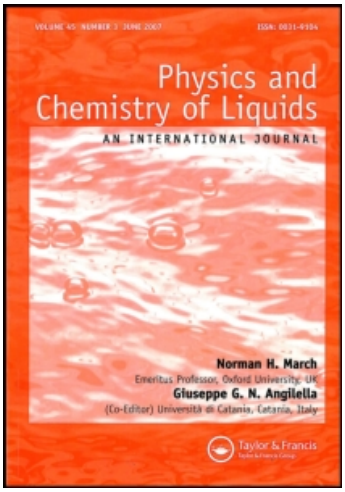

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Alluraiah, G. , Ramanjaneyulu, K. and Krishnaiah, A.(1989) 'Volumetric and Ultrasonic Behaviour of 1-Heptanol with Some Chloroethanes and Chloroethenes at 303.15 K', Physics and Chemistry of Liquids, 20: 4, 187 — 193
To link to this Article: DOI: 10.1080/00319108908028449
URL: http://dx.doi.org/10.1080/00319108908028449

Phys. Chem. Liq., 1989, Vol. 20, pp. 187-193
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VOLUMETRIC AND ULTRASONIC BEHAVIOUR OF 1-HEPTANOL WITH SOME CHLOROETHANES AND CHLOROETHENES AT 303.15 K

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(Received 28 November 1988)

Excess volumes (V^E) and deviations in isentropic compressibilities (K_s) were reported over the entire mole fraction range for mixtures of 1-heptanol with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene, at 303.15 K. The values of V^E and K_s are positive for the systems, 1-heptanol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + trichloroethene and + tetrachloroethene. Inversion in sign of V^E and K_s from positive to negative is observed in mixtures of 1-heptanol with 1,1,2,2-tetrachloroethane. The experimental data were used to explain the effect of successive chlorination and unsaturation of ethane molecule on V^E and K_s.

KEY WORDS: Excess volumes, isentropic compressibilities.

INTRODUCTION

The present paper forms a part of our programme on the measurement of thermodynamic properties of mixtures containing chlorinated hydrocarbons as one of the components[1-3]. We report here new experimental data on excess volumes and deviations in isentropic compressibilities for the mixtures 1-heptanol with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene at 303.15 K. We have undertaken this work to investigate the effect of successive chlorination and unsaturation of ethane molecule on excess volumes and deviations in isentropic compressibilities.

EXPERIMENTAL

1-Heptanol (Koch-Light) is further purified by fractional distillation. 1,2-dichloroethane (BDH), 1,1,1-trichloroethane (Koch-Light) and 1,1,2,2-tetrachloroethane (Riedel) were purified by the methods described by Ramanjaneyulu *et al.*[3]. Trichloroethene (BDH) and tetrachloroethene (BDH) were purified using the method

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described by Riddick and Bunger[4]. The measured densities and boiling points of the purified components were in good agreement with the literature values.

Excess volumes (V^E) were measured directly using a single composition per loading type dilatometer described by Rao and Naidu[5]. Five dilatometers with different capacities were used to cover the entire composition range. The values of V^E are accurate to ± 0.003 cm^3 mol^{-1}. Isentropic compressibilities were calculated from the relation

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

where U and ρ denote sound speed and density. Sound speeds of liquids and liquid mixtures were measured with a single crystal ultrasonic interferometer working at a fixed frequency. The densities of the mixtures were computed from experimental excess volume data (Table 1) using the relation,

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^0 + V^E} \tag{2}$$

where x_1 and x_2 denote mole fractions and M_1 and M_2 stand for the molecular weights of the components 1 and 2 respectively. V^0 and V^E represent ideal molar volume and excess molar volume of the mixture. Densities of the pure components were determined using a bicapillary pycnometer. Deviation in isentropic compressibility was calculated using the relation

$$K_s = k_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \tag{3}$$

where k_s, $k_{s,1}$ and $k_{s,2}$ are the isentropic compressibilities of the mixture and the pure components 1 and 2 respectively. ϕ_1 and ϕ_2 are the volume fractions. K_s represents the deviation in isentropic compressibility from the ideal behaviour. K_s values are accurate to $\pm 1.5\%$.

