Ultrasonic study of molecular interaction in binary liquid mixtures of n-hexane with alcohols

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ABSTRACT

Ultrasonic velocity, viscosity and density of alcohol[s] in n-hexane have been measured at various temperatures in the range of 303.15 - 318.15K. From the experimental data, the acoustical parameters such as molar volume, adiabatic compressibility, intermolecular free length and their excess values have been computed and presented as functions of compositions. The deviations from ideality of the acoustical parameters are explained on the basis of molecular interactions between the components of the mixtures. The variations of these parameters with composition of the mixture suggest the strength of interactions in these mixtures.

Keyword:
n-hexane; alcohol; acoustical parameters; mixtures

1. INTRODUCTION

The liquid mixtures containing two or more liquids are ideal when there is no volume or enthalpy change on mixing. However, in actual practice, mixtures of liquids are not ideal. The deviation from ideality is explained on the basis of molecular interaction between the components of liquid mixtures. The study of intermolecular interaction has attracted the attention of many workers¹-¹⁰. The extensive investigation on liquid systems has been carried out by infrared, raman effect, magnetic susceptibility, nuclear magnetic resonance and ultrasonic methods. In recent years, ultrasonic technique has become a powerful tool in providing valuable information regarding the molecular behavior of liquids.

Excess properties are the measure of nonideality in liquid mixtures as a consequence of association or other types of interactions. The various types of molecular interactions that may operate between molecules of different types are dispersion forces, charge transfer, hydrogen bonding and dipole and dipole-induced dipole interactions. More than one type of interaction may be concerned in any given system. Dispersion forces, which are likely to be operative in every case, should make positive contribution to excess values. Charge transfer,
dipole-induced dipole and dipole-dipole interactions and hydrogen bonding between unlike components should make negative contributions. The magnitudes of the contributions made by these different types of interactions will vary with the components present and the composition of the mixture. Dissociation of a component, which is associated in the pure state, should make a positive contribution to excess values. The change from positive to increasingly negative excess values shows that the strength of the interaction between the components increases; this increase may be qualitatively interpreted in terms of closer approach of unlike molecules leading to reduction in compressibility and volume.

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in design process (flow, mass transfer or heat transfer calculations) in many chemical and industrial processes \(^{11}\). The excess properties derived from these physical property data reflect the physicochemical behavior of the liquid mixtures with respect to the solution structure and intermolecular interactions between the component molecules of the mixture \(^{12-14}\).

The variation of ultrasound velocities, adiabatic compressibilities and free volumes of binary liquid mixtures of protic, aprotic and associating liquids with changing mole fraction of one of the components has been investigated by earlier workers \(^{15-17}\). The trends of changes have been interpreted by these workers in terms of differences in size of the molecules and the strength of interactions taking place between the components of the mixtures. The non-ideal behaviour of liquid mixtures has been predicted by Tuomikoski and Numi \(^{18}\), Fort and Moore \(^{6,19}\), Flory and Coworkers \(^{20,21}\), Prakash et al., \(^{22,23}\) and Raman and Naidu \(^{24}\). The velocity of sound through liquid mixtures could be helpful in assessing the degree of association between the molecules \(^{25,26}\). The molar sound velocity of non-associated liquids has been found to be independent, while that for associated liquid is dependent on temperature \(^{27}\).

n-Hexane is a very good non-polar solvent. Alcohols are self-associated organic liquids and are widely used for the synthesis of other organic compounds. n-Propyl and iso-propyl alcohols are widely used as coupling and dispersing agents in the chemical, pharmaceutical and household industries and as carrier and extraction solvent for natural products. Branching of alkyl group attached to the hydroxyl group results in abnormal behaviour of alcohols.

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\(^+\)). The order of acidity in alcohols is: 1\(^{-}\)-alcohol > 2\(^{-}\)-alcohol > 3\(^{-}\)-alcohol. This order is due to +I effect \(^{28}\). While the interacting ability of alcohols is well established no such opinion is suggested from literature with regards to n-hexane. Keeping this in view, five binary liquid mixtures n-propyl alcohol, iso-propyl alcohol, n-butyl alcohol, sec-butyl alcohol and tert-butyl alcohol with n-hexane were selected to study their molecular interactions through their acoustical behaviour.

