

## Research Article

# Ultrasonic Investigations of Molecular Interaction in Binary Mixtures of Cyclohexanone with Isomers of Butanol

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Ultrasonic speed,  $u$ , and density,  $\rho$ , have been measured in binary liquid mixtures of cyclohexanone with the isomers of butanol (*n*-butanol, *sec*-butanol, and *tert*-butanol) at 308.15 K over the entire range of composition. Molar volume ( $V_m$ ), adiabatic compressibility ( $k_s$ ), intermolecular free length ( $L_f$ ), acoustic impedance ( $z$ ), and their excess/deviation along with  $\Delta u$  have been calculated from the experimental data. These values have been fitted to Redlich-Kister type polynomial equation. Positive values of  $V_m^E$ ,  $\Delta k_s$ ,  $L_f^E$  and negative values of  $z^E$ ,  $\Delta u$  have been observed for all the liquid mixtures indicating the existence of weak interactions between components. Rupture of H-bond or reduction in H-bond strength of isomers of butanol or breaking of the structure of one or both of the components in a solution causes the existence of dispersions in the present investigated binary mixtures. The data obtained from  $\bar{V}_{m,1}$ ,  $\bar{V}_{m,2}$ , and excess partial molar volumes  $\bar{V}_{m,1}^E$ ,  $\bar{V}_{m,2}^E$ , reflects the inferences drawn from  $V_m^E$ . Furthermore, FTIR spectra support the conclusions drawn from excess/deviation properties. The measured values of ultrasonic speed for all the investigated mixtures have been compared with the theoretically estimated values using empirical relations such as, Nomoto, Van Dael and Vangeels, Impedance and Rao specific sound speed.

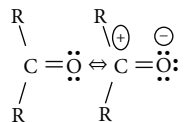
## 1. Introduction

Ultrasonic measurements are very useful in chemical and food processing, pharmaceuticals, material testing, and underwater ranging and cleaning and are also commonly employed in mechanical machinery of materials [1], preparation of colloids or emulsions, the pregermination of seeds, imaging of biological tissues [2], activation energy of metabolic process [3], formation and destruction of azeotropes in petrochemical industries [4], and nondestructive testing (NDT).

Alcohols are self-associated organic liquids, used for the synthesis of other organic compounds. They are also widely used as coupling and dispersing agents in the chemical, pharmaceutical, and household industries and as carrier and extraction solvents for natural products. Cyclohexanone and its derivatives are used for the synthesis of pharmaceuticals,

dyes, herbicides, pesticides, plasticizers, and rubber chemicals. Ketones are a class of an organic compound that contains a carbonyl group and two aliphatic or aromatic substituents containing the chemical formula  $\text{RCOR}^1$  (general chemical formula of Ketones). The chemical reactivity of the carbonyl group plays vital role in chemical reactions and is influenced considerably by steric effects. The greater electronegativity of  $\text{O}^-$  and high dipole moment value make Cyclohexanone polar. Scheme 1 illustrates this polarity. Further the presence of oxygen with its nonbonding electron pairs makes cyclohexanone H-bond acceptors. Thus a study on thermophysical properties data of binary liquid mixtures containing ketones has attracted considerable interest in the literature [5–9].

Literature survey reveals that Tsierkezos et al. [10] studied molecular interactions in cyclohexanone with methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol at 293.15 K and Sri Lakshmi et al. [11] studied molecular interactions in



Resonance structure

SCHEME 1

cyclohexanone with *n*-heptanol, *n*-octanol, and isooctanol at temperatures 303.15, 308.15, 313.15, and 318.15 K over the entire range of composition. Keeping these important aspects in mind, the present study deals with ultrasonic and thermodynamic study of cyclohexanone (CH) with the isomers of butanol (*n*-butanol, *sec*-butanol, and *tert*-butanol) at 308.15 K. The liquids under investigation have been chosen on the basis of their multifold applications.

## 2. Experimental Section

High purity analytical reagent (AR) grade compounds of cyclohexanone (mass fraction purity > 99%) and *n*-butanol, *sec*-butanol, and *tert*-butanol (mass fraction purity > 99.5%) obtained from S D Fine Chemicals are used in the present study. The chemicals are further purified by standard methods mentioned in [12, 13]. The weighing of solutions has been made using METTLER TOLEDO (Switzerland make) ABB5-S/FACT digital balance with an accuracy of  $\pm 0.01$  mg. The uncertainty in the mole fraction is  $10^{-4}$ . The ultrasonic speeds of pure liquids and liquid mixtures have been measured using an ultrasonic interferometer (Mittal type, Model F-82) working at 2 MHz fixed frequency with an accuracy of  $\pm 0.2\%$ . The temperature of liquid sample in the interferometer cell is maintained constant by circulating water pumped from constant temperature water bath. In the present study the constant temperature water bath (digital electronic) supplied by Concord Instruments Co. Ltd., Chennai (RAAGA type), has been used. The instrument can maintain temperature to  $\pm 0.01$  K as per its specifications.

Densities of pure liquids and their mixtures have been determined by using a  $5 \text{ cm}^3$  two-stem double-walled Parker & Parker type pycnometer [15]. This pycnometer is calibrated with triply distilled water. The pycnometer filled with air bubble free experimental liquids was kept in a transparent walled constant temperature bath for 20 to 30 min to attain thermal equilibrium. The positions of the liquid levels in the two arms are recorded with the help of traveling microscope. At least three to four measurements are performed, from which an average value of density of the experimental liquid is determined. The estimated accuracy in the density measurement is 3 in  $10^5$  parts. The ultrasonic speeds,  $u$ , and densities,  $\rho$ , measured at 308.15 K for the pure liquids used in this investigation are compiled in Table 1 together with the literature data [11, 14] available. These results are in good agreement with the reported data.

## 3. Theory

Thermodynamic and acoustical parameters such as molar volume ( $V_m$ ), adiabatic compressibility ( $k_s$ ), intermolecular

TABLE 1: Comparison of experimental values of density,  $\rho$ , and ultrasonic speed,  $u$ , of pure liquids with the corresponding literature values at 308.15 K.

