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ULTRASONIC STUDIES IN BINARY MIXTURES OF 1-2-DIBROMOETHANE WITH ALCOHOLS AT 303.15 K

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Isentropic compressibility data, K_s of 1,2-Dibromoethane + Propan-1-ol, + butan-1-ol, + pentan-1-ol, hexan-1-ol, heptan-1-ol and octan-1-ol at 303.15 K are reported. Deviations in isentropic compressibility, K_s values are found to be negative for mixtures of 1,2-dibromoethane with propan-1-ol over the entire range of composition and while in butan-1-ol the ΔK_s values are negative at lower molefractions and positive at higher molefractions. Therefore as the chain length increases it is showing the positive deviations. The data are interpreted in terms of specific interactions between the components.

KEY WORDS: Excess volume, isentropic compressibility.

INTRODUCTION

Though many binary liquid mixtures have been studied ultrasonically, it appears that very few binary mixtures of associated liquids have been studied. It has been shown that mixtures of associated liquids generally show non-ideal behaviour in respect of properties like excess volume and isentropic compressibility. Raman *et al.*^{1–3} have studied excess volume extensively the binary mixtures containing 1,2-Dibromoethane as common component. Like excess volume, isentropic compressibility also throws a light on the nature and degree of molecular interactions present in the binary mixture. Hence our work is extended to ultrasonic studies of the binary mixtures of 1,2-Dibromoethane with ketones⁴. The present paper reports Sound velocities, densities and isentropic compressibilities for the binary mixtures of 1,2-Dibromoethane with alcohols. Alcohols include propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol.

EXPERIMENTAL

The liquids were purified as described in our earlier work¹. The purity of the final samples were checked by density measurements. Ultrasonic sound velocities were

measured with a single crystal interferometer working at a fixed frequency of $2MH_2$. The temperature of the experimental liquid in the cell was maintained by circulating water from a thermostatic bath through the double walled liquid container. Densities were measured using a bi-capillary type pycnometer of Naidu *et al.*⁵ The densities and sound velocities were accurate to ± 0.00005 gcm⁻³ and $\pm 0.15\%$ respectively. All the measurements were made at 303.15 ± 0.01 K.

RESULTS AND DISCUSSION

Isentropic compressibilities K_s were derived from the expression

$$K_{s} = U^{-2} \rho^{-1} \tag{1}$$

where U and ρ denotes sound velocity and density respectively. The deviation in isentropic compressibility ΔK_s has been calculated from the equation

$$\Delta K_{s} = K_{s} - \phi_{1} K_{s_{1}} - \phi_{2} K_{s_{2}}$$
⁽²⁾

where K_s , K_{s_1} and K_{s_2} are the isentropic compressibilities of the mixture and pure components and ϕ_1 and ϕ_2 are volume fractions. Densities, Sound velocities were accurate to ± 0.00005 gcm⁻³ and $\pm 0.15\%$ are given in Table 1.

The experimental ΔK_s values against volume fraction ϕ_1 may be represented by

$$\Delta K_{\rm S} = \phi_1 \phi_2 [b_0 + b_1 (\phi_1 - \phi_2) + b_2 (\phi_1 - \phi_2)^2] \tag{3}$$

The values of b_0 , b_1 and b_2 obtained by least squares are included in Table 2 along with standard deviation $\sigma(\Delta K_s)$.

The values of ΔK_s are negative in the mixture 1,2-Dibromoethane-propan-1-ol over the entire range of composition, while in butan-1-ol it is negative at lower molefractions and positive at higher molefractions and pentan-1-ol onwards upto octan-1-ol it is showing positive nature. Therefore as the chain length increases the trend is changing from negative towards positive Alcohols⁶⁻⁸ are self-associated in the pure state. The values of ΔK_s may be ascribed to the relative strengths of opposing effects which influence the free space defined by Jacobson⁹. Mutual breaking up of hydrogen bonds in the alcohol and in the 1,2-Dibromoethane by each other leads to an increase in free spaces in mixtures contributing to positive deviations in sound velocity and negative deviations in compressibility. However, this effect will be counteracted by the interaction due to the hydrogen bond by Br-H-O, type between dibromoethane and alcohol, which leads to positive deviation in compressibility. The actual values of K_s , therefore, would depend upon relative strengths of these two opposing effects. The positive values of K_s in all the mixtures suggest the predominating hydrogen bond interaction between dibromoethane and alcohol and also supports the contention made previously¹ that Br-H-O bonding is relatively stronger. These are attributed to weak dipolar interactions between unlike molecules which leads to decrease in free length, increase in sound speed and negative deviations in isentropic compressibility. These interactions are infected decrease with increase in chain length.

