ULTRASONIC STUDY OF MOLECULAR INTERACTION IN
BINARY MIXTURES OF TETRAHYDROFURAN WITH
1-BUTANOL AND TERT-BUTANOL AT 30°C

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ABSTRACT

Intermolecular interaction between the components of binary mixtures of tetrahydrofuran (THF) with 1-butanol and tert-butanol was investigated using the experimental values of densities and ultrasonic speeds of the above binary mixtures at 30°C, over entire composition range. The derived parameters such as isentropic compressibility, $K_s$, intermolecular free length, $L_i$, relative association, $R$, excess isentropic compressibility, $K_e$, excess volume, $V_e$ and deviation in sound speed, $\Delta u$ were calculated using the experimental values of densities and ultrasonic speeds of the binary mixtures. 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.

Introduction

The studies of molecular interactions in non-aqueous binary solvent systems is of great importance owing to the practical applications of these systems in various industrial and technological processes, as they provide a wide range of solutions with appropriate properties. At present we are involved in a systematic study of the thermodynamic, acoustic and transport properties of non-aqueous binary solvent systems containing alcohols mixed with other protic and aprotic solvents$^{1-5}$. Here, we report the results of our study on the binary mixtures of tetrahydrofuran with 1-butanol and tert-butanol, covering the entire composition range, at 30°C. THF is a very useful compound having applications as reaction solvent and used commercially for the production of many useful compounds. The uses of alcohols are well-known. Moreover, literature survey indicates that no ultrasonic study on these binary systems has been reported. Therefore, the present study was undertaken in order to have a deeper understanding of the intermolecular interaction between the components of the above binary mixture.

In the present study we report densities and ultrasonic speeds of the mixtures of THF with 1-butanol and tert-butanol including pure liquids at 30°C covering the entire
composition range. From these experimental data, the isentropic compressibility, $K_s$, intermolecular free length, $L_f$, relative association, $R_A$, excess isentropic compressibility, $K_s^e$, excess volume, $V^e$, and deviation in sound speed, $\Delta u$, were calculated. The variation of these parameters with composition of the mixture was found to be helpful in understanding the nature and extent of interaction between unlike molecules in the mixture.

**Experimental**

THF (Qualigens fine chemicals, HPLC grade, 99.8%) was used without further purification, except drying over molecular sieves. 1-Butanol and tert-butanol (s.d. fine chemicals, AR grade, 99.5 and 99.0%, respectively) were purified by standard procedure. The mixtures were prepared by weight and were kept in special airtight bottles. The weighings were done on a Mettler-ER-120A electronic balance with a precision of 0.1 mg. The probable error in mole fraction was estimated to be less than ± 0.0001. The densities of pure liquids and binary mixtures were measured using a single-capillary pycnometer (made of Borosil glass) of bulb capacity $8 \times 10^{-3}$ dm$^3$.

The marks on the stem were calibrated with triple distilled water. The accuracy in density measurements was found to be ± 0.0001 g cm$^{-1}$. The ultrasonic speeds were measured using ultrasonic interferometer (Mittal Enterprise, New Delhi, Model-M-82) at 2 MHz with an accuracy of ± 0.05%. The temperature of samples was maintained at 30 ± 0.1°C in an electronically controlled thermostatic water bath.

**Results and Discussion**

From the measured density, $\rho$ and ultrasonic speed, $u$, the isentropic compressibility, $K_s$, intermolecular free length, $L_f$ and relative association, $R_A$ were calculated using the following standard relations:

\[
K_s = \frac{1}{u^2 \rho} \quad (1)
\]

\[
L_f = K_s \rho u \quad (2)
\]

\[
R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{u_0}{u}\right)^{1/3} \quad (3)
\]

where $K$ is temperature dependent constant [$ = (93.875 + 0.375T) \times 10^{-8}$]; $T$ is the absolute temperature; $\rho_0$, $\rho$ and $u_0$, $u$ are the densities and ultrasonic speeds of solvent and solution, respectively.
Table 1: Densities, \( \rho \), ultrasonic speeds, \( u \), isentropic compressibilities, \( K_s \), intermolecular free lengths, \( L_f \) and relative associations, \( R_A \) of binary mixtures of THF with 1-butanol and tert-butanol at 30°C.