From the measured ultrasonic velocity, viscosity and density, the acoustical parameters such as molar volume, adiabatic compressibility, intermolecular free length and their excess values are computed for all the mixtures at various temperatures. The dependence of these parameters on composition has been used to explain the nature and extent of intermolecular interactions in these mixtures. The degree of association of alcohols in n-hexane is also calculated.
2. EXPERIMENTAL PROCEDURE

Ultrasonic velocity of pure liquids and liquid mixtures were measured at 3MHz with variable path single beam interferometer having gold plated quartz crystal at the bottom and double walled gold plated cell having grooves at inside walls to check the overlapping of stationary waves to produce clarity nodes and internodes. The accuracy of velocity measurements is ± 0.1 ms$^{-1}$. The densities of pure liquids and liquid mixtures were determined from the weight measurements on using the specific gravity bottle immersed in the thermostat at the experimental temperature and the accuracy in the measurements is ± 0.1 Kgm$^{-3}$. The viscosities of the mixtures were measured using an Ostwald’s viscometer and were accurate to ± 0.001 Nsm$^{-2}$.

The liquids were of best available grade n-Hexane (BDH), n-propyl alcohol (BDH), iso-propyl alcohol (SD’s fine chemicals), n-butyl alcohol (BDH), secondary butyl alcohol (Emerck), tertiary butyl alcohol (BDH) and purified by standard methods described by Weissberger$^{29}$. The liquid mixtures were prepared by mixing calculated amount of pure liquids.

2.1. Theory

From experimental data, the adiabatic compressibility, Molar volume, intermolecular free length$^{30}$ and their excess values were computed by the following relations.

- Molar volume, $V = \frac{M_{\text{eff}}}{\rho}$
- Adiabatic compressibility, $\beta = \frac{1}{u^2 \rho}$
- Intermolecular free length, $L_f = K \beta^{1/2}$

Where $M_{\text{eff}}$ is the effective molecular weight given by, $M_{\text{eff}} = x_1 M_1 + x_2 M_2$, $M_1$ and $M_2$ being the molecular weights, $x_1$ and $x_2$ are mole fractions of components 1 and 2, $\rho$ is the density, $u$ is the ultrasonic velocity, $K$ is the temperature dependent Jacobson constant.

The excess values of all the parameters are computed by the expression, $A^E = A_{\text{exp}} - [x_1 A_1 + x_2 A_2]$

A represents various parameters, $A^E$ being the excess value and $A_{\text{exp}}$ the experimentally determined value.

3. RESULTS AND DISCUSSION

The experimental density, ultrasonic velocity, viscosity, the computed molar volume, adiabatic compressibility and free length data and their excess values for the alcohol [s] + n-hexane at various temperatures are given in Table 1 to 5. All the excess values of these parameters $V^E$, $\eta^E$, $\beta^E$ and $L_f^E$ at various temperatures are represented graphically in Fig. 1 to 4. The $V^E$, $\eta^E$ and $L_f^E$ are positive and $\eta^E$ is negative for all the systems (n-Hexane + alcohol[s]) under study over the whole composition range of n-hexane (Fig. 1 to 4).

The positive values of $V^E$ show that the interaction between alcohol[s] and n-hexane is weak, may be attributed to breaking of hydrogen bonds between alcohols. Prakash et al.$^{31}$ observed that $V^E$ are positive, involving the weak dispersion forces between molecules of dichloromethane and aromatic hydrocarbon molecules. This similar behaviour is also
The values of $\eta^E$ are negative over the whole concentration range for all the mixtures at all temperatures (Fig.2) suggesting weak interaction between the components\cite{19}. The $\eta^E$ values increase with increasing chain length of alcohols\cite{32}. The excess viscosities show a systematic decrease with increase of temperature (Table 1 to 5).

The excess adiabatic compressibilities are positive over the whole composition range for all mixtures at all the temperatures, indicating the breaking of hydrogen bonds\cite{32}. The variation of excess adiabatic compressibility with the composition of alcohols at 303.15K is given in Fig. 3. Such behaviour is also investigated by Venkatesulu et al\cite{33} in trichloroethylene with 3-methyl-1-butanol, 2-butanol and 2-methyl-2-propanol. The study of
the adiabatic compressibility provides better understanding of the medium. The electrostatic field produced by the interacting atoms in the mixture influences the structural arrangement of molecules which inturn pronounces the effect of adiabatic compressibility. A negative value of adiabatic compressibility indicates strong interaction between the components of the mixture, while the positive values are indicative of weaker interaction\textsuperscript{34}. Gour et al.\textsuperscript{35} pointed out that positive values in excess properties correspond mainly to the existence of dispersion forces.

