
0.4000	0.2000	810.7	0.9776	1256.4
0.5000	0.0998	806.3	1.0101	1249.6
0.6001	0.0000	800.22	1.1010	1241.4

Alkanols are liquids which are associated through the hydrogen bonding and in the pure state, they exhibit an equilibrium between the monomer and multimer species. Also, they can be associated with any other groups having some degree of polar attractions²¹. Similarly, *N-N* dimethylacetamide (DMA) is belonging to the amide group which is highly polar, aprotic solvent and its molecules are associated through dipolar interactions²². Mixing of DMA with alkanols would release the dipoles of alkanols due to the breaking of hydrogen bonds.

As a result, the free dipoles released from the alkanols in association with DMA molecules forming strong hydrogen bonds, hence stronger molecular association existing between the DMA and alkanols molecules through hydrogen bonding²². Further, mixing of such DMA with 1-alkanols causes dissociation of hydrogen bonded structure of 1-alkanols and

subsequent formation of (new)H-bond (C=O –H...O) between proton acceptor oxygen atom (with lone pair of electrons) of C=O group of DMA and proton of OH- group of 1-alkanols²³.

Table 3. Adiabatic compressibility (β), free length (L_f) free volume (V_f), internal pressure (π_i) and Acoustic impedance (Z).

Mole Fraction		Adiabatic compressibility $\beta / \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Free length $L_f / \times 10^{-10} \text{ m}$	Free volume $V_f / \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$	Internal pressure $\pi_i / \times 10^6 \text{ Nm}^{-2}$	Acoustic impedance $Z / \times 10^6 \text{ kg m}^2 \text{ s}^{-1}$
X_1	X_3					
System-I - 1-Propanol + toluene + dimethylacetamide (DMA)						
0.0000	0.6001	7.5694	0.5484	2.4750	111.37	1.0627
0.0998	0.5002	7.6900	0.5533	2.2208	117.35	1.0290
0.2000	0.4000	7.8079	0.5575	2.0165	118.17	1.0184
0.3000	0.3000	7.9165	0.5614	1.8137	120.47	1.0099
0.3999	0.2000	8.0261	0.5653	1.6555	121.91	1.0009
0.5000	0.1000	8.1257	0.5688	1.5072	123.89	0.9928
0.6001	0.0000	8.3850	0.5778	1.3418	126.68	0.9692
System-II - 1- Butanol + toluene + dimethylacetamide (DMA)						
0.0000	0.5999	7.3773	0.5419	1.9429	121.52	1.0592
0.0998	0.5000	7.5059	0.5466	1.6043	130.31	1.0471
0.1998	0.4004	7.6059	0.5503	1.4583	135.55	1.0388
0.3035	0.2918	7.7189	0.5544	1.3186	141.26	1.0287
0.4000	0.2000	7.8141	0.5332	1.2652	144.08	1.0186
0.5000	0.0998	7.9426	0.5623	1.1668	148.89	1.0076
0.6001	0.0000	8.1089	0.5682	0.9871	158.05	0.9933
System-III - 1-Propanol + toluene + dimethylacetamide (DMA)						
0.0000	0.6099	7.2872	0.5386	1.7962	123.69	1.0672
0.0999	0.5000	7.3899	0.5421	1.6797	127.37	1.0577
0.2010	0.3971	7.4990	0.5464	1.6096	128.52	1.0465
0.3000	0.3000	7.5922	0.5472	1.5528	129.57	1.0376
0.4000	0.1997	7.6994	0.5536	1.4724	131.50	1.0286
0.4900	0.0998	7.8146	0.5578	1.0880	149.49	1.0183
0.6000	0.0000	7.9372	0.5621	0.9806	149.55	1.0092

As 1-alkanols are associated through hydrogen bonding.

Further, the addition of *N, N*-Dimethylacetamide (DMA)) with mixtures causes dissociation of hydrogen bonded structure of 1-alkanols as well as decrease in interaction between toluene and alkanols. The subsequent formation of new hydrogen bonding between proton acceptor oxygen atoms of >C=O group of DMA and proton of –OH group of 1-alkanols²⁰.

The same trend was observed in free length too in all the three systems, which are tabulated in Table 3. The increase in free length in all the three liquid systems is due to the loose packing of the molecules inside the shield, which may be brought by weakening of molecular interactions²⁴.

Further, a decrease in free volume (V_f) and an increase in internal pressure (π_i) with increase in concentration of the primary alcohols in all the three liquid systems is observed, which are listed in Table 3. Such an increase in internal pressure generally indicates association through hydrogen bonding²⁵ and hence supports the present investigation. Similar results were observed by earlier workers¹⁴ in which an increase in internal pressure generally indicates association through hydrogen bonding.