RESULTS AND DISCUSSION

The experimental V^E values for the five binary liquid mixtures are included in Table 1. Dependence of V^E on mole fraction is graphically presented in Figure 1. The values of density (ρ), sound speed (U), isentropic compressibility (k_s) and deviation in isentropic compressibility (K_s) are included in Table 2. Volume fraction versus K_s plots are included in Figure 2. The V^E values are fitted to an empirical equation of the form,

$$V^E = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{4}$$

where a_0, a_1 and a_2 are adjustable parameters. The values of the parameters, obtained by the method of least squares, are given in Table 3 along with the values of standard deviation, $\sigma(V^E)$.

The values of K_s are also represented by a polynomial similar to Eq. (4) wherein the mole fraction is replaced by volume fraction (ϕ) and the constants a_0, a_1 and a_2 are by b_0, b_1 and b_2. The values of the empirical constants b_0, b_1 and b_2, evaluated by least

Table 1 Excess volumes (V^E) of 1-Heptanol with some chlorinated ethanes and ethenes at 303.15 K.

X_1	V^E / $cm^3\ mol^{-1}$	X_1	V^E / $cm^3\ mol^{-1}$
1-Heptanol + 1,2-dichloroethane			
0.1082	0.068	0.6220	0.072
0.1749	0.085	0.7104	0.062
0.3034	0.090	0.7978	0.050
0.4560	0.086	0.8642	0.038
0.5496	0.072	0.9346	0.023
1-Heptanol + 1,1,1-trichloroethane			
0.1177	0.008	0.5911	0.013
0.2075	0.014	0.6407	0.012
0.3311	0.018	0.7497	0.008
0.4385	0.017	0.8365	0.005
0.5262	0.015	0.9206	0.002
1-Heptanol + 1,1,2,2-tetrachloroethane			
0.1082	0.015	0.5205	0.028
0.2331	0.032	0.6548	0.008
0.3041	0.036	0.7810	−0.008
0.3444	0.038	0.8562	−0.008
0.4479	0.035	0.9304	−0.005
1-Heptanol + trichloroethene			
0.1161	0.017	0.5714	0.020
0.2045	0.025	0.6298	0.018
0.2949	0.028	0.7370	0.012
0.3792	0.027	0.8161	0.008
0.4884	0.024	0.9242	0.003
1-Heptanol + tetrachloroethene			
0.1320	0.012	0.5927	0.014
0.2375	0.020	0.6534	0.012
0.3539	0.024	0.7637	0.006
0.4634	0.020	0.8512	0.003
0.5262	0.018	0.9246	0.001

square analysis, are shown in Table 4 along with the values of standard deviation, $\sigma(K_s)$.

The data included in Tables 1 and 2 shows that the values of V^E and K_s are positive for all the systems over the entire composition range, except in the system 1-heptanol with 1,1,2,2-tetrachloroethane, wherein an inversion in sign from positive to negative is observed.

The values of V^E and K_s may be explained on the basis of two effects, (1) depolymerization of self associated alcohol and (2) formation of weak hydrogen bond of the form O—H···Cl.The actual values of V^E and K_s depend upon the relative strength of the two opposing effects. The experimental results suggest that the former effect determines V^E and K_s in mixtures of 1-heptanol with 1,2-dichloroethane,

