

## Isentropic Compressibilities of Binary Mixtures of 1-Bromobutane with Propan-2-ol, Butan-2-ol and 3-Methyl butan-1-ol

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Ultrasonic sound velocities and densities in binary mixtures of 1-bromobutane with propan-2-ol, butan-2-ol, and 3 methyl butan-1-ol, have been experimentally determined at 303.15 K. Isentropic compressibilities (Ks) and deviation in isentropic compressibilities ( $\Delta K_s$ ) have been computed from the experimentally determined densities and velocity of sound. The results show that  $\Delta K_s$  is almost positive over volume fraction range studied in the system. The experimental results are explained in terms of depolymerisation of hydrogen bonded alcohol aggregates, decrease in dipolar association and weak hydrogen bonding interaction of the type Br . . . H—O between unlike molecules.

### INTRODUCTION

Many attempts have been made to measure ultrasonic behaviour of binary mixtures of bromobutane with aromatic hydrocarbons<sup>1-3</sup>, chloroalkane with alkane<sup>4</sup> and alcohol<sup>5-9</sup> have investigated the binary systems containing haloalkane as common component. Choudary *et al*<sup>10-12</sup> have studied extensively the binary mixtures containing chloro alkane as common component. Recently we have reported the volumetric behaviour of an alcohol with bromobutane<sup>13</sup>. However no attempt has been made to study the interactions between 1-bromobutane with propan-2-ol, butan-2-ol and 3-methyl butan-1-ol. Hence we measured sound velocities for the mixtures of bromobutane with propan-2-ol, butan-2-ol and 3-methyl butan-1-ol at 303. 15 K, which exhibit dipole-dipole interactions in pure state. These alcohols have been chosen to study the effect of chain length on the properties studied.

### EXPERIMENTAL

1-Bromobutane (BDH) was refluxed with concentrated sulphuric acid, washed several times with water, dried over two portions of calcium chloride and finally fractioned. Propan-2-ol (AR) butan-2-ol (AR) and 3-methyl butan-1-ol (AR) were purified by the methods described by Riddick and Bunger<sup>14</sup>. The purity of the samples was checked by comparing the measured densities of the samples with those reported in the literature<sup>15</sup>. Densities of the pure components were measured using a bicapillary Pyknometer<sup>16</sup> which gave an accuracy of 2 parts in 10<sup>5</sup>. Mixture densities were computed from the measured excess volume data<sup>13</sup>.

Ultrasonic velocity was measured with a single crystal interferometer at a frequency of 2 MHz and was accurate 1 to  $\pm 0.15\%$ . All the measurements were made at a constant temperature employing a thermostat that could maintain the temperature constant to  $\pm 0.1$  K.

### RESULTS AND DISCUSSION

Isentropic compressibilities ( $K_s$ ) were calculated from the measured ultrasonic velocities and precise density values at 303.15 K using the relation.

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

Where  $u$  and  $\rho$  denote sound velocity and density respectively. The deviation in ( $\Delta K_s$ ) from linear dependence of isentropic compressibility on volume fraction was calculated using the relation.

$$\Delta K_s = K_s - (\phi_1 K_{s_1} + \phi_2 K_{s_2}) \quad (2)$$

Where  $K_s$ ,  $K_{s_1}$  and  $K_{s_2}$  are isentropic compressibilities of mixture and pure components respectively.  $\phi_1$  and  $\phi_2$  are volume fractions of the component. The experimental data for the density, sound velocity, isentropic compressibility and deviation in isentropic compressibility are included in Table 1 and also graphically represented in Fig. 1. The  $\Delta K_s$  values may be fitted to an empirical equation of the form

$$\Delta K_s = \phi_1 \phi_2 [b_0 + b_1 (1 - \phi_1) + b_2 (1 - \phi_2)^2] \quad (3)$$

The values of  $b_0$ ,  $b_1$  and  $b_2$  computed by the method of least square, as shown in Table 2 along with standard deviation  $\sigma$  ( $\Delta K_s$ ).

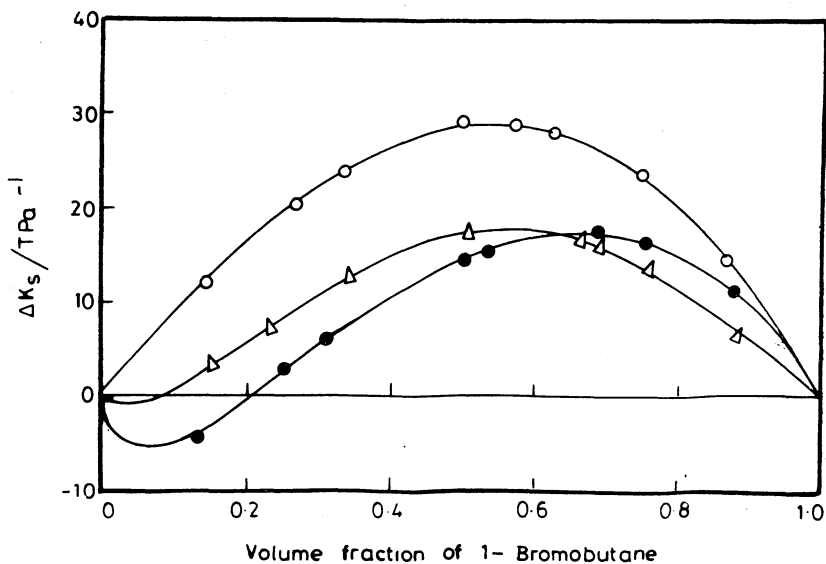


Fig. 1. Volume fraction  $\phi_1$  against deviation in isentropic compressibility at 303.15 K  
 ○ Propan-2-ol; ● butan-2-ol; Δ 3-methyl butan-1-ol