<table>
<thead>
<tr>
<th>( x(\text{THF}) )</th>
<th>( \rho ) (kg m(^{-3}))</th>
<th>( u ) (m s(^{-1}))</th>
<th>( K_s ) (10(^{-10}) m(^{2}) N(^{-1}))</th>
<th>( L_f ) (10(^{-11}) m)</th>
<th>( R_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>801.7</td>
<td>1228.0</td>
<td>8.2716</td>
<td>5.9678</td>
<td>1.0000</td>
</tr>
<tr>
<td>0.0996</td>
<td>806.9</td>
<td>1230.3</td>
<td>8.1876</td>
<td>5.9374</td>
<td>1.0059</td>
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<tr>
<td>0.1993</td>
<td>812.9</td>
<td>1232.3</td>
<td>8.1008</td>
<td>5.9059</td>
<td>1.0128</td>
</tr>
<tr>
<td>0.2990</td>
<td>819.5</td>
<td>1234.0</td>
<td>8.0135</td>
<td>5.8739</td>
<td>1.0205</td>
</tr>
<tr>
<td>0.3989</td>
<td>826.1</td>
<td>1236.3</td>
<td>7.9199</td>
<td>5.8395</td>
<td>1.0281</td>
</tr>
<tr>
<td>0.4989</td>
<td>833.2</td>
<td>1238.3</td>
<td>7.8271</td>
<td>5.8052</td>
<td>1.0364</td>
</tr>
<tr>
<td>0.5989</td>
<td>840.8</td>
<td>1240.6</td>
<td>7.7276</td>
<td>5.7682</td>
<td>1.0452</td>
</tr>
<tr>
<td>0.6990</td>
<td>848.5</td>
<td>1244.0</td>
<td>7.6157</td>
<td>5.7263</td>
<td>1.0538</td>
</tr>
<tr>
<td>0.7993</td>
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<td>1248.2</td>
<td>7.4912</td>
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<td>1.0629</td>
</tr>
<tr>
<td>0.8996</td>
<td>866.1</td>
<td>1252.6</td>
<td>7.3588</td>
<td>5.6289</td>
<td>1.0732</td>
</tr>
<tr>
<td>1.0000</td>
<td>876.4</td>
<td>1256.3</td>
<td>7.2295</td>
<td>5.5792</td>
<td>1.0849</td>
</tr>
</tbody>
</table>

The values of \( \rho \), \( u \), \( K_s \), \( L_f \) and \( R_A \) as function of mole fraction \( x \) of THF at 30°C are listed in Table 1. It is observed (Table 1) that the value of \( u \) and \( R_A \) increase, while those of \( K_s \) and \( L_f \) decrease with mole fraction of THF for both the systems under study. The variation of \( u \) through the mixture depends on the increase or decrease of \( L_f \). In general, \( u \) and \( L_f \) have been reported to vary inverse of each other with composition of the mixture\(^1,4,7\), as in the present systems. The non-linear decrease of \( K_s \) and \( L_f \) and also an increase in \( R_A \) (Table 1) with the mole fraction of THF in both the systems indicate the presence of molecular interaction\(^8\) between unlike molecules.
Table 2: Coefficients $A_i$ of equation (6) along with standard deviations $\sigma(Y^E)$ of binary mixtures.

<table>
<thead>
<tr>
<th>Properties</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
<th>$\sigma(Y^E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>THF + 1-Butanol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_s^E$ ($10^{-11}$ m$^2$ N$^{-1}$)</td>
<td>3.0118</td>
<td>-1.5146</td>
<td>0.0165</td>
<td>1.8429</td>
<td>-1.3820</td>
<td>0.009</td>
</tr>
<tr>
<td>$V^E$ ($10^{-6}$ m$^3$ mol$^{-1}$)</td>
<td>1.4890</td>
<td>-0.2621</td>
<td>0.4628</td>
<td>0.2144</td>
<td>0.5306</td>
<td>0.009</td>
</tr>
<tr>
<td>$\Delta u$ (ms$^{-1}$)</td>
<td>-15.524</td>
<td>11.349</td>
<td>4.533</td>
<td>-13.844</td>
<td>12.629</td>
<td>0.142</td>
</tr>
<tr>
<td><strong>THF + tert-Butanol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_s^E$ ($10^{-11}$ m$^2$ N$^{-1}$)</td>
<td>3.5660</td>
<td>-0.6269</td>
<td>-3.3230</td>
<td>-3.3451</td>
<td>4.8431</td>
<td>0.023</td>
</tr>
<tr>
<td>$V^E$ ($10^{-6}$ m$^3$ mol$^{-1}$)</td>
<td>5.5728</td>
<td>1.1369</td>
<td>-2.1546</td>
<td>-1.8618</td>
<td>3.6803</td>
<td>0.006</td>
</tr>
<tr>
<td>$\Delta u$ (ms$^{-1}$)</td>
<td>-32.166</td>
<td>19.183</td>
<td>4.215</td>
<td>11.534</td>
<td>-12.317</td>
<td>0.071</td>
</tr>
</tbody>
</table>

The excess isentropic compressibility, $K_s^E$ and excess volume, $V^E$ have been calculated from the relation

$$Y^E = Y_{\text{mixture}} - \left[ (1 - x) Y_1 + xY_2 \right]$$

(4)

where $x$ is the mole fraction of THF (volume fraction, $\phi$ is used in case of $K_s^E$), $Y$ is $K_s$ or $V$ and subscript 1 and 2 denote 1-butanol/tert-butanol and THF, respectively.

