

Ultrasonic studies on binary mixtures of associated liquids (1-bromobutane + alcohol) at 303·15K

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Abstract. Ultrasonic sound velocities and densities of binary mixtures of 1-bromobutane with propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol and octan-1-ol have been experimentally determined at 303·15 K. Isentropic compressibilities (K_S) and deviations in isentropic compressibilities (ΔK_S) have been calculated from the results. The values of ΔK_S are almost positive over the entire range of composition in all six binary liquid mixtures. 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.

Keywords. Interferometer; isentropic compressibilities; sound velocity; 1-bromobutane; normal alcohols; hydrogen bonding; depolymerisation.

1. Introduction

Isentropic compressibilities find extensive application in characterising the various aspects of physico-chemical behaviour of liquid mixtures such as molecular association, deassociation and complex formation. Diaz Pena *et al* (1983), and Lainez *et al* (1984) studied the excess functions of bromobutane with aromatic hydrocarbons. Doan-Nguesan *et al* (1978) have studied the binaries of chloro-alkane with alkane and alcohol. Raman and co-workers (Venkateswarlu *et al* 1984, 1986, 1987; Venkateswarlu and Raman 1985) have investigated binary systems containing haloalkanes as common components. Choudary and co-workers (Choudary and Naidu 1981; Choudary *et al* 1982; Mouli *et al* 1982) have extensively studied binary mixtures containing chloro-alkane as the common component. Recently we have reported the volumetric behaviour of an alcohol with bromobutane (Rambabu *et al* 1989). However no attempt has been made to study the interactions between 1-bromobutane and alcohol. Hence we measured sound velocities for the mixtures of bromobutane with normal alcohols which exhibit dipole-dipole interactions in the pure state. The alcohols include propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol and octan-1-ol. These alcohols have been chosen to study the effect of chain length on the properties studied.

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2. Experimental

1-Bromobutane (BDH) was refluxed with concentrated sulphuric acid, washed several times with water, dried over two portions of calcium chloride and finally fractionated (Riddick and Bunger 1970). Propan-1-ol (BDH), butan-1-ol (BDH), pentan-1-ol (J J Baker, AR) and hexan-1-ol (BDH) were purified using procedures reported previously (Riddick and Bunger 1970). Heptan-1-ol and octan-1-ol (Koch-Light Lab, England) was used without further purification. The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (Timmermans 1950). Densities were determined using a bicapillary-type pycnometer which gave an accuracy of 2 parts in 10^5 . Density was computed from the measured excess volume data (Ram Babu *et al* 1989). Ultrasonic velocity was measured with a single crystal interferometer at a frequency of 2 MHz and was accurate to $\pm 0.15\%$. All the measurements were made at a constant temperature employing a thermostat that could maintain the temperature constant to ± 0.01 K.

3. Results and discussion

Isentropic compressibilities were calculated using the relation

$$K_S = U^{-2} \rho^{-1}, \quad (1)$$

where U and ρ denote the sound velocity and the density, respectively. The deviation in isentropic compressibility from the ideal value, assumed to be additive in terms of volume fraction, is estimated by using the equation

$$\Delta K_S = K_S - (\phi_1 K_{S_1} + \phi_2 K_{S_2}) \quad (2)$$

where K_S , K_{S_1} and K_{S_2} are isentropic compressibilities of the mixture and the pure components, respectively, and ϕ_1 and ϕ_2 are volume fractions of the components. The experimental plots of the volume fraction ϕ_1 versus deviation in isentropic compressibility are shown in figure 1. The ΔK_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 were computed by the method of least squares and are shown in table 1 along with standard deviations $\sigma(\Delta K_S)$.

The results included in table 1 show that values of ΔK_S are almost positive over the entire range of mole fractions in all the six binary mixtures. The ΔK_S 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 contributing to an increase in free lengths as described by Jacobson (1953). This leads to negative deviation in μ and positive deviation in K_S . The second effect, on the other hand, contributes to positive deviation in μ and negative deviation in K_S . The actual value and sign of the deviation would depend upon the relative strengths of the two opposing effects. The experimental values of ΔK_S , which are positive, indicate that the first effect is stronger than the second. The data also show that ΔK_S is maximum over the mole fraction range (0.6 to 0.7) of 1-bromobutane. This may be explained as follows.