Liquid	$\rho/(\text{kg m}^{-3})$		$u/(\text{m s}^{-1})$	
	Present work	Literature	Present work	Literature
Cyclohexanone	939.60	939.6 [11]	1362.00	1362.0 [11]
<i>n</i> -Butanol	796.50	796.5 [14]	1209.30	1209.3 [14]
<i>sec</i> -Butanol	793.20	793.2 [14]	1174.80	1174.8 [14]
<i>tert</i> -Butanol	768.40	768.3 [14]	1086.00	1086.0 [14]

free length ( $L_f$ ), and acoustic impedance ( $z$ ) are evaluated using the relations given below:

$$V_m = \frac{M_{\text{eff}}}{\rho}, \quad (1)$$

where  $M_{\text{eff}}$  is given by  $M_{\text{eff}} = (x_1 M_1 + x_2 M_2)$ , where  $M_1$  and  $M_2$  are the molar masses of pure components, and  $\rho$  is the density of the liquid mixture.

The speed of sound ( $u$ ) and the density of the medium ( $\rho$ ) are related by using Newton and Laplace equation as

$$k_s = \frac{1}{\rho u^2}, \quad (2)$$

$$L_f = K k_s^{1/2}.$$

Here  $K$  is the temperature dependent constant which is equal to  $K = (93.875 + 0.375T) \times 10^{-8}$  where  $T$  is absolute temperature. Consider

$$z = u\rho. \quad (3)$$

In order to understand the nature of the molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Nonideal liquid mixtures show considerable deviation from linearity in their concentrations and this has been interpreted to arise from the presence of strong or weak interactions. The difference between the properties of the real mixtures ( $Y_{\text{real}}$ ) and those corresponding to ideal mixture ( $Y_{\text{ideal}} = \sum x_i Y_i$ ) values, namely, excess properties ( $Y^E$ ), such as excess molar volume ( $V_m^E$ ), free length ( $L_f^E$ ), acoustic impedance ( $z^E$ ), and deviations in ultrasonic speed ( $\Delta u$ ), is computed by the relation

$$Y^E = Y_{\text{real}} - \sum x_i Y_i, \quad (4)$$

where  $Y^E = V_m^E, L_f^E, z^E$  and  $\Delta u$ ;  $x_i$  is the mole fraction and  $Y_i$  is the value of the property of the  $i$ th component liquid of mixture.

The deviation in adiabatic compressibility ( $\Delta k_s$ ) has been calculated from the equation

$$\Delta k_s = k_s - (\Phi_1 k_{s1} + \Phi_2 k_{s2}), \quad (5)$$

where  $\Phi_1$ ,  $\Phi_2$ , and  $k_{s1}$ ,  $k_{s2}$  are the volume fractions and adiabatic compressibilities of components 1 and 2, respectively. Since  $k_s$  is not additive on mole fraction but is additive on volume fraction, such values are calculated using volume fraction ( $\Phi$ ):

$$\Phi_i = \frac{x_i V_i}{\sum x_i V_i} \quad (6)$$

The experimentally measured values of ultrasonic speed ( $u$ ) and density ( $\rho$ ) and calculated properties of molar volume ( $V_m$ ), adiabatic compressibility ( $k_s$ ), intermolecular free length ( $L_f$ ), and acoustic impedance ( $z$ ) and excess/deviation thermodynamic properties  $V_m^E$ ,  $L_f^E$ ,  $z^E$ ,  $\Delta u$ , and  $\Delta k_s$  are presented in Table 2 for all binary systems over the entire composition range of CH.

The excess/deviation properties have been fitted to a Redlich-Kister type polynomial equation [16]

$$Y^E = x_1 x_2 \sum_{i=0}^n A_i (x_2 - x_1)^i, \quad (7)$$

where  $Y^E = V_m^E, L_f^E, z^E, \Delta u$  and  $\Delta k_s$ ;  $x_1$  is the mole fraction of the solute.

The values of  $\Delta k_s$  have been fitted to Redlich-Kister type polynomial with volume fraction instead of mole fraction in the above polynomial and  $A_i$  are the adjustable parameters of the function and are determined using the least square method. In the present investigation “ $i$ ” values are taken from 0 to 4. The corresponding standard deviation  $\sigma(Y^E)$  was calculated using the expression

$$\sigma(Y^E) = \left[ \frac{\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{(m - n)} \right]^{1/2}, \quad (8)$$

where “ $m$ ” is the total number of experimental points and “ $n$ ” is the number of coefficients in (7). The calculated values of the coefficients  $A_i$  along with the standard deviations ( $\sigma$ ) have been presented in Table 3.

#### 4. Results and Discussion

Figure 1 represents the variation of excess molar volume ( $V_m^E$ ) with mole fraction of CH. The sign of  $V_m^E$  depends upon the contraction and expansion of volume of the liquids due to mixing. The factors that are mainly responsible for the expansion of molar volume, that is, positive values of  $V_m^E$ , are the following: (i) breaking of the structure of one or both of the components in a solution, that is, the loss of dipolar association between the molecules (dispersion forces); (ii) H-bond rupture and stretching of self-associated molecules (like alcohols); (iii) the geometry of molecular structures which does not favour the fitting of molecules of one component into void space of another molecule; (iv) steric hindrance of the molecules. The negative values of  $V_m^E$  are due to the (i) association of molecules through the formation of hydrogen bond, that is, strong specific interactions, and (ii) accommodation of molecules because of large differences in their