TABLE 1

VOLUME FRACTION ( $\phi_1$ ) OF 1-BROMOBUTANE, DENSITY ( $\rho$ ), SOUND VELOCITY ( $u$ ), ISENTROPIC COMPRESSIBILITY ( $K_s$ ), CALCULATED FROM EQUATION (1) AND DEVIATION IN ISENTROPIC COMPRESSIBILITY ( $\Delta K_s$ ) FROM EQUATION (2) FOR THE BELOW SYSTEMS AT 303.15 K

1	$\frac{\rho}{\text{gcm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{K_s}{\text{Tpa}^{-1}}$	$\frac{\Delta K_s}{\text{Tpa}^{-1}}$
1-bromobutane + Propan-2-ol				
0.0000	0.77691	1127	1013	0
0.1503	0.84846	1089	994	11
0.2558	0.89865	1065	981	20
0.3286	0.13335	1050	971	24
0.4942	1.01261	1024	942	28
0.5663	1.04727	1014	928	29
0.6184	1.07237	1009	916	28
0.7483	1.13551	997	886	24
0.8728	1.19694	990	852	15
1.0000	1.26130	989	811	0
1-bromobutane + butan-2-ol				
0.0000	0.79439	1172	916	0
0.1284	0.85393	1142	898	-5
0.2446	0.90784	1111	893	3
0.3124	0.93938	1094	889	6
0.5029	1.02767	1053	877	14
0.5326	1.04146	1047	875	15
0.6830	1.11134	1022	861	17
0.7533	1.14408	1012	853	16
0.8747	1.20114	998	836	12
1.0000	1.26130	989	811	0
1-bromobutane + 3 methyl butan-1-ol				
0.0000	0.80177	1220	838	0
0.1543	0.87253	1170	837	3
0.2312	0.90758	1146	839	7
0.3358	0.95517	1115	842	13
0.5124	1.03564	1071	842	18
0.6689	1.10739	1040	835	15
0.6833	1.11407	1037	835	15
0.7640	1.15132	1022	831	14
0.8840	1.20713	1005	820	6
1.0000	1.26130	989	811	0

The results included in Table 2 show that the values of  $\Delta Ks$  are almost positive over the entire range of mole fraction range in all the three binary mixtures. The  $\Delta Ks$  values may be explained in terms of the following. (i) Break up of hydrogen bonds present in alcohol aggregates and (ii) Weak interactions of the type O-H...Br between unlike molecules. The first factor contributes to an increase in free lengths described by Jacobson<sup>17</sup>. This leads negative deviation in  $u$  and positive deviation in  $Ks$ .

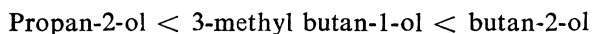
TABLE 2  
VALUES OF PARAMETERS IN EQUATION (3) AND THE STANDARD  
DEVIATION  $\sigma(\Delta Ks)$  AT 303.15 K

1-bromobutane	$b_0$	$b_1$	$b_2$	$\frac{\sigma(\Delta Ks)}{Tpa^{-1}}$
Propan-2-ol	116.089	29.093	-8.991	1
butan-2-ol	58.129	88.736	-42.316	2
3-methyl butan-1-ol	70.232	28.142	-54.760	1

The second effect, on the other hand, contributes to positive deviation in  $u$  and negative deviation in  $\Delta Ks$ . The actual value and sign of the deviation would depend upon the relative strengths of the two opposing effects. The experimental values of  $\Delta Ks$ , which are positive arise due to the breaking of hydrogen bonds in self-associated alcohols and physical dipole-dipole interactions between alcohol monomers and multimers. It is also clear that the first effect is stronger than the second.

The data in Table 1 also point out that  $\Delta Ks$  is maximum over the range (0.5 to 0.6) mole fraction of 1-bromobutane. This may be explained as follows.

In solutions, rich in alcohols, the bromoalkane molecules get interstitial accommodation in alcohol aggregates. This factor will mitigate the effect of depolymerization of alcohol aggregates. Hence  $\Delta Ks$  will be smaller in these solutions. On the other hand it will be maximum in solutions rich in 1-bromobutane because the contribution due to interstitial accommodation will be absent. The aforesaid factors account for the maximum values observed for  $\Delta Ks$  over the mole fraction range 0.5 to 0.6 of bromobutane. The algebraic values of  $Ks$  are in the order:



This order may be ascribed to the effect of chain length on the degree of polymerization of alcohols in the pure state and strength of complex formed between unlike molecules. The degree of polymerization of an alcohol increases with decreases in chainlength. The strength of hydrogen bond in the aggregates and also the complex formation increases with decrease in chain length.

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