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Sound Velocities and Isentropic Compressibilities of 1,2-Dichloroethane with Isomeric and Branched Alcohols

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Sound velocities for binary mixtures of 1,2-dichloroethane with isopropanol, isobutanol, *sec*-butanol, *tert*-butanol, isopentanol, isohexanol and cyclohexanol were determined at 303.15 K. Isentropic compressibilities were computed from sound velocity and density data derived from excess volume. The deviation in isentropic compressibility exhibits negative values of dichloroethane with isopropanol and *tert*-butanol, but are positive in the mixtures of dichloroethane with isobutanol, isopentanol, isohexanol, *sec*-butanol and cyclohexanol. The results are explained in terms of interactions between unlike molecules.

INTRODUCTION

Isentropic compressibilities have extensive application in characterising the aspects of physico-chemical behaviour of liquid mixtures such as molecular association, deassociation and complex formation. A survey of the literature shows that attempts have been made to measure the sound velocity of binary mixtures of halo alkane with alcohols[1–4], alkanes[5, 6], and ketones[7–10] but no attempt has been made to measure the sound velocity of dichloroethane with iso and branched alcohols. Hence we report the sound velocities of dichloroethane with isopropanol, isobutanol, *sec*-butanol, *tert*-butanol, isopentanol, isohexanol and cyclohexanol at 303.15 K.

Experimental

1,2-Dichloroethane was purified by the method reported earlier[11]. Alcohols were purified by the methods described by Reddick and Bunger[12]. The purity of the samples was checked by comparing the measured densities of the samples with those reported in the literature[13]. Ultrasonic sound velocities were measured with a single crystal interferometer working at a fixed frequency of 3 MHz. 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 of pure component were measured using a bi-capillary pyknometer[14]. 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.

Densities of liquid mixtures were computed from the measured excess volume data, using the relation

$$\rho = \frac{X_1 M_1 + X_2 M_2}{V + V^E} \qquad (1)$$

X_1 and X_2 denote the mole fraction of two components and M_1 and M_2 stand for molecular weights. V represents molar volume of the mixture.

RESULTS AND DISCUSSION

Isentropic compressibilities were calculated using the relation

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

where u and ρ denote the sound velocity and density. The values of k_s are accurate to ± 2 TPa^{-1}. The deviation in isentropic compressibility from the ideal value assumed to be additive in terms of volume fraction is estimated using the equation

$$\Delta k_s = k_s - (\phi_1 k_{s1} + \phi_2 k_{s2}) \tag{2}$$

where k_s, k_{s1} and k_{s2} are isentropic compressibilities of mixture and pure components respectively. ϕ_1 and ϕ_2 are volume fractions of the components. 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 Δk_s values may

TABLE 1

VOLUME FRACTION (ϕ_1) OF 1,2-DICHLOROETHANE, DENSITY (ρ), SOUND VELOCITY (u), ISENTROPIC COMPRESSIBILITY (k_s), CALCULATED FROM EQUATION (2) AND DEVIATION IN ISENTROPIC COMPRESSIBILITY (Δk_s) FROM EQUATION (3) FOR 1,2-DICHLOROETHANE + AN ISO-ALCOHOL AND BRANCHED ALCOHOLS AT 303.15 K

ϕ_1	ρ / g cm^{-3}	u / ms^{-1}	k_s / TPa^{-1}	Δk_s / TPa^{-1}
		1,2-dichloroethane + isopropanol		
0.0000	0.77741	1127	1013	0
0.1425	0.84025	1122	945	−8
0.2484	0.88857	1123	893	−14
0.3422	0.93057	1126	848	−19
0.4338	0.97191	1129	807	−21
0.5568	1.02782	1131	761	−14
0.6797	1.08455	1135	716	−7
0.8164	1.14902	1144	665	1
0.9117	1.19496	1156	626	2
1.0000	1.23836	1174	536	0
		1,2-dichloroethane + isobutanol		
0.0000	0.79435	1172	917	0
0.1333	0.85194	1157	877	4

TABLE 1 (cont.)

ϕ_1	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{k_s}{\text{TPa}^{-1}}$	$\frac{\Delta k_s}{\text{TPa}^{-1}}$
0.2020	0.88159	1152	855	5
0.2851	0.91756	1146	830	7
0.3828	0.96002	1143	798	8
0.5510	1.03395	1139	746	11
0.5717	1.04311	1140	738	10
0.7456	1.12112	1145	680	10
0.8352	1.16197	1152	649	8
1.0000	1.23836	1174	586	0
	1,2-dichloroethane + *sec*-butanol			
0.0000	0.97888	1195	877	0
0.1770	0.87352	1172	833	8
0.3162	0.93255	1157	801	16
0.3720	0.95636	1153	786	17
0.4211	0.97733	1151	772	18
0.5666	1.04048	1147	731	19
0.6092	1.05910	1145	720	20
0.7578	1.12547	1152	670	14
0.8823	1.18661	1159	627	7
1.0000	1.23836	1174	586	0
	1,2-dichloroethane + *tert*-butanol			
0.0000	0.77653	1105	1055	0
0.1224	0.82961	1101	955	−3
0.2620	0.89130	1101	926	−6
0.3429	0.92755	1102	887	−7
0.4382	0.97062	1106	842	−8
0.5485	1.02114	1114	789	−9
0.6800	1.08245	1125	730	−6
0.7310	1.10655	1128	710	−2
0.8270	1.15260	1140	668	1
1.0000	1.23836	1174	586	0
	1,2-dichloroethane + isopentanol			
0.0000	0.86769	1220	838	0
0.1492	0.86538	1190	815	15

TABLE 1 (cont.)