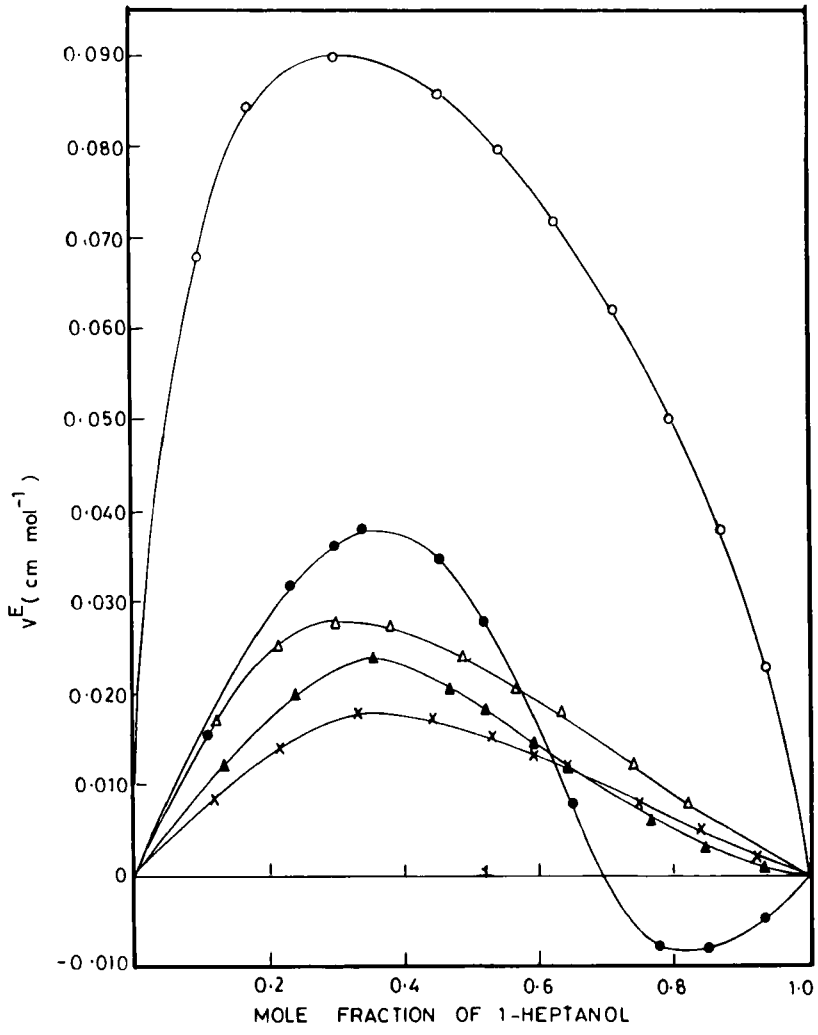

Figure 1 1-Heptanol + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (×), + 1,1,2,2-tetrachloroethane (●), + trichloroethene (△) and + tetrachloroethene (▲).

Table 2 Volume fraction (ϕ_1), density (ρ), sound speed (U), isentropic compressibility (k_s) and deviation in isentropic compressibility (K_s) at 303.15 K.

ϕ_1	ρ / g cm^{-1}	U / m s^{-1}	k_s / TPa^{-1}	K_s / TPa^{-1}
	1-Heptanol + 1,2-dichloroethane			
0.0000	1.23828	1173.3	586.6	—
0.1778	1.16219	1168.2	630.5	21.4
0.2742	1.12132	1171.2	650.1	28.9
0.4371	1.05261	1183.5	678.3	36.5
0.5991	0.98433	1206.0	698.5	36.2
0.6851	0.94812	1222.2	706.1	33.0
0.7111	0.92257	1237.5	707.8	31.4
0.8139	0.89390	1252.2	713.5	24.1
0.8755	0.86797	1269.6	714.8	17.6
0.9190	0.84969	1282.8	715.2	12.5

Table 2 (*continued*)