The deviations in the measured speeds of sound from their linear dependence of ultrasonic speeds were calculated from the equation

$$\Delta u = u - \sum x_i u_i^*$$

(5)

where $u_i^*$ are the ultrasonic speeds of pure components. The values of $K_s^E$, $V^E$ and $\Delta u$ for each mixture have been fitted to Redlich-Kister's polynomial equation

$$Y^E = x(1 - x) \sum_{i=0}^{4} A_i (1 - 2x)^i$$

(6)

The values of coefficients $A_i$, evaluated by the method of least-squares are given in Table 2 along with the standard deviations $\sigma(Y^E)$. The variations in $K_s^E$, $V^E$ and $\Delta u$ with mole fraction, $x$ of THF are shown graphically in Figs. 1-3.

Figures 1 and 2 show that $K_s^E$ and $V^E$ are positive for both the systems (THF + 1-butanol/tert-butanol) under study over the whole composition range of THF in these mixtures. In general, $K_s^E$ and $V^E$ can be considered as arising from two types of interactions between component molecules:
Fig. 1: Variation of excess isentropic compressibility, $K_E^s$ with mol fraction of tetrahydrofuran for the binary mixtures at 30°C.

Fig. 2: Variation of excess volume, $V_E^v$ with mol fraction of tetrahydrofuran for the binary mixtures at 30°C.
(i) physical interaction consisting of mainly of dispersion forces or weak dipole-dipole interaction and making a positive contribution, and

(ii) chemical or specific interaction, which include charge-transfer forces, forming of H-bonds and other complex forming interactions, resulting a negative contribution.

It is well known that alkanols are associated through hydrogen bond in pure state. The mixing of THF with alkanols tends to break associates present in alkanol molecules with subsequent increase in $K_s^E$ and $V^E$. On the other hand, there is possibility of H-bonding between oxygen atom of THF (with its lone pair of electrons) and the hydrogen atom of -OH group of alkanols. The observed positive values of $K_s^E$ and $V^E$ over the whole composition range (Figs. 1 and 2) suggest that the effect due to the rupture of hydrogen bonded chains of alkanols dominates over that of hydrogen bond between the unlike molecules, making the $K_s^E$ and $V^E$ values positive. Another main contribution leading to positive $K_s^E$ and $V^E$ values comes from the shapes and sizes of the component molecules in
the mixtures. The molecular size of THF (molar volume = 8.228 x 10^-5 m^3 mol^-1), 1-butanol (molar volume = 9.245 x 10^-5 m^3 mol^-1) and tert-butanol (molar volume = 9.549 x 10^-5 m^3 mol^-1) are not too different, it seems that the component molecules do not pack well into each other's structure. This results in expansion in volume, hence, positive K^E_s and V^E values. Fort and Moore suggested that the liquids of almost equivalent molecular size usually mix with positive excess compressibilities and volumes. Similar trends in K^E_s and V^E were also reported by others for methanol + 1-butanol, toluene + 1-butanol, tert-butanol and bromoform + 1-butanol/tert-butanol/THF binary mixtures.

The deviations in sound speeds, Δu are negative (Fig. 3), over the whole composition range, for both the systems. This is in good agreement with the opposite trends in K^E_s (K_s = 1/μ^2 p) shown in Fig. 1. Thus, we may conclude that the factors responsible for the variation of K^E_s with x are the same as for Δu in these systems, which is good agreement with the results reported by others.

From the plots of K^E_s, V^E and Δu vs x (Fig. 1, 2 and 3) it is clearly evident that the extent of positive deviations in K^E_s and V^E and negative deviations in Δu are larger for THF + tert-butanol mixtures than those in THF + 1-butanol mixtures. It has been reported that increasingly positive values of K^E_s and V^E and a reverse trend of Δu with composition are indicative of decrease in the strength of interaction between the component molecules in the mixture. Therefore, it may be concluded that the strength of interaction decreases on moving from 1-butanol to tert-butanol. It may be pointed out that the presence of three methyl groups at 3° carbon atom in tert-butanol, as compared to butyl group in 1-butanol, creates more crowding, hence, more steric hindrance for the formation of H-bonds between OH group of tert-butanol and THF. As a result, relatively weak H-bonding is expected between tert-butanol and THF molecules, than that between 1-butanol and THF molecules, yielding more positive K^E_s and V^E values in the former system.

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REFERENCES