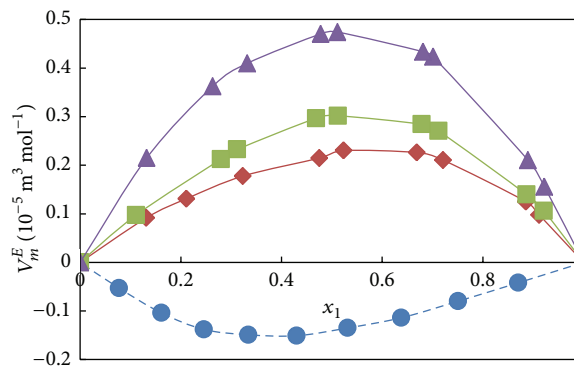


FIGURE 1: Variation of excess molar volume,  $V_m^E$ , with mole fraction,  $x_1$ , of cyclohexanone in (◆), *n*-butanol/(■), *sec*-butanol/(▲), and *tert*-butanol at 308.15 K and Tsierkezos et al. [10] for cyclohexanone + 1-butanol (dotted lines) at 293.15 K.

molar volumes. In other words,  $V_m^E$  arises due to the result of physical, chemical, and structural contributions. Physical interactions involving mainly nonspecific interactions such as dispersion or weak forces (breaking of the liquid order on mixing, i.e., loss of dipolar association between the molecules) contribute to positive  $V_m^E$ . The chemical or specific interactions such as complex formation and hydrogen bond formation between constituent molecules contribute to negative  $V_m^E$ . The structural effects arise from interstitial accommodation due to the difference in the molar volumes and free volumes between the liquid components on mixing contributing to negative  $V_m^E$  [17]. The variation of  $V_m^E$  is found to be positive over the entire composition range in the present investigation which indicates that weak forces exist. Sri Lakshmi et al. [11] reported similar results in CH with *n*-heptanol, *n*-octanol, and *iso*-octanol at temperatures of 303.15, 308.15, 313.15, and 318.15 K. The  $V_m^E$  data obtained by Tsierkezos et al. [10] for CH + 1-butanol binary system are negative at 293.15 K whereas in our investigations they are found to be positive when performed at 308.15 K. Such behaviour may arise due to the fact that as temperature increases the effective collision between the component molecules increases. Thus larger number of free dipoles of component molecules may be available due to declustering of molecules in the pure state.

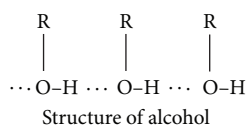
The nature of interaction in binary liquids can be analysed by knowing their chemical and physical properties (physicochemical properties). Generally, butanols are associated through the hydrogen bonding as shown below and in the pure state, they exhibit equilibrium between the monomer and multimer species. Also, they can be associated with any other groups having some degree of polar attractions. As discussed earlier, butanol exhibits strong intermolecular interactions (H-bond). Alcohol size, chain length, and physical properties (boiling point, density, hydrophobic property, viscosity, insolubility, and refractive index) are important parameters that must be taken into account to explain the behaviour of the interactions (Scheme 2).

CH is a polar molecule because of the presence of carbonyl group (C=O); this is due to the fact that oxygen is more electronegative ( $O^-$ ) than carbon ( $C^+$ ). Thus they

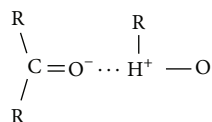


TABLE 3: Coefficients  $A_i$  of Redlich-Kister type polynomial equation (7) and the corresponding standard deviations,  $\sigma$ , of all the systems at 308.15 K.

	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
CH + <i>n</i> -butanol						
$V_m^E/(10^{-5} \text{ m}^3 \text{ mol}^{-1})$	24.7625	-5.7880	3.6945	-3.1381	-0.8351	0.0019
$\Delta k_s/(10^{-10} \text{ Pa}^{-1})$	0.0183	-0.0020	0.0075	0.0029	-0.0004	0.0091
$L_f^E/(10^{-10} \text{ m})$	0.8201	-0.1460	0.2529	0.0638	0.1066	0.0009
$z^E/(10^6 \text{ kg m}^{-2} \text{ s}^{-1})$	-0.2875	0.0836	-0.1081	0.0006	-0.0202	0.0002
$\Delta u/(\text{ms}^{-1})$	-1.40	0.58	-0.31	-0.03	-0.18	0.0024
CH + <i>sec</i> -butanol						
$V_m^E/(10^{-5} \text{ m}^3 \text{ mol}^{-1})$	27.5896	-9.594	4.2809	-2.2460	-0.7780	0.0018
$\Delta k_s/(10^{-10} \text{ Pa}^{-1})$	0.0267	-0.001	0.0001	0.0033	0.0034	0.0001
$L_f^E/(10^{-10} \text{ m})$	1.1507	-0.1810	0.0576	0.1082	0.0684	0.0011
$z^E/(10^6 \text{ kg m}^{-2} \text{ s}^{-1})$	-0.3733	0.1252	-0.0791	0.0092	-0.0110	0.0001
$\Delta u/(\text{ms}^{-1})$	-1.94	0.59	-0.04	-0.01	-0.04	0.0006
CH + <i>tert</i> -butanol						
$V_m^E/(10^{-5} \text{ m}^3 \text{ mol}^{-1})$	36.4535	-12.3900	-0.6780	0.1003	-0.2750	0.0009
$\Delta k_s/(10^{-10} \text{ Pa}^{-1})$	0.0428	0.0120	0.0024	0.0019	0.0011	0.0001
$L_f^E/(10^{-10} \text{ m})$	1.8117	0.1253	0.1393	0.0862	-0.0290	0.0006
$z^E/(10^6 \text{ kg m}^{-2} \text{ s}^{-1})$	-0.5484	0.1374	-0.0850	0.0123	-0.0032	0.0001
$\Delta u/(\text{ms}^{-1})$	-2.96	0.62	-0.54	0.01	-0.01	0.0001



