



## STUDY OF SPEEDS OF SOUND AND ISENTROPIC COMPRESSIBILITY'S OF BINARY MIXTURES OF WATER WITH SOME ALIPHATIC ALCOHOLS AT 298.15 K

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### ABSTRACT

Isentropic compressibility's for the binary mixtures of water with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol have been computed from the experimentally measured densities and sound speeds at 298.15 K over the entire composition range. All the systems studied exhibit contraction on mixing. The results have been discussed in terms of the specific interactions between the component molecules of the binary mixtures.

#### Key words:

Isentropic compressibility, speed of sound, water, aliphatic alcohols, unlike reactions.

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## INTRODUCTION

The thermodynamic properties of binary mixtures containing a self-associated component exhibit a significant deviation from ideality, arising not only from differences in molecular size but also from the changes in the hydrogen bonding between like and unlike molecules. As an extension to our studies on the thermodynamic properties of binary mixtures containing a self-associated component, the isentropic compressibility's,  $k_s$ , of binary mixtures of water with six aliphatic alcohols, namely, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol have been determined at 308.15 K over the entire composition range and reported in this paper. These studies are aimed to provide information on the binary mixtures with a view to understanding the nature of interactions present in these mixtures.

#### Experimental Setup

Analytical reagent grade samples of methanol, ethanol, 1-butanol and 2-butanol supplied by E. Merck and Laboratory reagent grade samples of 1-propanol and 2-propanol supplied by BDH were purified by following the standard established procedures (1-2). The liquids are fractionally distilled immediately before use. The densities ( $\rho$ ) of the purified liquids agreed closely with the accepted literature values (3-7). The excess molar volumes of mixing have been calculated from the experimental density data.

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The solutions for the measurement of densities were prepared by weight and corrections for buoyancy are applied. The details of experimental techniques for the preparation of solutions have been described elsewhere (7). The densities are measured using a vibrating tube flow densimeter (Model DMA 601602). Water from a thermostat was circulated through the densimeter module at a flow rate of 2-3 L min<sup>-1</sup>. The temperature of the thermostat was maintained at 20.01 K by using a precision temperature controller. The densimeter was calibrated with nitrogen gas and degassed ion exchanged water by using the densities of Kell (8). Duplicate densities of liquids and the liquid mixtures are reproducible to within  $5 \times 10^{-5}$  g cm<sup>-3</sup>. The isentropic compressibility's were computed from the ultrasonic speeds of sound,  $u$ , using the relation:

$$k_s = (u^2 \rho)^{-1}$$

The speeds of sound are measured using a single crystal interferometer (Model F-81, Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz. The maximum error in the measurement of  $u$  was estimated to be around 0.15%. This renders the  $k_s$  values uncertain by  $\pm 2$  T Pa<sup>-1</sup>.

Table 1 Comparison of the measured densities,  $\rho$  for the various liquids with their corresponding literature values at 298.15  $\pm$  0.01K

Liquids	Density $\rho$ (gm cm <sup>-3</sup> )	
	Experimental	Literature
Methanol	0.78663	0.78664 <sup>3</sup>
Ethanol	0.78508	0.78509 <sup>3</sup>
Propan-1-ol	0.79978	0.79976 <sup>4</sup>
Propan-2-ol	0.7809	0.78095 <sup>4</sup>
Butan-1-ol	0.80975	0.80979 <sup>5</sup>
Butan-2-ol	0.80254	0.80250 <sup>6</sup>
Water	0.99705	0.99708 <sup>7</sup>

### Determination of speed of sound

The speeds of sound<sup>9</sup> values for the various organic liquids and their mixtures have been determined with the help of an ultrasonic interferometer (M/S Mittal Enterprises, India).

#### Working principle

The principle used in the measurement of speed of sound is based on accurate determination of wavelength ( $\lambda$ ) in the medium. If ultrasonic waves of known frequency ' $\nu$ ' (produced by a quartz plate fixed at the bottom of the cell) are reflected by a movable metallic plate kept parallel to the quartz plate, standing waves are then formed in the medium if the separation between these two plates is exactly a whole number multiple of the sound wavelength. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half the wavelengths ( $\lambda/2$ ) or multiple of it, then anodic current again becomes maximum. From the knowledge of wavelength ( $\lambda$ ), the velocity ( $u$ ) can be obtained from the relation.

$$u = \lambda \nu \quad (1)$$

(Where  $\nu$  is the frequency of the generator.)

