Ultrasonic Studies of Molecular Interactions in Organic Binary Liquid Mixtures

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Abstract: The ultrasonic velocity, density and viscosity have been measured for the mixtures of 1-alkanols such as 1-propanol and 1-butanol with *N-N* dimethylformamide (DMF) 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 the above parameters are also evaluated and discussed in the light of molecular interaction existing in the mixtures. It is obvious that there is a formation of hydrogen bonding between DMF and 1-alkanols. Further, the addition of DMF causes dissociation of hydrogen bonded structure of 1-alkanols. The evaluated excess values confirm that the molecular association is more pronounced in system-II comparing to the system-I.

Keywords: Adiabatic compressibility, Intermolecular free length, Hydrogen bonding, Internal pressure

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 liquids, binary and ternary mixture⁴⁻⁸. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components⁹ as well as strongly interacting components¹⁰.

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 bond¹¹ and can be associated with any other group having some degree of polar attractions¹².

Although several investigations¹³⁻¹⁵ were carried out in liquid mixtures having alcohol as one of the components, a systematic study in a series of primary alcohols in binary as well as in ternary systems has been scarcely reported. Since, no effort appears to have been made to collect the ultrasonic velocity data for the binary mixtures of 1-alkanols with DMF at 303K. These experimental studies were carried out by the authors and reported the present investigation.

The present binary liquid systems taken up for study at 303K are

System – I	1-propanol + DMF
System – II	1-butanol + DMF

Experimental

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 binary liquid mixtures were prepared in terms of mole fraction, such as 1-propanol with DMF and 1-butanol with DMF varied from 0.1 to 0.9 in steps 0.3. The density of pure liquids and liquid mixtures were 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 was used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within $\pm 0.01\text{s}$. An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 3MHz with an overall accuracy of $\pm 2 \text{ ms}^{-1}$ 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 $\pm 0.1\text{K}$.

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 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 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

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

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 density (ρ), viscosity (η) and ultrasonic velocity (U) of two systems at 303 K are represented in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of the above two systems are evaluated and are presented Table 2. The respective excess values of above parameters have been also evaluated and presented in the Table 3.

In the present investigation, in all the two liquid systems, except viscosity and all the other parameters such as density and ultrasonic velocity decreases with increasing molar concentrations of alcohols. It is observed that as number of hydrocarbon group or chain-length of alcohol increases, a gradual decrease in ultrasonic velocity is noticed. This behaviour at such concentrations is different from the ideal mixtures behaviour can be attributed to intermolecular interactions in the systems studied¹⁶⁻¹⁷. The value of adiabatic compressibility (β) shows an inverse behaviour as compared to the ultrasonic velocity (U). The adiabatic compressibility (β) increases with increase of concentration of molar concentration of 1-alkanols. It is primarily the compressibility that increases due to structural changes of molecules in the mixture leading to a decrease in ultrasonic velocity¹⁸⁻²⁰.

Table 1. Density (ρ), viscosity (η) and ultrasonic velocity (U) at 303 K

Mole fractions		Density (ρ) / kg/m ³	Viscosity (η) / x10 ⁻³ Nsm ⁻²	Ultrasonic velocity (U) m/s
X ₁	X ₂			
System - I				
0.1000	5.2515	933.79	0.7648	1428.4
0.2995	5.8757	901.49	0.8204	1374.2
0.4997	6.5390	871.48	0.9120	1324.6
0.7013	7.3256	841.46	1.0338	1273.6
0.9000	8.3375	809.92	1.3562	1216.92
System – II				
0.09966	0.9003	923.87	0.7651	1419.17
0.30016	0.6998	895.64	0.8966	1370.9
0.5000	0.4999	866.13	1.0247	1325.3
0.70076	0.29924	837.89	1.3348	1279.9
0.9002	0.0997	814.7	1.7053	1253.7

Table 2. Adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at 303 K

Mole fraction		Adiabatic compressibility $\beta/10^{-10} \text{ m}^2 \text{ N}^{-1}$	Free length $L_f/10^{-10} \text{ m}$	Free volume $V_f/10^{-7} \text{ m}^3 \text{ mol}^{-1}$	Internal pressure $\pi_i/10^6 \text{ N}^{-2} \text{ m}$
X_1	X_2				
System - I					
0.1000	5.2515	5.2515	0.4572	1.7508	315.40
0.2995	5.8757	5.8757	0.4835	1.4094	339.97
0.4997	6.539	6.539	0.5102	1.0744	374.10
0.7013	7.3256	7.3256	0.5401	0.07904	416.81
0.9000	8.3375	8.3374	0.5761	0.0265	500.85
System - II					
0.09966	0.9003	5.3742	0.4656	1.7864	307.08
0.30016	0.6998	5.9409	0.4864	1.3427	330.89
0.5000	0.4999	6.5733	0.5116	1.0489	351.47
0.70076	0.29924	7.2850	0.5386	0.6724	398.81
0.9002	0.0997	7.8080	0.5576	0.4534	446.45