SCHEME 2

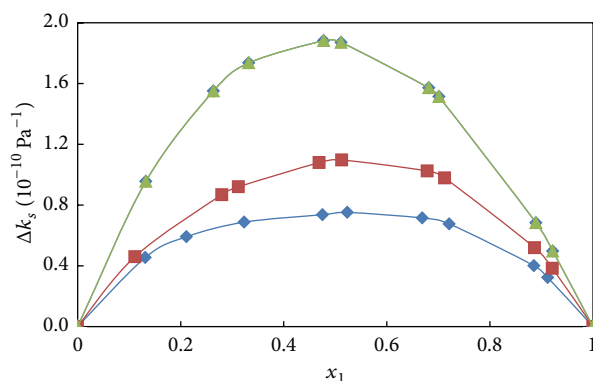


Resonance structure

SCHEME 3

cause strong dipole-dipole interactions in chemical reactions. Moreover CH lacks hydroxyl groups, so it is incapable of creating intermolecular hydrogen bonds. In CH + isomers of butanol binary systems, the negatively charged oxygen ( $\text{O}^-$ ) in CH tries to drag the positively charged  $\text{H}^+$  which were bounded in very strong intermolecular interactions of butanol (Scheme 3). An equilibrium stage is reached where rupturing of hydrogen bond or reduction in H-bond strength of butanol or breaking of the structure of one or both of the components in a solution, that is, the loss of dipolar association between the molecules (dispersion forces) [18], will be favourable leading to weak interactions. This causes increase in volume of binary liquid and explains the observed positive values  $V_m^E$  in the systems.

Kiyohara and Benson [19] have suggested that  $\Delta k_s$  is the resultant of several opposing effects. Negative values of  $\Delta k_s$  contribute to charge transfer, dipole-induced dipole and

FIGURE 2: Variation of deviation in adiabatic compressibility,  $\Delta k_s$ , with mole fraction,  $x_1$ , of cyclohexanone in ( $\blacklozenge$ ), *n*-butanol/( $\blacksquare$ ), *sec*-butanol/( $\blacktriangle$ ), and *tert*-butanol at 308.15 K.

dipole-dipole interactions, interstitial accommodation, and breaking up of the alcohol structures leads to positive values of  $\Delta k_s$ . From Figure 2, the observed positive values of  $\Delta k_s$  for binary mixtures of CH with *n*-butanol, *sec*-butanol, and *tert*-butanol are due to declustering of alcohols in the presence of CH. The positive deviation in  $\Delta k_s$  for the binary systems follows the order CH +, *tert*-butanol > *sec*-butanol > *n*-butanol. Figure 3 represents the variation of  $L_f^E$  with mole fraction ( $x_1$ ) of CH. The observed values of  $L_f^E$  are positive. According to Fort and Moore [20], positive  $L_f^E$  should be attributed to the dispersive forces. As mentioned earlier, positive values of  $\Delta k_s$  and  $L_f^E$  are mainly attributed to weak forces between the component molecules in the mixture [21].



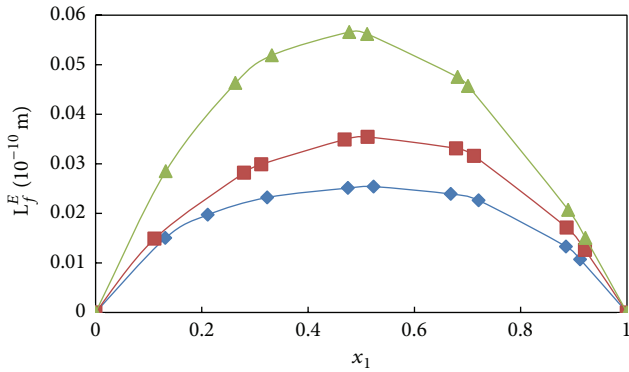


FIGURE 3: Variation of excess free length,  $L_f^E$ , with mole fraction,  $x_1$ , of cyclohexanone in (◆), *n*-butanol/(■), *sec*-butanol/(▲), and *tert*-butanol at 308.15 K.

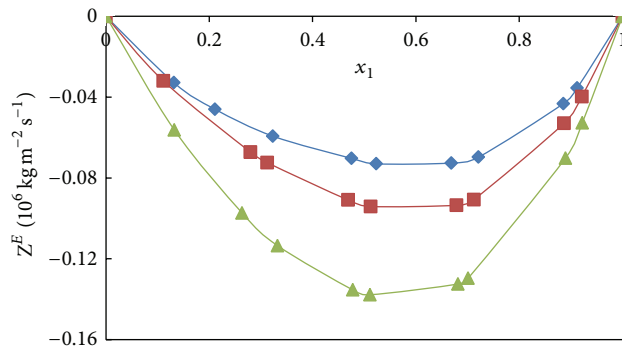


FIGURE 4: Variation of excess acoustic impedance,  $z^E$ , with mole fraction,  $x_1$ , of cyclohexanone in (◆), *n*-butanol/(■), *sec*-butanol/(▲), and *tert*-butanol at 308.15 K.

The variations of excess acoustic impedance ( $z^E$ ) and deviation in ultrasonic speed ( $\Delta u$ ) have been presented in Figures 4 and 5, respectively. From Figure 4, it has been observed that the values of  $z^E$  are negative over the entire mole fraction range indicating the decreasing strength of interactions between component molecules of the mixture. According to Gowrisankar et al. [22], the negative values for  $\Delta u$  indicate the decrease in the strength of interaction between the molecules and the negative deviations in  $\Delta u$  from linear dependence suggest the presence of weak interaction between the component molecules. These deviation/excess properties further support the conclusions drawn from  $V_m^E$ ,  $L_f^E$ , and  $\Delta k_s$ .