#### Description of ultrasonic interferometer

The ultrasonic interferometer consists of the following two parts:

1. High frequency generator
2. The measuring cell.

#### High frequency generator

It is designed to generate ultrasonic waves in the experimental liquid filled in the measuring cell by exciting the quartz crystal fixed at the bottom of the measuring cell, at its resonance frequency. It is also provided with a micrometer (to observe the changes in current,  $C$ ) and two control knobs (for the purpose of sensitivity regulating and initial adjustment of the micrometer). The position of the needle on the ammeter is adjusted with the knob marked "Adj." and the knob marked "Gain" is used to increase the sensitivity of the instrument. The ammeter is used to notice the number of maximum deflections while the micrometer is moved up and down in the liquid.

#### Measuring cell

It is a specially designed double walled cell having a quartz crystal at its. Two chutes in the double walled construction allow water to be circulated to maintain the liquid in the cell at the desired temperature. It has further been provided with a fine micrometer screw at the top which can lower or raise the reflector plate in the liquid in the cell through a known distance.

#### Experimental procedure

The measuring cell of appropriate frequency was connected to the output terminal of the "high frequency generator" through a shielded coaxial cable. The knurled cap of the cell was unscrewed to lift it away from the double walled cell, which is then filled with the experimental liquid. The knurled cap was then screwed back. The cell was inserted in the square base socket and was clamped to it with the help of the screw provided on one of its side. The generator was then switched

on and an appropriate frequency was selected. The water (from a thermostat was maintained at the appropriate temperature) was then circulated through the two chutes of the cell and the micrometer is slowly moved till the anode current on an ammeter (M/S MOTWANE, INDIA) showed a maxima. The micrometer reading is noted. The screw was moved again and the micrometer reading was again noted when the anode current was maximum. A number of such maximum readings of anode current were recorded and their number ' $n$ ' was counted. The total distance " $d$ " (which measures the distance through which the micrometer screw moves through any two successive anode current maxima) was then utilized to calculate the wave length ' $\lambda$ ' of the ultrasonic waves of the appropriate frequency through the liquid under examination, using the relation

$$d = n \lambda / 2 \quad (2)$$

The velocity ' $u$ ' at the appropriate frequency in the liquid was then calculated utilizing the relation

$$u = \lambda \nu \quad \{\nu = 2 \text{ MHz (fixed frequency)}\} \quad (3)$$

After making the measurements, the liquid was taken out of the cell, washed with water followed by distilled alcohol and acetone and cell was then dried under vacuum.

## RESULTS AND DISCUSSION

### Speeds of sound, isentropic compressibility's and excess isentropic compressibility's

Speed of sound ( $u$ ) in pure liquids water, methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol (Table- II), and in binary mixtures Water (i) + methanol or ethanol or propan-1-ol or propan-2-ol or butan-1-ol or butan-2-ol (j) binary mixtures measure over the whole mole fraction range at 298.15K are reported in Table III – Table VIII respectively.

**Table II** Comparison of the measured Ultrasonic speeds of sound,  $u$  for the various liquids with their corresponding literature values at 298.15  $\pm$  0.0

Liquid	Speed, $u$ (m.s <sup>-1</sup> )	
	Experimental	Literature
Methanol	1097.6	1096 <sup>19</sup>
Ethanol	1144.3	1143 <sup>20</sup>
Propan-1-ol	1239.9	1240 <sup>21</sup>
Propan-2-ol	1344.8	1343 <sup>22</sup>
Butan-1-ol	1309.3	1311 <sup>21</sup>
Butan-2-ol	1304.8	1306 <sup>19</sup>
Water	1520.1	1519 <sup>23</sup>

The isentropic compressibility values,  $\kappa_s$  were calculated from experimentally measured speed of sound values for various binary mixtures using Eq. (4).

$$\kappa_s = (\rho_{ij} u^2)^{-1} \quad (4)$$

The density,  $\rho_{ij}$  of binary (i + j) mixtures were determined from their experimental molar excess volumes,  $V^E$  data via Eq. (5)

$$V^E = \sum_{i=1}^j x_i M_i (\rho_{ij})^{-1} - \sum_{i=1}^j (x_i M_i) (\rho_i)^{-1} \quad (5)$$

Where  $x_i$ ,  $M_i$ ,  $\rho_i$  etc. are mole fraction, molecular mass and density of pure component (i) of the binary mixtures.