Table 3. Excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) at 303 K

Mole fraction		Excess Adiabatic compressibility (β^E)	Excess Free length (L_f^E)	Excess Free volume (V_f^E)	Excess Internal pressure (π_i^E)
X_1	X_2				
System- I					
0.1000	5.2515	-0.1816	5.6120	0.1668	-22.361
0.2995	5.8757	-0.3117	8.3009	0.8527	-45.392
0.4997	6.539	-0.3966	10.299	1.533	-59.039
0.7013	7.3256	-0.3651	9.3450	2.8767	-64.43
0.9000	8.3375	-0.0977	1.6985	3.2722	-27.54
System - II					
0.09966	0.9003	-0.0139	-4.055	-0.1066	-24.80
0.30016	0.6998	-0.100	-5.377	-0.8479	-37.181
0.5000	0.4999	-0.188	-5.838	-1.4383	-52.687
0.70076	0.29924	-0.060	-1.0268	-2.110	-41.577
0.9002	0.0997	-0.186	-5.217	-2.6277	-29.921

Such a continuous increase in adiabatic compressibility with respect to the solute concentration has been qualitatively ascribed to the effect of hydrogen bonding or dipole-dipole interactions²¹.

N-N dimethylformamide (DMF) is a non-aqueous solvent of particular interest, because it has no hydrogen bonding in pure state. Therefore, it acts as an aprotic protophilic medium with high dielectric constant and it is considered as a dissociating solvent. Further, the addition of *N, N*-Dimethylformamide (DMF) with mixtures causes dissociation of hydrogen bonded²² structure of 1-alkanols.

Further, mixing of such DMF with 1-alkanols causes dissociation of hydrogen bonded structure of 1-alkanols and subsequent formation of (new) H-bond ($C=O \dots H-O$) between proton acceptor oxygen atom (with lone pair of electrons) of $C=O$ group of DMF and hydrogen atom of $-OH$ group of 1-alkanol molecules. This dissociation effect leads to an decrease in volume and hence an increase in adiabatic compressibility. Further, the molecules of alkanols are self-associated in pure state through hydrogen bonding. However mixing of DMF with alkanols would release the dipoles²³ of alkanols and interact with DMF molecules forming strong hydrogen bonds, leading to contraction in volume which makes an increase in free length in all the two liquid systems. Such an increase in free length may also be attributed due to the loose packing of 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 is noticed in all the two systems. The increase in internal pressure generally indicates association through hydrogen bonding and hence supports the present investigation. Similar results were observed by earlier workers²⁵ in which an increase in internal pressure generally indicates association through hydrogen bonding.

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 behaviour 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 negative excess values is an indication of strong molecular interaction in the liquid mixtures, whereas positive excess values attributed to weak interactions, which mainly results from the dispersion forces.

As far as excess values are concerned, in the system-I, excess adiabatic compressibility (β^E) values are negative and however, the excess values of free length (L_f^E) and free volume (V_f^E) are all positive. These are represented in the Table 3. Such a positive deviation show that the mixtures are behaving as non-ideal ones, on the basis of sound propagation given by Eyring *et.al*²⁶. The positive values of free volume indicate that weakening of hydrogen bonding between alkanols and DMF and also dissociation of alkonal molecule. The negative excess internal pressure (π_i^E) in the all the two systems clearly confirms this. As far as the system-II concerned, since all the excess parameters (Table 3) exhibit negative values which strongly suggest that strong molecular interaction taking place in this system comparing to the system-I. Hence, the molecular interactions is of the order by comparing the two systems are of the following

$$\begin{array}{l} \text{1-Propanol-DMF} \angle \text{1-Butanol-DMF} \\ \text{System - I} \angle \text{System - II} \end{array}$$

Conclusion

From ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixtures of 1-alkanols with DMF at 303 K, it is concluded that there is a formation of hydrogen bonding between DMF and 1-alkanols. Further, the addition of DMF causes dissociation of hydrogen bonded structure of 1-alkanols. The evaluated excess values clearly confirm that that the molecular interaction is more pronounced in system-II comparing to the system-I

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