The existing molecular interactions in the systems are well reflected in the properties of partial molar volumes. The partial molar volumes  $\bar{V}_{m,1}$  of component 1 (CH) and  $\bar{V}_{m,2}$  of component 2 (isomers of butanol) in the mixtures over the entire composition range have been calculated by using the following relations:

$$\bar{V}_{m,1} = V_m^E + V_1^* + x_2 \left( \frac{\partial V_m^E}{\partial x} \right)_{T,P},$$

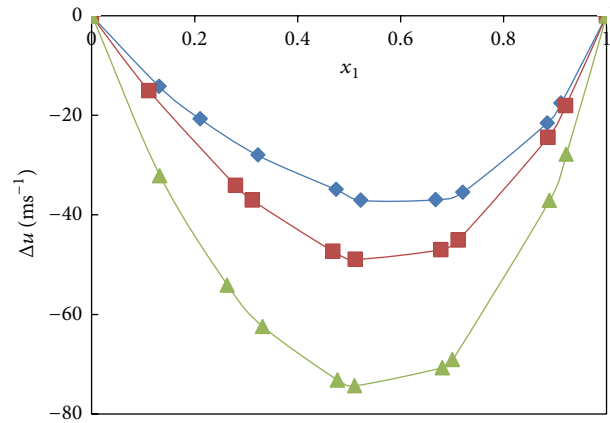


FIGURE 5: Variation of deviation in ultrasonic speed,  $\Delta u$ , with mole fraction,  $x_1$ , of cyclohexanone in (◆), *n*-butanol/(■), *sec*-butanol/(▲), and *tert*-butanol at 308.15 K.

$$\bar{V}_{m,2} = V_m^E + V_2^* + x_1 \left( \frac{\partial V_m^E}{\partial x} \right)_{T,P}, \quad (9)$$

where  $V_1^*$  and  $V_2^*$  are the molar volumes of the pure components of CH and butanols, respectively. The derivatives in the above equations are obtained by differentiating Redlich-Kister equation (7) which leads to the following equations for  $\bar{V}_{m,1}$  and  $\bar{V}_{m,2}$ :

$$\bar{V}_{m,1} = V_1^* + x_2^2 \sum_{i=0}^j A_i (x_2 - x_1)^i - 2x_1 x_2^2 \sum_{i=1}^j A_i (x_2 - x_1)^{i-1}, \quad (10)$$

$$\bar{V}_{m,2} = V_2^* + x_1^2 \sum_{i=0}^j A_i (x_2 - x_1)^i + 2x_2 x_1^2 \sum_{i=1}^j A_i (x_2 - x_1)^{i-1}; \quad (11)$$

using the above equations  $\bar{V}_{m,1}^E$ ,  $\bar{V}_{m,2}^E$  have been calculated using

$$\begin{aligned} \bar{V}_{m,1}^E &= \bar{V}_{m,1} - V_1^*, \\ \bar{V}_{m,2}^E &= \bar{V}_{m,2} - V_2^*. \end{aligned} \quad (12)$$

The pertinent values of  $\bar{V}_{m,1}$  and  $\bar{V}_{m,2}$  are furnished in Table 4. From this table, the values of  $\bar{V}_{m,1}$  and  $\bar{V}_{m,2}$  for both the components in the mixtures are greater than their respective molar volumes in the pure state; that is, an expansion of volume takes place on mixing alcohols with ketone. These results also support the observed positive values of  $V_m^E$  in all the binary systems. Figures 6 and 7 represent the variation of excess partial molar volumes of  $\bar{V}_{m,1}^E$  (CH),  $\bar{V}_{m,2}^E$  (isomers of butanol) in the binary mixtures. Examination of these figures reveals that dispersion forces exist between the unlike molecules. These figures support the conclusions drawn from  $V_m^E$ . The partial molar volumes and excess partial

TABLE 4: Partial molar volumes of CH ( $\bar{V}_{m,1}/10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ) and butanols ( $\bar{V}_{m,2}/10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ) of all the binary systems with mole fraction ( $x_1$ ) of CH at 308.15 K.

CH + <i>n</i> -butanol			CH + <i>sec</i> -butanol			CH + <i>tert</i> -butanol		
$x_1$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$x_1$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$x_1$	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$
1.0000	7.210	42.676	1.0000	7.210	49.234	1.0000	7.210	54.612
0.9121	7.699	32.512	0.9212	7.681	38.378	0.9221	7.606	44.590
0.8854	7.999	30.035	0.8867	8.130	34.445	0.8895	7.997	40.788
0.7211	10.600	19.303	0.7121	11.586	20.460	0.7012	12.366	23.413
0.6687	11.554	17.041	0.6786	12.354	18.636	0.6814	12.989	22.023
0.5232	14.365	12.385	0.5123	16.219	12.221	0.5112	19.004	13.087
0.4752	15.378	11.198	0.4688	17.234	11.058	0.4777	20.247	11.893
0.3231	19.092	8.232	0.3121	20.995	8.043	0.3321	25.389	8.416
0.2112	22.264	6.843	0.2797	21.794	7.619	0.2635	27.459	7.562
0.1313	24.403	6.314	0.1112	25.586	6.406	0.1323	30.211	6.874
0.0000	25.905	6.128	0.0000	26.462	6.307	0.0000	30.421	6.823

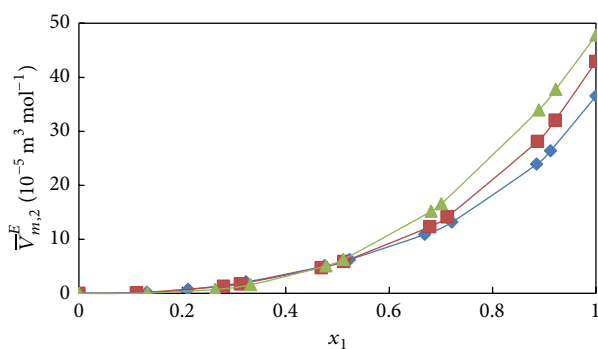


FIGURE 6: Variation of excess partial molar volume,  $\bar{V}_{m,2}^E$ , with mole fraction,  $x_1$ , of cyclohexanone in ( $\blacklozenge$ ), *n*-butanol/( $\blacksquare$ ), *sec*-butanol/( $\blacktriangle$ ), and *tert*-butanol at 308.15 K.

