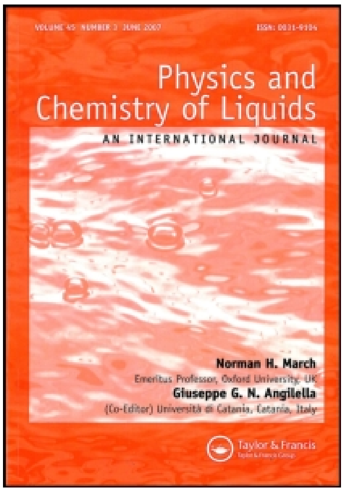

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Sound Speeds and Isentropic Compressibilities of Tetrachloroethylene With *N*-Alcohols

Comparison With Theories

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Sound velocities for binary mixtures of tetrachloroethylene with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol were determined at 303.15 K. The results were analysed in terms of the free length theory (FLT) due to Jacobson and Collision factor theory (CFT) due to Schaaffs. The analyses showed that both theories predict satisfactorily sound velocities of the mixtures. Further, isentropic compressibilities, k_s, of the mixtures were computed by combining sound velocities and density data derived from excess volumes. The deviation in isentropic compressibility, K_s, is negative over the whole range of composition for all the mixtures formed by tetrachloroethylene with alcohols. An inversion in the sign of K_s is observed certain ranges of concentration of tetrachloroethylene with 1-octanol. The deviation in isentropic compressibility was found to decrease with increase in chain length of the alcohol.

1 INTRODUCTION

A survey of the literature has shown that no effort has been made to measure the sound velocity and isentropic compressibility of binary mixtures of alcohols with tetrachloroethylene at 303.15 K, though the other thermodynamic properties have been measured.[1,2] Hence, we report new experimental data for sound velocities and isentropic compressibilities of mixtures of a homologous series of 1-alcohols with tetrachloroethylene. The *n*-alcohols include: 1-propanol; 1-butanol; 1-pentanol; 1-hexanol; 1-heptanol and 1-octanol. Sound velocity data have been analysed in terms of free length theory (FLT) due to Jacobson[3,4] extended to binary mixtures by Kaulgud[5–8] and Collision factor (CFT) theory developed by Schaaffs[9] extended to binary mixtures by Nutsch-Kuhnkies.[10]

THEORETICAL

(a) Free length theory (FLT)

Sound velocity is calculated using Jacobson's formula

$$U_{\mathrm{mix}} L_{\mathrm{mix}} \rho_{\mathrm{mix}}^{1/2} = K \tag{1}$$

where K is temperature dependent constant, U_{mix} and ρ_{mix} are sound velocity and density respectively and L_{mix} is the free length in the mixture. Free length (L_f) for pure liquids is calculated using the following relation,

$$L_f = \frac{K}{U_{\mathrm{exp}} \rho_{\mathrm{exp}}^{1/2}} \tag{2}$$

where U_{exp} and ρ_{exp} are experimentally determined sound velocity and density respectively. The value of K at 303.15 K is taken as 631, given by Jacobson. The surface areas per mole for the pure components is calculated using the following expression

$$Y = \frac{2V_a}{L_f} \tag{3}$$

and $V_a = V_T - V_0$ where V_a is the available volume per mole and V_0 and V_T and the molar volumes at absolute zero and at absolute temperature, T, as shown below:

$$V_0 = V_T\left(1 - \frac{T}{T_c}\right)^{0.3} \tag{4}$$

L_{mix} is calculated employing the expression

$$L_{\mathrm{mix}} = \frac{2[V_m - (n_1 V_0^1 + n_2 V_0^2)]}{n_1 Y_1 + n_2 Y_2} \tag{5}$$

where n's represent mole fraction and V_m represents molar volume of the mixtures.

(b) Collision factor theory (CFT)

On the basis of CFT Schaaffs developed the following formula for sound velocity in pure liquids

$$U = U_\infty S r_f = U_\infty S \frac{B}{V_m} \tag{6}$$

All the symbols in Eq. (6) have the usual significance described elsewhere.[11] Nutsch-Kuhnkies[10] extended this concept to the binary mixtures as given below

$$U_{\text{mix}} = U_{\infty} S_{\text{mix}} r_{f\,\text{mix}} \tag{7}$$

This may be written as,

$$U_{\text{mix}} = U_{\infty}[n_1 S_1 + n_2 S_2] \frac{(n_1 B_1 + n_2 B_2)}{V_m} \tag{8}$$

The actual volume of the molecule per mole for the pure components denoted by (B_1 and B_2) is calculated using the following equation

$$B = \frac{4\pi}{3} r_m^3 N \tag{9}$$

where N is the Avogadro's number and r_m is the molecular radius. The value of r_m is the average of those calculated using the semi-empirical equation of Schaaffs,[9] the expression described by Gopala Rao and Venkataseshaiah[12] and equation derived by Chaturvedi and Pratap.[13]