Table 1 Volume factors (ϕ_1) , densities (ρ) , sound velocities (u) and isentropic compressibilities (K_S) and deviation in isentropic compressibilities ΔK_S of binary liquid mixtures of 1,2-dibromoethane with alcohols at 303.15 K.

ϕ_1	ρ	U	Ks	ΔK_s
	g cm ⁻³	mg^{-1}	TPa^{-1}	TPa ⁻¹
	1,2-dibron	noethane + p	ropan-1-ol	
0.0000	0.79604	984	884	0
0.1270	0.96856	1121	822	- 11
0.2130	1.08564	1086	781	-17
0.4126	1.35606	1035	688	- 28
0.5081	1.48564	1008	663	- 21
0.5861	1.59177	998	631	- 16
0.6352	1.65828	992	613	- 14
0.7726	1.84556	980	564	-07
0.8859	1.99972	977	524	- 1
1.0000	2.15967	984	479	0
	1,2-dibroi	moethane + t	outan-1-ol	
0.0000	0.80201	1232	821	0
0.0960	0.93128	1168	787	- 1
0.2026	1.07488	1113	751	- 1
0.3373	1.25673	1063	705	- 2
0.3594	1.28631	1057	696	-2
0.5207	1.50420	1017	643	0
0.5578	1.55430	1011	630	0
0.7822	1.85870	985	555	2
0.8802	1.99304	980	522	2
1.0000	2.15967	984	479	0
	1,2,dibron	noethane + p	entan-1-ol	
0.0000	0.80760	1270	768	0
0.0998	0.94115	1185	757	18
0.2217	1.10442	1120	722	18
0.2743	1.17483	1100	704	17
0.3777	1.28200	1062	692	16
0.3972	1.33960	1058	667	15
0.5457	1.53902	1022	662	12
0.7732	1.84681	989	554	9
0.8878	2.00381	982	518	7
1.0000	2.15967	984	479	0
	1,2-dibror	noethane + h	exan-1-ol	
0.0000	0.81204	1288	742	0
0.1191	0.97071	1201	714	3
0.2081	1.08916	1150	694	7
0.2613	1.16008	1126	680	7
0.3863	1.32672	1075	652	12
0.5453	1.53937	1032	610	11
0.5910	1.60678	1025	595	8
0.7500	1.81550	998	553	7
0.8881	2.02545	982	512	4
1.0000	2.15967	984	479	0

(continued)

ϕ_1	ρ	U	Ks	ΔK_s
	$g cm^{-3}$	$\overline{MG^{-1}}$	$\overline{TPa^{-1}}$	TPa^{-1}
	1,2-diobro	moethane + h	eptan-1-ol	
0.0000	0.81573	1310	714	0
0.1226	0.97800	1220	687	2
0.1928	1.07112	1172	680	11
0.2794	1.18605	1128	663	15
0.3252	1.24690	1108	653	15
0.5065	1.48855	1049	611	16
0.5594	1.55924	1035	599	16
0.7949	1.87715	992	541	14
0.8749	1.98656	989	515	7
1.0000	2.15967	984	479	0
	1,2 dibro	moethene + o	ctan-1-ol	
0.0000	0.94160	1330	688	0
0.0765	0.92253	1265	677	5
0.1638	1.03753	1204	665	11
0.2185	1.10960	1172	656	14
0.3758	1.31737	1100	627	18
0.4765	1.45103	1064	609	21
0.5288	1.52055	1050	597	20
0.6705	1.71007	1019	563	15
0.8922	2.01087	990	507	6
1.0000	2.15967	984	479	0

Table 1 (continued)

Table 2 Values of parameters in Eq. (3) and the standard deviation $\sigma(\Delta K_s)$ at 303.15 K.

1,2-Dibromoethane +	bo	b_1	<i>b</i> ₂	$\sigma(\Delta K_S)$
Propan-1-ol	- 88.622	61.392	58.257	± 3
butan-1-ol	- 2.374	19.091	11.611	± 1
Pentan-1-ol	41.074	- 59.594	144.049	± 2
hexan-1-ol	42.346	1.888	-11.861	± 1
heptan-1-ol	75.471	16.870	- 37.133	± 3
octan-1-ol	79.380	- 9.797	- 18.572	± 1

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