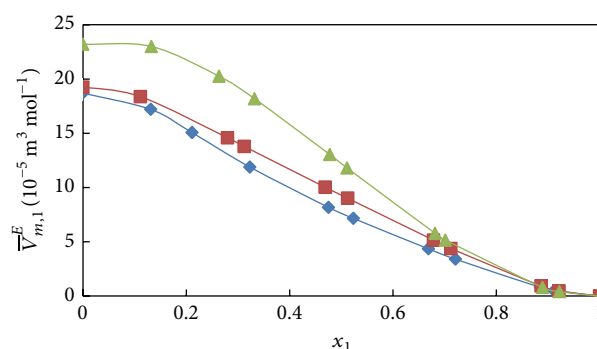


FIGURE 7: Variation of excess partial molar volume,  $\bar{V}_{m,1}^E$ , with mole fraction,  $x_1$ , of cyclohexanone in ( $\blacklozenge$ ), *n*-butanol/( $\blacksquare$ ), *sec*-butanol/( $\blacktriangle$ ), and *tert*-butanol at 308.15 K.

molar volumes of CH and isomers of butanols in all the binary liquid mixtures at infinite dilution,  $\bar{V}_{m,1}^\infty$ ,  $\bar{V}_{m,2}^\infty$ ,  $\bar{V}_{m,1}^{E,\infty}$ , and  $\bar{V}_{m,2}^{E,\infty}$ , respectively, were obtained by putting  $x = 0$  in (10) and  $x = 1$  in (11). Consider

$$\begin{aligned} \bar{V}_{m,1}^{E,\infty} &= A_0 + A_1 + A_2 + A_3 + \dots = \bar{V}_{m,1}^\infty - V_1^*, \\ \bar{V}_{m,2}^{E,\infty} &= A_0 - A_1 + A_2 - A_3 + \dots = \bar{V}_{m,2}^\infty - V_2^*. \end{aligned} \quad (13)$$

The pertinent values of  $\bar{V}_{m,1}^\infty$ ,  $\bar{V}_{m,2}^\infty$ ,  $\bar{V}_{m,1}^{E,\infty}$ , and  $\bar{V}_{m,2}^{E,\infty}$  are reported in Table 5. From this table it is seen that these values are positive, from which we conclude that weak interactions exist among the unlike molecules of the liquid mixtures.

FT-IR spectra of pure CH, butanols, and binary mixtures of CH with butanols at equal concentrations are depicted in Figures 8, 9, and 10. According to Karunakar and Srinivas [23], the intensity of an absorption in the IR spectrum is related to the change in dipole moment that occurs during the vibration. Consequently, vibrations that produce a large change in dipole moment (e.g., C=O stretch) result in a more intense absorption than those that result in a relatively modest change in dipole (e.g., C=C). Vibrations that do not result in a change in dipole moment (e.g., a symmetrical

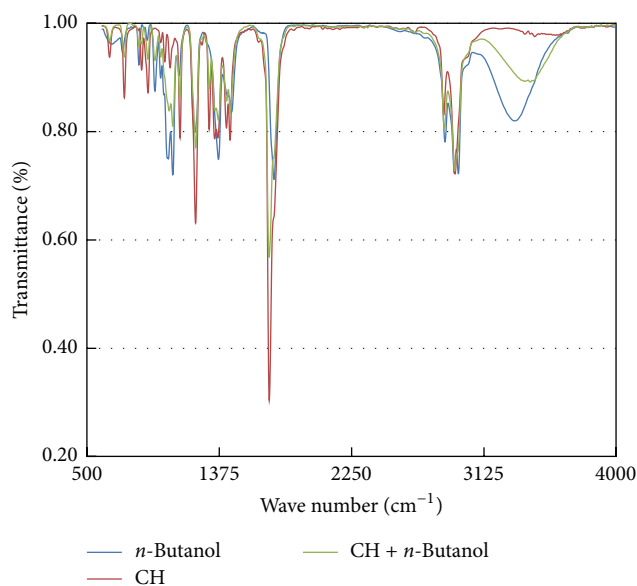


FIGURE 8: Fourier transform infrared spectra of pure cyclohexanone (red), cyclohexanone and *n*-butanol in the ratio 5:5 (green), and pure *n*-butanol (blue).

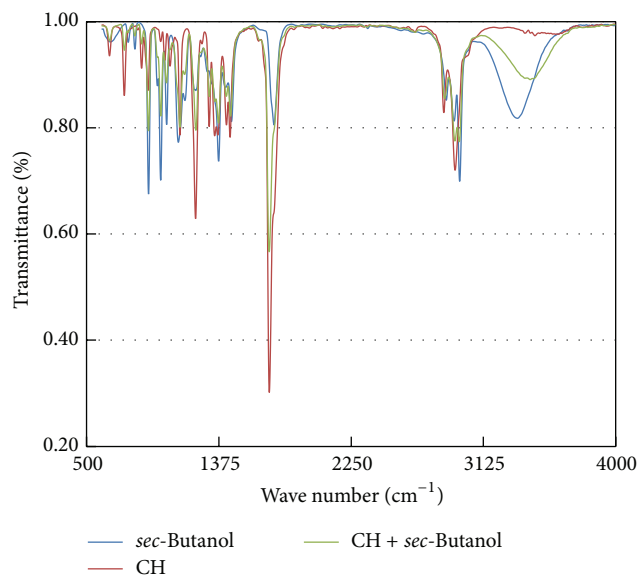


FIGURE 9: Fourier transform infrared spectra of pure cyclohexanone (red), cyclohexanone and *sec*-butanol in the ratio 5:5 (green), and pure *sec*-butanol (blue).