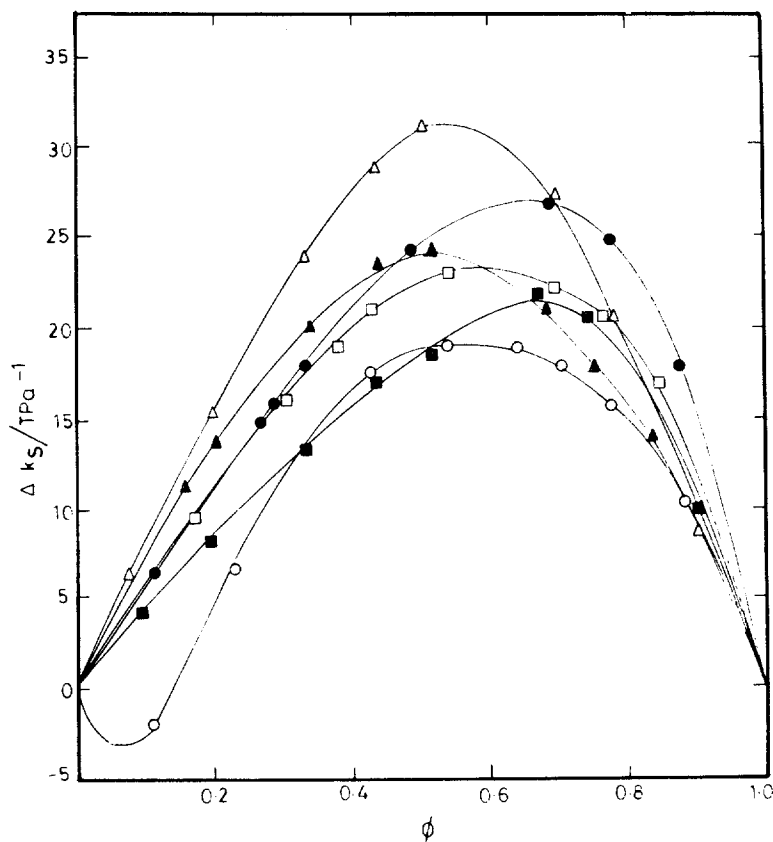


Figure 1. Volume fraction of 1-bromobutane with ○ - propan-1-ol; ● - butan-1-ol; △ - pentan-1-ol; ▲ - hexan-1-ol; □ - heptan-1-ol; ■ - octan-1-ol.

Table 1. Values of parameters in (4) and the standard deviation $\sigma(\Delta K_S)$ at 303.15 K.

System:	b_0	b_1	b_2	$\sigma(\Delta K_S)$
1-bromobutane +	(TPa ⁻¹)			
Propan-1-ol	74.301	65.179	-61.636	1
Butan-1-ol	99.919	58.272	22.638	1
Pentan-1-ol	118.859	-4.158	-44.722	2
Hexan-1-ol	93.814	15.085	-5.742	1
Heptan-1-ol	88.929	46.840	14.554	1
Octan-1-ol	74.484	53.180	24.584	1

In solutions rich in alcohols, the bromoalkane molecules get interstitial accommodation in alcohol aggregates. This factor mitigates the effect of depolymerization of alcohol aggregates. Hence K_S is smaller in these solutions. On the other hand it is maximum in solutions rich in 1-bromobutane because the contribution due to interstitial accommodation is absent. The aforesaid factors account for the maximum values observed for ΔK_S over the mole fraction range 0.6-0.7 of 1-bromobutane.

The values of the ΔK_S of 1-alcohols are in the order:

pentan-1-ol > butan-1-ol > propan-1-ol,

and

pentan-1-ol > hexan-1-ol > heptan-1-ol > octan-1-ol.

The above order indicates that deviation in compressibility increases with increase in chain length upto pentan-1-ol and decreases with increase in chain length from then on. This may be attributed to steric hindrance in the chain.

The results may be explained in terms of the structure-breaking and structure-making effects on free-lengths, as defined by Jacobson (1953). The results show that structure-breaking is dominant in all the mixtures.

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