The positive $\beta^E$ values for hexane + alcohols systems follow the order: n-butyl alcohol $<$ sec-butyl alcohol $<$ tert-butyl alcohol $<$ n-propyl alcohol $<$ iso-propyl alcohol. This order shows that deviation in compressibility decreases with increased in chain length of the alcohol[s]. The excess free length values displayed in Fig.4, are positive for all the mixtures at all temperatures. Positive value of $L_f^E$ indicates weak interaction, and this positive value is attributed to the molecular dissociation of an associated species caused by addition of an inert or an active solvent,

\begin{table}[h]
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\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Mole fraction $x_i$ & $\rho$ Kgm\textsuperscript{-3} & $\eta$ x 10\textsuperscript{8} Nms\textsuperscript{-1} & $u$ mms\textsuperscript{-1} & $V$ x 10\textsuperscript{6} m\textsuperscript{3}mol\textsuperscript{-1} & $\beta$ x 10\textsuperscript{9} Pa\textsuperscript{-1} & $L_f$ x 10\textsuperscript{10} m & $\eta$ x 10\textsuperscript{8} Nms\textsuperscript{-1} & $V$ x 10\textsuperscript{6} m\textsuperscript{3}mol\textsuperscript{-1} & $\beta$ x 10\textsuperscript{9} Pa\textsuperscript{-1} & $L_f$ x 10\textsuperscript{10} m \\
\hline
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 \\
\hline
0.0000 & 649.8 & 0.3139 & 1052.0 & 132.61 & 1.3906 & 0.7458 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\
0.1664 & 663.7 & 0.3556 & 1059.9 & 123.30 & 1.3412 & 0.7325 & -0.1751 & 0.2157 & 0.0354 & 0.0120 \\
0.3032 & 677.1 & 0.3949 & 1070.0 & 115.59 & 1.2900 & 0.7183 & -0.3140 & 0.3427 & 0.0539 & 0.0186 \\
0.4344 & 691.9 & 0.4810 & 1080.2 & 108.17 & 1.2386 & 0.7039 & -0.3988 & 0.4402 & 0.0694 & 0.0242 \\
0.5499 & 707.0 & 0.5512 & 1091.1 & 101.60 & 1.1881 & 0.6894 & -0.4791 & 0.4853 & 0.0777 & 0.0272 \\
0.6409 & 721.1 & 0.6712 & 1105.2 & 96.32 & 1.1353 & 0.6739 & -0.4776 & 0.4201 & 0.0713 & 0.0256 \\
0.7274 & 736.1 & 0.7891 & 1121.3 & 91.30 & 1.0805 & 0.6574 & -0.4724 & 0.3475 & 0.0605 & 0.0223 \\
0.8070 & 751.5 & 0.9415 & 1136.8 & 86.66 & 1.0297 & 0.6418 & -0.4237 & 0.2738 & 0.0502 & 0.0187 \\
0.8770 & 766.6 & 1.1623 & 1152.3 & 82.57 & 0.9824 & 0.6269 & -0.2941 & 0.1951 & 0.0387 & 0.0145 \\
0.9427 & 782.3 & 1.3553 & 1171.9 & 78.73 & 0.9308 & 0.6102 & -0.1867 & 0.1110 & 0.0205 & 0.0078 \\
1.0000 & 797.7 & 1.7166 & 1192.8 & 75.33 & 0.8811 & 0.5937 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\
\hline
0.0000 & 645.1 & 0.2980 & 1030.1 & 133.58 & 1.4609 & 0.7702 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\
0.1664 & 658.9 & 0.3359 & 1038.2 & 124.20 & 1.4081 & 0.4561 & -0.1479 & 0.2231 & 0.0372 & 0.0124 \\
0.3032 & 672.1 & 0.3701 & 1048.2 & 116.45 & 1.3542 & 0.7415 & -0.2665 & 0.3737 & 0.0574 & 0.0196 \\
0.4344 & 686.8 & 0.4451 & 1059.3 & 108.97 & 1.2976 & 0.7258 & -0.3380 & 0.4739 & 0.0719 & 0.0248 \\
0.5499 & 701.9 & 0.5167 & 1071.3 & 102.34 & 1.2414 & 0.7099 & -0.3954 & 0.5064 & 0.0782 & 0.0273 \\
0.6409 & 715.9 & 0.6121 & 1084.9 & 97.02 & 1.1868 & 0.6942 & -0.4016 & 0.4438 & 0.0729 & 0.0260 \\
0.7274 & 730.9 & 0.7175 & 1100.8 & 91.95 & 1.1291 & 0.6771 & -0.3928 & 0.3602 & 0.062 & 0.0227 \\
0.8070 & 746.2 & 0.8612 & 1116.2 & 87.28 & 1.0756 & 0.6609 & -0.3380 & 0.2885 & 0.0516 & 0.0191 \\
0.8770 & 761.1 & 1.0166 & 1131.3 & 83.17 & 1.0266 & 0.6456 & -0.2607 & 0.2227 & 0.0405 & 0.0150 \\
0.9427 & 776.9 & 1.2091 & 1148.5 & 79.27 & 0.9758 & 0.6295 & -0.1416 & 0.1189 & 0.0253 & 0.0093 \\
1.0000 & 792.3 & 1.4147 & 1171.6 & 75.85 & 0.9195 & 0.6110 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\
\hline
0.0000 & 641.0 & 0.2836 & 1010.0 & 134.43 & 1.5293 & 0.7939 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\
0.1664 & 654.6 & 0.3178 & 1018.5 & 125.01 & 1.4727 & 0.7790 & -0.1267 & 0.2610 & 0.0389 & 0.0129 \\
0.3032 & 667.9 & 0.3510 & 1028.9 & 117.18 & 1.4143 & 0.7634 & -0.2257 & 0.3909 & 0.0591 & 0.0201 \\
\hline
\end{tabular}
\caption{Experimental Density ($\rho$), viscosity ($\eta$) and Ultrasonic Velocity ($u$) Data and Computed Parameters ($V$, $\beta$ and $L_f$) and Their excess values for the n-Propyl alcohol (1) – n-Hexane (2) system at Different Temperature}
\end{table}
### Table 2: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V, β and Lₜ) and Their excess values for the iso-Propyl alcohol (1) – n-Hexane (2) system at Different Temperatures.