ϕ_1	ρ / g cm^{-1}	U / m s^{-1}	k_s / TPa^{-1}	K_s / TPa^{-1}
	1-Heptanol + 1,2-dichloroethane			
0.9622	0.83153	1298.7	713.0	4.9
1.0000	0.81573	1311.3	712.9	—
	1-Heptanol + 1,1,1-trichloroethane			
0.0000	1.32094	942.1	852.9	—
0.1584	1.24086	981.9	835.9	5.8
0.2697	1.18454	1011.3	825.4	10.8
0.4112	1.11306	1054.8	807.5	12.6
0.5236	1.05597	1094.7	790.2	11.0
0.6104	1.01244	1128.6	775.4	8.3
0.6710	0.98185	1153.8	765.1	6.4
0.7155	0.94465	1181.7	758.1	5.6
0.8086	0.91235	1215.0	742.5	3.0
0.8783	0.87716	1248.9	730.9	1.1
0.9424	0.84480	1281.0	721.4	0.5
1.0000	0.81573	1311.3	712.9	—
	1-Heptanol + 1,1,2,2-tetrachloroethane			
0.0000	1.57857	1132.8	493.7	—
0.1398	1.47171	1136.7	525.9	1.6
0.2894	1.35743	1147.5	559.5	2.4
0.3693	1.29647	1157.1	576.1	1.4
0.4133	1.26288	1163.1	585.3	1.0
0.5208	1.18091	1181.1	607.0	−0.9
0.5926	1.12628	1194.6	622.2	−1.4
0.7176	1.03105	1224.3	647.1	−3.9
0.8269	0.94779	1253.4	671.6	−3.4
0.8886	0.90073	1272.3	685.8	−2.7
0.9471	0.85608	1291.8	700.0	−1.3
1.0000	0.81573	1311.3	712.9	—
	1-Heptanol + trichloroethene			
0.0000	1.45134	1015.1	668.1	—
0.1713	1.34223	1034.7	695.9	20.1
0.2880	1.26795	1055.7	707.6	26.6
0.3969	1.19873	1081.8	712.8	26.9
0.4901	1.13949	1108.2	714.5	24.4
0.6004	1.06951	1143.0	715.6	20.6
0.6772	1.02072	1170.0	715.6	17.2
0.7280	0.98842	1189.2	715.3	14.6
0.8151	0.93312	1224.0	715.2	10.6
0.8747	0.89527	1251.0	713.7	6.4
0.9505	0.84717	1286.4	713.3	2.6
1.0000	0.81573	1311.3	712.9	—
	1-Heptanol + tetrachloroethene			
0.0000	1.60636	1024.5	593.1	—
0.1734	1.46901	1043.1	625.6	11.7
0.3006	1.36840	1063.2	646.6	17.4
0.4305	1.26571	1091.1	663.6	18.9
0.5437	1.17624	1122.0	675.3	17.1
0.6051	1.12772	1141.5	680.5	14.9
0.6676	1.07841	1163.1	685.5	12.4
0.7223	1.03513	1183.2	690.1	10.5
0.8168	0.96046	1221.9	697.3	6.3
0.8876	0.90458	1254.3	702.7	3.3
0.9442	0.85981	1282.2	707.4	1.2
1.0000	0.81573	1311.3	712.9	—