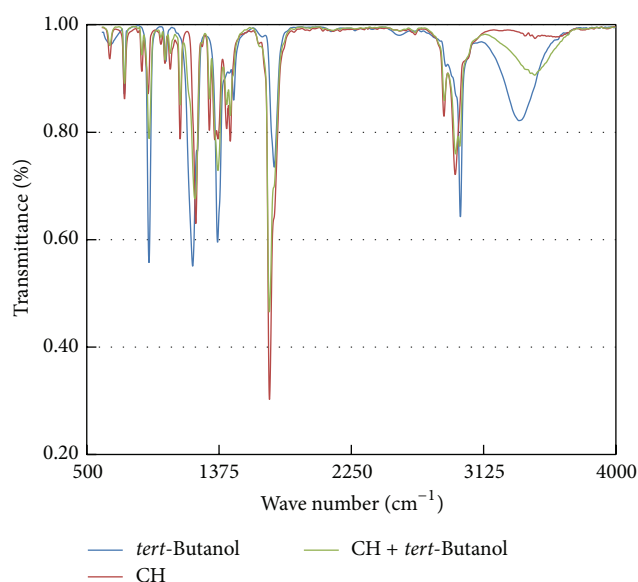


FIGURE 10: Fourier transform infrared spectra of pure cyclohexanone (red), cyclohexanone and *tert*-butanol in the ratio 5:5 (green), and pure *tert*-butanol (blue).

alkyne  $C\equiv C$  stretch) will show little or no absorption for this vibration. In the present FT-IR spectra liquid mixture shows very small variations in the intensity of the respective bonds, that is, dipole moment, and hence it supports that weak interactions take place between the components of liquid molecules.

Theoretical evaluation of ultrasonic speed in binary liquid mixtures and its correlation to study molecular interaction has been successfully done in recent years. Ultrasonic speeds in liquid mixtures have been calculated and compared with

TABLE 5: Partial molar volumes ( $\bar{V}_{m,1}^{\infty}, \bar{V}_{m,2}^{\infty}$ ) and excess partial molar volumes ( $\bar{V}_{m,1}^{E,\infty}, \bar{V}_{m,2}^{E,\infty}$ ) of the components at infinite dilution for all the systems at 308.15 K.

System	$\bar{V}_{m,1}^{\infty}$	$\bar{V}_{m,2}^{\infty}$	$\bar{V}_{m,1}^{E,\infty}$	$\bar{V}_{m,2}^{E,\infty}$
	/( $10^{-5} \text{ m}^3 \text{ mol}^{-1}$ )			
CH + <i>n</i> -butanol	25.519	43.758	18.696	36.548
CH + <i>sec</i> -butanol	25.561	50.9205	19.253	42.933
CH + <i>tert</i> -butanol	30.034	55.000	23.211	47.790

experimental values using various theories. Such an evaluation offers a simple method to investigate molecular interactions besides verifying the applicability of various theories to liquid mixtures.

Nomoto [24] established the following relation for sound speed ( $U_N$ ) based on the assumption of the linearity of the molecular sound speed and the additivity of molar volume:

$$U_N = \left\{ \frac{(\sum x_i R_i)}{(\sum x_i V_i)} \right\}^3, \quad (14)$$

where  $R_i$  is molar sound speed and  $V_i$  is molar volume.

van Dael and Vangeel [25] obtained the ideal mixture relation

$$\sum \left( \frac{x_i M_i}{u_i^2} \right) = \left\{ \frac{1}{\sum x_i M_i} \right\} \left\{ \frac{1}{U_V} \right\}^2. \quad (15)$$

Baluja and Parsania [26] have given impedance relation on the basis of force of resistance for sound speed by the interacting molecules

$$U_{\text{imp}} = \frac{\sum x_i Z_i}{\sum x_i \rho_i}. \quad (16)$$

Rao's (specific sound speed) [27] relation is given by

$$U_R = \left( \sum x_i r_i \rho \right)^3, \quad (17)$$

where  $r_i = u_i^{1/3} / \rho_i$  is Rao's specific sound speed of  $i$ th component of the mixture.

Percentage deviation in ultrasonic speed is given by

$$\% \Delta u = 100 * \left[ 1 - \frac{U_{\text{cal}}}{u_{\text{exp}t}} \right]. \quad (18)$$

Table 6 shows the values of ultrasonic speed computed by various theories along with their percentage error for all the systems. The variations between the evaluated and experimental values may be due to interactions occurring between the hetero molecules of the binaries. From the observed values of all three systems, there is a good agreement between theoretical and experimental values through van Deal and Vangeel relation. It can be seen from Table 6 that the theoretical values of ultrasonic speed calculated by using various theories show deviation from experimental values. The limitations and approximation incorporated in these theories



TABLE 6: Theoretical values of ultrasonic speed from various equations and percentage error with mole fraction  $x_1$  of CH for all binary systems at 308.15 K.