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<th>Mole fraction x₁</th>
<th>ρ (Kgm⁻³)</th>
<th>η (x10⁸) Nms⁻¹</th>
<th>U (ms⁻¹)</th>
<th>V x 10¹⁰ m³ mol⁻¹</th>
<th>βₚₜ x 10¹⁰ Pa⁻¹</th>
<th>Lₜ x 10¹⁰ m</th>
<th>η' x 10⁸ Nms⁻¹</th>
<th>V' x 10¹⁰ m³ mol⁻¹</th>
<th>βₑₜ' x 10¹⁰ Pa⁻¹</th>
<th>Lₑₜ x 10¹⁰ m</th>
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- **ρ (Kgm⁻³)**: Density
- **η (x10⁸ Nms⁻¹)**: Viscosity
- **U (ms⁻¹)**: Ultrasonic Velocity
- **V x 10¹⁰ m³ mol⁻¹**: Molar Volume
- **βₚₜ x 10¹⁰ Pa⁻¹**: Thermoelastic Coefficient of Volume
- **Lₜ x 10¹⁰ m**: Speed of Sound
- **η' x 10⁸ Nms⁻¹**: Reduced Viscosity
- **V' x 10¹⁰ m³ mol⁻¹**: Reduced Molar Volume
- **βₑₜ' x 10¹⁰ Pa⁻¹**: Reduced Thermoelastic Coefficient of Volume
- **Lₑₜ x 10¹⁰ m**: Reduced Speed of Sound
Table 3: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V, β and L_f) and Their excess values for the n-Butyl alcohol (1) – n-Hexane (2) system at Different Temperatures.

<table>
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<th>Mole fraction (x_1)</th>
<th>(\rho) Kgm(^{-3})</th>
<th>(\eta \times 10^3) Nms(^{-1})</th>
<th>(U) ms(^{-1})</th>
<th>(V \times 10^6) m(^3)mol(^{-1})</th>
<th>(\beta_{ad} \times 10^7) Pa(^{-1})</th>
<th>(L_f \times 10^{10}) m</th>
<th>(\eta' \times 10^3) Nms(^{-1})</th>
<th>(V' \times 10^6) m(^3)mol(^{-1})</th>
<th>(\beta_{ad}' \times 10^8) Pa(^{-1})</th>
<th>(L_{f}' \times 10^{10}) m</th>
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</table>

| 303.15K              | 308.15K             | 303.15K             | 308.15K           | 303.15K                  | 308.15K             | 303.15K             | 308.15K             | 303.15K                  | 308.15K             | 303.15K             | 308.15K             |
Table 4: Experimental Density (ρ), viscosity (η) and Ultrasonic Velocity (u) Data and Computed Parameters (V, β and Lₚ) and Their excess values for the sec-Butyl alcohol (1) – n-Hexane (2) system at Different Temperature.