ϕ_1	ρ / g cm^{-3}	u / ms^{-1}	k_s / TPa^{-1}	Δk_s / TPa^{-1}
0.2191	0.89532	1179	804	21
0.2604	0.91306	1175	794	22
0.3504	0.95151	1162	778	28
0.4454	0.99262	1157	753	27
0.5606	1.04241	1151	724	27
0.7363	1.11925	1154	671	19
0.8592	1.17402	1159	634	13
1.0000	1.23836	1174	586	0
	1,2-dichloroethane + isohexanol			
0.0000	0.81573	1282	743	0
0.1512	0.87914	1240	740	21
0.2503	0.91925	1217	734	30
0.3664	0.96663	1196	723	38
0.4589	1.00487	1184	710	39
0.5748	1.05335	1173	690	37
0.5933	1.06116	1172	686	36
0.6434	1.08235	1170	675	33
0.8606	1.17627	1169	622	14
1.0000	1.33836	1174	586	0
	1,2-dichloroethane + cyclohexanol			
0.0000	0.94160	1446	508	0
0.0949	0.96866	1384	539	24
0.2057	1.00014	1338	559	35
0.3064	1.02874	1318	560	38
0.4529	1.07058	1272	577	38
0.5335	1.09384	1250	585	36
0.6397	1.12509	1228	589	31
0.7280	1.15165	1204	599	26
0.8658	1.19449	1188	593	18
1.0000	1.23836	1174	586	0

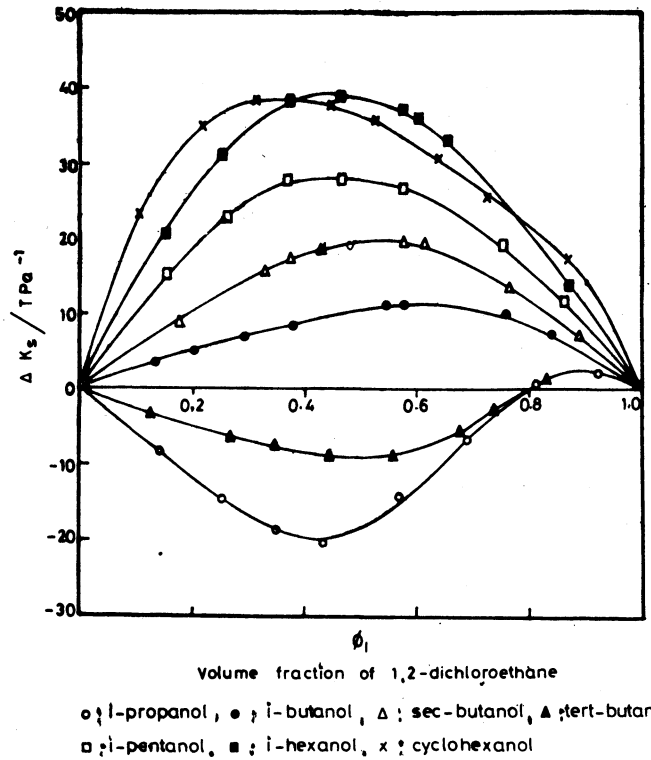

Fig. 1 The values of Δk_s plotted against volume fraction (ϕ_1) of 1,2-dichloroethane with 150 and branched alcohols at 303.15 K.

be fitted to an empirical equation of the form

$$\Delta k_s = \phi_1\phi_2 [b_0 + b_1 (\phi_1 - \phi_2) + b_2 (\phi_1 - \phi_2)^2)] \quad (4)$$

The values of parameters b_0, b_1 and b_2 as obtained by a least square method are given in Table 2 along with standard deviation σ (Δk_s).

TABLE 2
STANDARD DEVIATION $\sigma(\Delta k_s)$ AND VALUES OF THE PARAMETERS IN EQ. (4) AT 303.15 K

1,2-dichloroethane +	b_0	b_1	b_2	$\frac{\sigma(\Delta k_s)}{TPa^{-1}}$
Isopropanol	−70.883	56.227	87.799	±2
Isobutanol	39.253	19.273	14.707	±1
Isopentanol	110.479	−13.327	3.892	±1
Isohexanol	155.720	−30.958	−31.660	±0
Sec-butanol	79.246	12.513	−36.250	±0
Tert-butanol	−33.754	23.616	48.893	±1
Cyclohexanol	142.214	−67.065	115.850	±1

Values of Δk_s are negative in the systems of 1,2-dichloroethane with isopropanol and *tert*-butanol but are positive in the systems of dichloroethane with isobutanol, isopentanol, isohexanol, *sec*-butanol and cyclohexanol. These values may be attributed the following factors: (i) The addition of chloroethane to the associated alcohols may cause the break up of the alcohol aggregates into monomers, leading to an increase in interspecies between the molecules in the mixtures compared with pure components. (ii) Specific and non-specific interactions may also be expected between monomers of alcohol and dichloroethane. The net resultant compressibility will depend on the relative magnitude of these two opposing contributions, which depend markedly on the relative molecular size of the components. The values of Δk_s of isomeric alcohols fall in the order: isopropanol > isobutanol > isopentanol > isohexanol. This order shows that increase in chain length of the alcohol increases the deviation in isentropic compressibility.

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