Further, in all three liquid systems, the values of acoustic impedance (Z) were found to be decreased, which are listed in Table 3. When an acoustic wave travels in a medium, there was a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it was observed that these acoustic impedance (Z) values decrease with increasing concentration of *n*-alkanols. Such a decreasing values of acoustic impedance (Z) further supports the possibility of molecular interactions between the unlike molecules.

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 terms of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures.

The excess values of adiabatic compressibility (β^E), intermolecular free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) for all the three liquid systems are furnished in Table 4. In the present investigation, it is observed that excess values of adiabatic compressibility (β^E) and excess free length (L_f^E) exhibit positive deviation over the entire range of composition in all three liquid systems.

It is learnt that negative values of β^E is an indication of strong intermolecular interactions in the liquid mixtures, which is attributed to charge transfer, dipole-induced dipole and dipole-dipole interactions and hydrogen bonding. While positive excess values to weak interactions which result from dispersion forces Rastogi²⁶ from his studies of excess thermodynamic function in ternary mixtures has shown that the addition of third component weakens the strength of the interaction and the ternary mixture tends to approach ideal behaviour. Further²⁷, it is also suggested that the negative excess compressibility has been due to a closed packed molecules and positive excess values to weak interaction between unlike

molecules. The Perusal of Table 4 shows the variation of the excess free volume as a function of concentration in all systems. The increasing values of free volume in all the systems with decreasing concentration of DMA resulting in weakening of hydrogen bonding interaction between unlike molecules. The negative values of excess internal pressure (π_i^E) in all the three liquid systems which are furnished in Table 4 clearly confirm this prediction. Further, it is again well supported by the excess values of acoustic impedance (Z^E) which are tabulated in Table 4 are all negative in all the liquid systems over the entire range of composition. The negative excess values of Z^E clearly suggest that there is a weak molecular interaction³² existing between the unlike molecules.

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) (Z^E).

Mole Fraction		Excess adiabatic compressibility $\beta^E/\times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	Excess free length $L_f^E/\times 10^{-10} \text{ m}$	Excess free volume $V_f^E/\times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$	Excess internal pressure $\pi_i^E/\times 10^6 \text{ Nm}^{-2}$	Excess acoustic impedance $Z^E/\times 10^6 \text{ kg m}^2 \text{ s}^{-1}$
X_1	X_3					
System-I - 1-propanol + toluene + dimethylacetamide (DMA)						
0.0000	0.6001	1.5410	0.0595	-0.0396	-274.22	-0.1933
0.0998	0.5002	1.2885	0.0509	-0.0639	-312.70	-0.1658
0.2000	0.4000	1.0314	0.0408	-0.1169	-356.56	-0.1362
0.3000	0.3000	0.7664	0.0307	-0.1684	-398.81	-0.1065
0.3999	0.2000	0.5027	0.0205	-0.1756	-441.87	-0.0763
0.5000	0.1000	0.2291	0.0086	-0.1720	-450.14	-0.0450
0.6001	0.0000	0.1146	0.0048	-0.1857	-526.29	-0.0293
System-II - 1- Butanol + toluene + dimethylacetamide (DMA)						
0.0000	0.5999	1.3485	0.0530	-0.4929	-264.06	-0.1747
0.0998	0.5000	1.1605	0.0461	-0.6788	-289.89	-0.1511
0.1998	0.4004	0.9378	0.0372	-0.6740	-319.68	-0.1245
0.3035	0.2918	0.7171	0.0287	-0.6599	-349.20	-0.0955
0.4000	0.2000	0.5138	0.0041	-0.5604	-380.48	-0.1698
0.5000	0.0998	0.3255	0.0129	-0.5048	-410.31	-0.0473
0.6001	0.0000	0.1706	0.0065	-0.5314	-435.98	-0.0260
System-III - 1-propanol + toluene + dimethylacetamide (DMA)						
0.0000	0.6099	1.1620	0.0543	-0.6784	-268.13	-0.1860
0.0999	0.5000	1.0924	0.6716	-0.6716	-286.38	-0.1439
0.2010	0.3971	0.9269	0.0031	-0.5171	-313.52	-0.1218
0.3000	0.3000	0.7569	0.0274	-0.4182	-450.63	-0.0992
0.4000	0.1997	0.5959	0.0233	-0.3434	-367.36	-0.0755
0.4900	0.0998	0.3879	0.0096	-0.7698	-389.21	-0.1087
0.6000	0.0000	0.2944	0.0107	-0.5261	-405.28	-0.0306

Conclusion

By analyzing exhaustively, the present investigation reveals that there exists a weak molecular association is identified. Mixing of DMA with 1-alkanols causes dissociation of

hydrogen bonded structures of 1-alkanols. It is also observed that further addition of DMA with the mixture not only causes dissociation of hydrogen boded structures of 1-alkanols but also a decrease in molecular association between toluene and 1-alkanols. The evaluated excess values too clearly predict weak molecular interactions existing between DMA-1-alkanols as well as toluene-1-alkanols.

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