<table>
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<tr>
<th>Mole fraction x₁</th>
<th>ρ</th>
<th>η x10⁴</th>
<th>U</th>
<th>V x 10⁶ m⁻¹mol⁻¹</th>
<th>βₚ x10⁹ Pa⁻¹</th>
<th>Lₚ x10¹⁰ m</th>
<th>η x10⁴</th>
<th>V x 10⁶ m⁻¹mol⁻¹</th>
<th>βₚ x10⁹ Pa⁻¹</th>
<th>Lₚ x10¹⁰ m</th>
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<td>m⁻¹mol⁻¹</td>
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313.15K

308.15K
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<th>Mole fraction $x_1$</th>
<th>$\rho$ Kgm$^{-3}$</th>
<th>$\eta x 10^4$ Nms$^{-1}$</th>
<th>$U$ m$^{-1}$</th>
<th>$V$ x $10^6$ m$^3$mol$^{-1}$</th>
<th>$\beta u x 10^6$ Pa$^{-1}$</th>
<th>$L_x x 10^{10}$ m</th>
<th>$\eta^2 x 10^6$ Nms$^{-2}$</th>
<th>$V^2 x 10^6$ m$^3$mol$^{-1}$</th>
<th>$\beta_{us} x 10^6$ Pa$^{-1}$</th>
<th>$L_x^2 x 10^{18}$ m</th>
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*Table 5:* Experimental Density ($\rho$), viscosity ($\eta$) and Ultrasonic Velocity ($U$) Data and Computed Parameters ($V$, $\beta$ and $L_x$) and Their excess values for the tert-Butyl alcohol (1) – n-Hexane (2) system at Different Temperatures.
producing considerable deviation\textsuperscript{36}. If a polar liquid is diluted with a non-polar one, the dipole-induced dipole interactions between the polar molecules and non-polar molecules of the diluent should result in an additional increase in free length and also compressibility and a corresponding decrease in velocity. Such a situation is already discussed by Orzechowki and Ernst\textsuperscript{37}. The magnitude of excess free length values of n-propyl alcohol and iso-propyl alcohol are almost same and also for butanol [s] systems at all temperatures. So these value change according to the sequence butanol[s] < propanol[s]. The effect of temperature on the
excess free length is small for all the system. Similar results are observed for this type (polar – nonpolar) of binary liquid mixtures\textsuperscript{38,39}.

Most of the $\beta^E$, $L_f^E$ and $V^E$ are positive and $\eta^E$ are found to be negative in these systems indicating weak interactions between the components of mixtures\textsuperscript{40}. Such weakly interacting components are already investigated by earlier workers\textsuperscript{41-43}. Dispersion forces are responsible for positive deviations. The observed values of these parameters indicate that dissociation of the alcohol aggregates predominates over association between unlike molecules. If a polar liquid is diluted with non-polar one, the dipole – induced dipole interaction takes place between the molecules\textsuperscript{44}. The Vander waal type of interactions are present in hexane, while alcohols are polar and associate strongly through hydrogen bonding. In alcohols + n-hexane mixtures, the alcohol molecules associate in inert hexane medium and form clusters\textsuperscript{45}. There are molecular size holds or voids in such structures.

There is a considerable evidence to show that alcohols exist as closed ring structures as dimmers and trimers as shown in Diagram 1.

\begin{center}
\textbf{Diagram 1.} Structural representation of dimmers and trimers.
\end{center}

Such a structural representation is already suggested in CCl\textsubscript{4} + Alcohol [s] by Subha rao and Gopalakrishnan\textsuperscript{45}. The addition of small quantity of passive diluent is usually to get into the interstices and causing a small degree of breaking of hydrogen bonds between the molecules of the alcohols. However the n-hexane molecules have no such clustering tendency. As the concentration of the alcohol molecule increases, some of the hexane molecules go to fill the voids in the alcohol structure.

4. CONCLUSION

The ultrasonic velocity, adiabatic compressibility, free length and viscosity with the mole fraction of alcohol for all the systems vary regularly without showing any maxima or minima and thereby corroborating the non existence of any complex formation. Same trend is seen at all the temperatures. In these systems, the magnitude of the excess acoustical parameters values are inferred only the weak interaction between alcohol [s] and n-Hexane molecule. This weak interaction may be due to rupture of hydrogen bonds via dissociation or dilution takes between the alcohol molecules.
References