The excess isentropic compressibility's for binary mixtures were determined using the relation:

$$\kappa_s^E = \kappa_s - \sum_{i=1}^j \phi_i (\kappa_s)_i \quad (6)$$

Where  $\phi_i$  and  $(\kappa_s)_i$  are the volume fraction and isentropic compressibility of the  $i^{\text{th}}$  component of binary mixtures. Such  $\kappa_s$  and  $\kappa_s^E$  values for the various binary (i + j) mixtures are recorded in the following Tables, i.e., Table III – Table VIII .

**Table III** Water (i) +Methanol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.0342	1496	443.6	-10.0
0.0984	1479	448.7	-29.8
0.1734	1471	450.4	-48.0
0.2940	1476	446.0	-73.1
0.3642	1480	443.7	-83.8
0.3987	1478	444.9	-87.1
0.4464	1480	444.5	-90.7
0.4989	1476	447.4	-91.9
0.5764	1465	455.3	-89.1
0.6301	1454	462.3	-85.1
0.6984	1438	473.7	-77.0
0.7643	1416	488.5	-65.0
0.8346	1391	507.0	-49.1
0.8992	1366	526.7	-31.6
0.9120	1361	530.7	-28.0
0.9580	1342	545.4	-14.6

**Table IV** Water (i) +Ethanol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.0524	1142	980.9	-16
0.1023	1156	941.2	-30.4
0.1624	1173	896.6	-44.9
0.2305	1192	850.4	-57.9
0.3106	1214	800.4	-69.1
0.398	1235	753.1	-74.9
0.4286	1243	737.4	-76.2
0.4961	1258	706.7	-75.2
0.5681	1271	678.3	-71
0.6203	1280	659.8	-65.9
0.6986	1290	636.7	-54
0.7261	1294	628.5	-50.1
0.896	1313	585.2	-19.8
0.9123	1315	581.5	-16.6

**Table V** Water (i) +Propan-1-ol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.0862	1203	851.8	-11.9
0.1325	1210	831.2	-18.8
0.2002	1222	801.8	-30
0.2306	1227	787.7	-33.1
0.2964	1238	759.7	-41.3
0.3624	1250	732.4	-48.6
0.4203	1260	709.8	-53.6
0.5106	1274	677.1	-58.5
0.5964	1285	650.7	-58.3
0.6401	1290	638.7	-56.6
0.7204	1296	619.8	-50.3
0.8246	1299	600.5	-36.4
0.8964	1298	590.6	-23.2
0.9362	1296	586	-14.9

**Table VI** Water (i) +Propan-2-ol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.071	1284	703.5	-6.7
0.1325	1286	694.4	-11.9
0.192	1288	685.7	-15.6
0.2113	1289	683.2	-16.6
0.2842	1290	673	-20.2

0.3012	1291	670.5	-20.8
0.361	1292	662.7	-22.9
0.4217	1293	654	-23.9
0.4617	1294	648.7	-24.3
0.5114	1295	642	-24.6
0.5968	1296	631.5	-23.2
0.6512	1297	624.2	-21.6
0.7019	1298	619.4	-19.6
0.8312	1290	600.5	-12.2

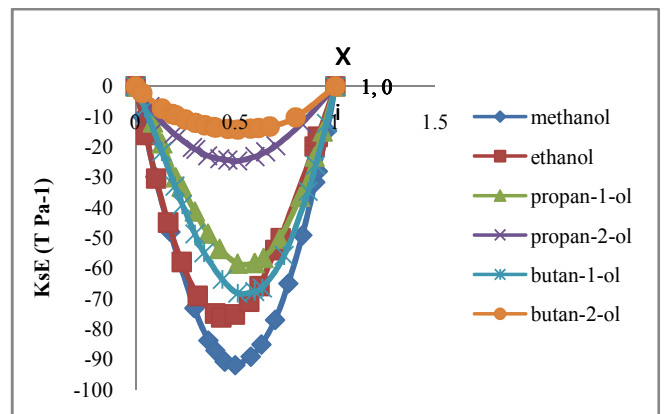
**Table VII** Water (i) +Butan-1-ol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.0462	1135	997.4	-7.2
0.1308	1150	948.2	-21.5
0.1966	1163	909.3	-32.9
0.234	1170	887.5	-39
0.2964	1184	851.2	-48.7
0.3423	1194	825.3	-54.9
0.434	1215	776.7	-63.7
0.5108	1232	738.4	-68.2
0.5964	1249	700.7	-67.7
0.6341	1256	684.9	-66.5
0.7442	1273	645.2	-55.8
0.8643	1286	610.4	-34.6
0.9013	1288	601.3	-26
0.9564	1291	589	-12.2