$x_1$	$U_N$	$U_V$	$U_{Imp}$	$U_R$	% $U_N$	% $U_V$	% $U_{Imp}$	% $U_R$
CH + <i>n</i> -butanol								
1.0000	1362.00	1362.00	1362.00	1362.00	0.00	0.00	0.00	0.00
0.9121	1350.01	1345.47	1350.43	1298.06	1.43	1.09	1.46	2.48
0.8854	1346.32	1340.60	1346.87	1283.17	1.77	1.33	1.81	3.01
0.7211	1323.09	1311.99	1324.27	1221.96	3.05	2.18	3.14	4.83
0.6687	1315.49	1303.34	1316.81	1209.73	3.22	2.27	3.32	5.08
0.5232	1293.86	1280.42	1295.42	1185.02	3.33	2.26	3.46	5.36
0.4752	1286.56	1273.19	1288.14	1178.71	3.17	2.10	3.30	5.48
0.3231	1262.83	1251.29	1264.29	1163.93	2.61	1.68	2.73	5.42
0.2112	1244.78	1236.09	1245.94	1161.66	1.96	1.25	2.05	4.85
0.1313	1231.58	1225.67	1232.39	1168.83	1.35	0.86	1.42	3.82
0.0000	1209.30	1209.30	1209.30	1209.30	0.00	0.00	0.00	0.00
CH + <i>sec</i> -butanol								
1.0000	1362.00	1362.00	1362.00	1362.00	0.00	0.00	0.00	0.00
0.9212	1348.36	1344.12	1349.36	1284.64	1.44	1.12	1.52	3.35
0.8867	1342.34	1336.50	1343.75	1258.30	1.98	1.53	2.08	4.41
0.7121	1311.30	1299.73	1314.35	1172.55	3.82	2.91	4.06	7.16
0.6786	1305.24	1293.00	1308.52	1162.63	4.02	3.04	4.28	7.35
0.5123	1274.65	1260.97	1278.60	1131.58	4.33	3.21	4.65	7.38
0.4688	1266.50	1252.96	1270.49	1127.05	4.22	3.10	4.55	7.26
0.3121	1236.66	1225.24	1240.27	1120.04	3.38	2.43	3.69	6.37
0.2797	1230.39	1219.72	1233.81	1120.51	3.13	2.23	3.41	6.08
0.1112	1197.22	1192.10	1199.01	1138.85	1.41	0.98	1.56	3.53
0.0000	1174.80	1174.80	1174.80	1174.80	0.00	0.00	0.00	0.00
CH + <i>tert</i> -butanol								
1.0000	1362.00	1362.00	1362.00	1362.00	0.00	0.00	0.00	0.00
0.9221	1340.13	1335.38	1344.13	1269.23	2.09	1.73	2.40	3.31
0.8895	1330.99	1324.56	1336.51	1236.00	2.83	2.33	3.25	4.51
0.7012	1278.40	1265.44	1290.65	1095.88	5.61	4.54	6.63	9.46
0.6814	1272.89	1259.53	1285.64	1085.50	5.78	4.67	6.84	9.80
0.5112	1225.70	1211.04	1240.87	1023.59	6.33	5.06	7.64	11.21
0.4777	1216.45	1201.95	1231.70	1016.61	6.27	5.01	7.61	11.19
0.3321	1176.38	1164.00	1190.36	1004.06	5.48	4.37	6.74	9.97
0.2635	1157.60	1146.96	1170.00	1007.94	4.80	3.84	5.92	8.75
0.1323	1121.83	1115.75	1129.39	1033.39	2.89	2.33	3.58	5.23
0.0000	1086.00	1086.00	1086.00	1086.00	0.00	0.00	0.00	0.00

are responsible for the deviations of theoretical values from experimental values. Nomoto's theory proposes that the volume does not change upon mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. Similarly, the assumption for the formation of ideal mixing relation is that the ratios of specific heats of ideal mixtures and the volumes are also equal. Again no molecular interactions are taken into account. But upon mixing, interactions between the molecules occur because of the presence of various types of forces such as dispersion forces, charge transfer, and hydrogen bonding dipole-dipole and dipole-induced dipole interactions. Thus, the observed deviation of theoretical values of speed from the experimental values

shows that the molecular interactions are taking place between the CH and isomers of butanol molecules. The deviations of experimental values and values calculated from impedance relation and Rao's relation imply nonadditivity of acoustic impedance and Rao's speed in the liquid mixtures. Among all the empirical theories van Dael and Vangeels relation gives better estimate of experimental values of sound speed in all the systems. In the present binary systems, the difference between experimental and theoretical speeds is greater where the mole fraction of CH varies in the region 0.3 to 0.6. Hence it can be qualitatively inferred that the strength of interaction in the binary mixtures is more in this range of composition of CH with isomers of butanol liquid system.

## 5. Conclusion

- (i) Ultrasonic speeds,  $u$ , and densities,  $\rho$ , of mixtures of cyclohexanone with *n*-butanol or *sec*-butanol or *tert*-butanol over the entire composition range have been measured at  $T = 308.15$  K.
- (ii) The values of  $V_m^E$ ,  $\Delta k_s$ ,  $L_f^E$ ,  $z^E$ , and  $\Delta u$  are calculated from experimental data of density and ultrasonic speed. The excess and deviation properties have been fitted to Redlich-Kister type polynomial and corresponding standard deviations have been evaluated. The observed positive values of  $V_m^E$ ,  $\Delta k_s$ , and  $L_f^E$  and negative values of  $z^E$ ,  $\Delta u$  for all the liquid mixtures studied clearly indicate the presence of weak interactions such as rupturing of hydrogen bond or reduction in H-bond strength of butanol or breaking of the structure of one or both of the components in a solution.
- (iii) The deviation/excess properties have been fitted to Redlich-Kister type polynomial and the corresponding standard deviations have been calculated.
- (iv) The calculated values of partial molar volumes have also been examined. The observed higher partial molar volumes in the liquid mixture when compared to the respective molar volumes of pure components indicate weak interactions present in the systems.
- (v) The strength of interaction in the mixtures follows the order CH +, *tert*-butanol > *sec*-butanol > *n*-butanol.
- (vi) FT-IR spectra for the present binary mixture also support the conclusions drawn from the  $V_m^E$ ,  $L_f^E$ ,  $\Delta k_s$ ,  $\Delta u$ , and  $z^E$ .
- (vii) Further theoretical values of sound speed in the mixtures have been evaluated using various theories and have been compared with experimental sound speeds to verify the applicability of such theories to the systems studied.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgment

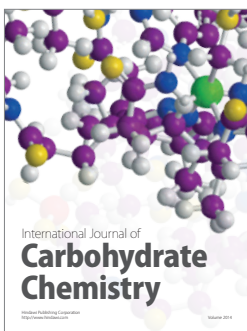
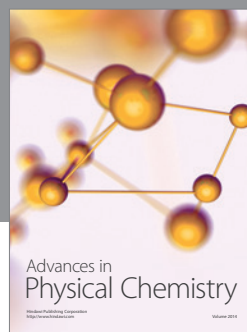
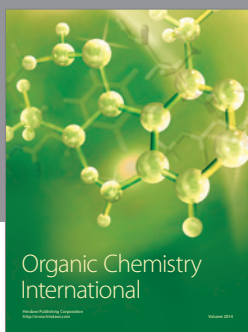
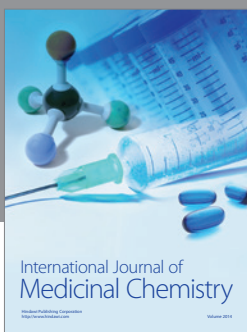
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