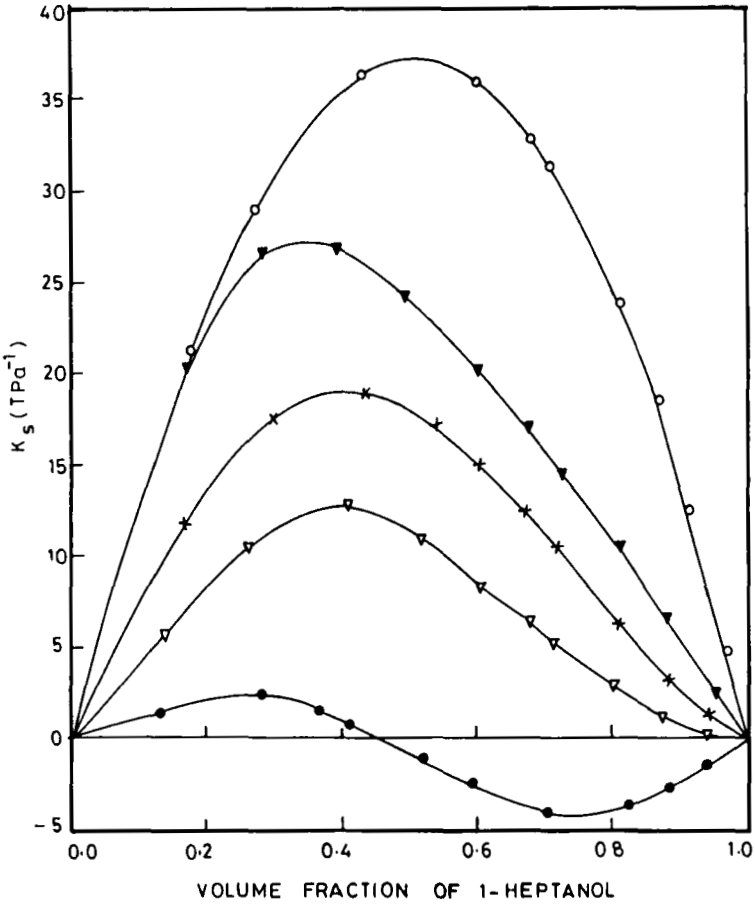

Figure 2 1-Heptanol + 1,2-dichloroethane (○), + 1,1,1-trichloroethane (▽), + 1,1,2,2-tetrachloroethane (●), + trichloroethene (▼) and + tetrachloroethene (×).

Table 3 Values of the parameters, a_0, a_1 and a_2 of the Eq. (4) and the standard deviation, $\sigma(V^E)$ at 303.15 K

1-*Heptanol* +	a_0	a_1	a_2	$\sigma(V^E)$
		$cm^3\ mol^{-1}$		
1,2-Dichloroethane	0.328	−0.213	0.309	0.003
1,1,1-Trichloroethane	0.070	−0.033	−0.036	0.001
1,1,2,2-Tetrachloroethane	0.113	−0.165	−0.106	0.004
Trichloroethene	0.094	−0.080	0.026	0.001
Tetrachloroethene	0.076	−0.063	−0.018	0.001

Table 4 Values of the parameters, b_0, b_1 and b_2 of the Eq. (4) and the standard deviation, $\sigma(K_s)$ at 303.15 K

1-*Heptanol* +	b_0	b_1	b_2	$\sigma(K_s)$
		TPa^{-1}		
1,2-Dichloroethane	152.237	8.639	−7.931	0.7
1,1,1-Trichloroethane	43.697	−23.645	−23.666	0.8
1,1,2,2-Tetrachloroethane	−2.041	−27.817	−3.812	0.5
Trichloroethene	98.638	−59.768	12.792	0.5
Tetrachloroethene	71.694	−32.960	−23.934	0.3

1,1,1-trichloroethane, trichloroethene, tetrachloroethene and also at lower concentrations of 1-heptanol in the system, 1-heptanol + 1,1,2,2-tetrachloroethane. The latter effects operate at higher mole fractions of 1,1,2,2-tetrachloroethane in the system, 1-heptanol + 1,1,2,2-tetrachloroethane. The former effect leads to increase of free lengths as described by Jacobson[6] and results in decrease of sound speed and increase of compressibility. Hence the positive deviations in isentropic compressibilities support the hypothesis used to explain V^E.

The algebraic values of V^E and K_s in mixtures containing chloroethanes and ethenes fall in the order.

1,2-dichloroethane < 1,1,1-trichloroethane < 1,1,2,2-tetrachloroethane
and trichloroethene < tetrachloroethene.

This order suggest that increase of number of chlorine atoms in ethane or ethene molecule results in decrease of V^E and K_s. The trend may be attributed to the increase of strength of interaction between unlike molecules as the number of chlorine atoms increases. V^E and K_s values are larger in mixtures containing chloroethenes than that of chloroethanes with same number of chlorine atoms. This may be ascribed to the partial saturation of interacting ability of chlorine atoms by the Π-electron of the alkene bond in chloroethenes.

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