**Table VIII** Water (i) +Butan-2-ol (j) T =298.15 K

Mole fraction ( $X_i$ )	u (m s <sup>-1</sup> )	$k_s(\text{T pa}^{-1})$	$k_s^E(\text{T pa}^{-1})$
0.0325	1258	728.2	-2.2
0.131	1263	710.7	-7.3
0.1825	1265	702.1	-9.1
0.201	1266	699.3	-9.5
0.248	1268	691.6	-10.9
0.299	1270	682.5	-12
0.3457	1272	676.1	-12.8
0.3912	1273	669	-13.4
0.401	1274	667.4	-13.6
0.4617	1276	658	-14
0.5112	1278	650.3	-14.2
0.5758	1280	640.6	-13.9
0.6152	1281	634.5	-13.7
0.6713	1284	625.9	-13.2
0.801	1275	610.2	-10.2

The speeds of sound values for the purified liquids (recorded in Table II) compare well with their corresponding experimental values<sup>10-16</sup>.



**Figure 1** Molar excess isentropic compressibilities,  $K_s^E$ . Speeds of sound data for Water (i) + propan-2-ol (j) binary mixture at 298.15K; Water (i) + butan-1-ol or butan-2-ol (j) binary mixtures at 298.15K and 313.15K have been reported in literature<sup>10,13,17,18</sup>. Our speeds of sound values for Water (i) + propan-2-ol mixtures; Water (i) + butan-1-ol or butan-2-ol (j) mixtures at 298.15K are 10-25 ms<sup>-1</sup> lower than those reported in literature<sup>22</sup>. We are unaware of any speed of sound data for

the remaining mixtures at 298.15K with which to compare our results.

Plot of  $k_s^E$  Vs  $x_i$ , mole fraction of component (i) for the various binary mixtures are shown in figure (1). The  $k_s^E$  values for various binary mixtures are fitted to Equation (7).

$$k_s^E = x_i x_j \left[ \sum_{n=0}^2 \kappa_s^{(n)} (2x_i - 1)^n \right] \quad (7)$$

Where  $\kappa_s^{(n)}$  ( $n = 0-2$ ) etc. are the adjustable parameters and were calculated using the least squares method. These parameters are recorded along with standard deviation,  $\sigma(\kappa_s^E)$  defined by

$$\sigma(k_s^E) = \left[ \sum (k_{s(\text{exp.})}^E - k_{s(\text{calc.})}^E)^2 (m - n)^{0.5} \right] \quad (8)$$

Where  $m$  is the number of data points;  $n$  is the number of adjustable parameters of Equation (8).

The  $K_s^E$  values for Water (i) + methanol or ethanol or propan-1-ol or propan-2-ol or butan-1-ol or butan-2-ol (j) binary mixtures are negative over the entire composition and for an equimolar mixture vary in the order butan-2-ol > butan-1-ol > propan-2-ol > propan-1-ol > ethanol > methanol.

The negative  $K_s^E$  values for (i+j) binary mixtures are due to the combination of several contributions:

1. Water (i) and methanol or ethanol or propan-1-ol or butan-1-ol (j) are associated molecular entities
2. Establishment of unlike i and j contacts
3. Formation of unlike contacts between i and j then leads to depolymerization of associated molecular entities to yield their respective monomer
4. Monomers of i and j undergo interaction to form i - j molecular complex.

The negative values of  $K_s^E$  for these binary mixtures suggest net contributions due to factors (1), (2) and (4) for outweigh the contribution due to factors (3), so that the overall  $K_s^E$  for (i + j) mixtures are negative. Further less negative values of Water (i) + butan-2-ol (j) mixture than those for Water (i) + methanol or ethanol (j) mixtures is due to the presence of bulky  $-CH_3$  groups at the adjacent carbon atoms of butan-2-ol or propan-2-ol which restrict the approach of Water (i) molecules. Thus contribution to  $K_s^E$  for Water (i) + butan-2-ol mixtures due to factor (3) should be less than those for Water (i) + propan-2-ol mixture. Hence  $K_s^E$  for Water (i) + butan-2-ol (j) must be less negative than those for Water (i) + propan-2-ol (j) mixture. This is indeed true. Excess isentropic compressibilities,  $K_s^E$  values have also been analyzed in terms of (i) graph theory and (ii) Flory theory.

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