2 EXPERIMENTAL

Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. Alcohols were purified by the methods described previously.[14] The purity of the compounds was checked by measuring densities and boiling points. The boiling points at 760 mm Hg were measured using a Swietoslawski type ebulliometer which gave an accuracy of ±0.2°C. The density of pure compounds at 303.15 K was measured using a bi-capillary pycnometer with an accuracy of 5 parts in 10^5. The measured values are reported in Table I along with the literature values.[15,16]

TABLE I

Boiling points and densities of the pure components at 303.15 K

	Boiling point (K)		Density, ρ ($\text{g} \cdot \text{cm}^{-3}$)	
Compound	Present work	Literature[14,15]	Present work	Literature[14]
Tetrachloroethylene	394.28	304.4	1.60634	1.60640
1-Propanol	370.25	370.34	0.79596	0.79600
1-Butanol	390.75	390.87	0.80201	0.80206
1-Pentanol	411.0	411.21	0.80755	0.80764
1-Hexanol	430.38	431.00	0.81195	0.81201
1-Heptanol	449.00	449.15	0.81572	—
1-Octanol	467.45	467.6	0.82188	0.82192

Ultrasonic sound velocities were measured with a single crystal interferometer working at a fixed frequency of 1 MHz and were accurate to ±0.075%. The temperature of the experimental liquid in the cell was maintained by circulating water from a thermostatic bath through the double walled liquid container. All the measurements were made at a constant temperature that could be maintained to ±0.01 K. Densities in respect of mixtures were computed from experimental excess volume data reported previously,[1] using the relation,

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^0 + V^{\mathrm{E}}} \tag{10}$$

where the subscripted x and M represent the mole fraction and molecular weight of the corresponding component. V^0 stands for ideal molar volume and V^E denotes excess molar volume.

RESULTS AND DISCUSSION

The surface area Y, and the collision factor S, of the pure components used in FLT and CFT were calculated using the experimentally determined sound velocities and densities. The remaining quantities, critical temperature, surface tension, and ratio of specific heats, which were used in the calculation of V_0 and r_m were taken from the literature.[15–17] Surface tension for 1-heptanol was calculated using Auerbach[18] relation. The values of molar volume V, available volume V_a, free length L_f, surface area Y, collision factor S, and the average radius of the molecule r_m, of the pure components are given in Table II.

Isentropic compressibilities k_s were computed using the relation,

$$k_s = u^{-2}\rho^{-1} \tag{11}$$

where u and ρ denotes sound velocity and density, respectively. The deviation isentropic compressibility K_s has been calculated from the equation,

$$K_s = k_s - \phi_1 k_{s,1} - \phi_s k_{s,2} \tag{12}$$

where k_s, $k_{s,1}$ and $k_{s,2}$ are the isentropic compressibilities of the pure components and ϕ_1 and ϕ_2 are the volume fractions. Experimental data for density, sound velocity, deviation isentropic compressibilities, K_s, defined by Eq. (12), and predicted sound velocities for the six binary liquid mixtures are included in Table III and the plots of K_s against volume fraction of tetrachloroethylene is presented in Figure 1. The dependence of K_s on volume fraction is expressed by an empirical equation of the form,

$$K_s = \phi_1(1 - \phi_1) \sum_{k=1}^{p} a_k (1 - 2\phi_1)^n \tag{13}$$

TABLE II

Molar volume (V), actual volume per molecule (V_0), available volume (V_a), free length (L_f), surface area (Y), collision factor (S) and average molecular radius (r_m) of the pure liquid compounds at 303.15 K.

Compound	V (cm^3 mol^{-1})	V_0 (cm^3 mol^{-1})	V_a (cm^3 mol^{-1})	L_f Å	Y	S	r_m Å
Tetrachloroethylene	103.235	84.414	18.821	0.4824	78.03	1.3396	2.7013
1-Propanol	75.519	58.837	16.682	0.5941	56.16	1.7296	2.3443
1-Butanol	92.418	73.283	19.135	0.5759	66.45	1.7126	2.5387
1-Pentanol	109.120	87.689	21.431	0.5586	76.73	1.7015	2.7139
1-Hexanol	125.845	102.411	23.434	0.5451	85.98	1.7352	2.8477
1-Heptanol	142.206	116.947	25.259	0.5332	94.74	1.7295	2.9889
1-Octanol	158.454	131.919	26.535	0.5229	101.49	1.7258	3.1171

TABLE III

Mole fraction x_1, volume fraction ϕ_1 of the tetrachloroethylene, density ρ, speed of sound u, isentropic compressibilities k_s calculated from Eq. (11), K_s calculated from Eq. (12), and predicted sound velocities for the binary liquid mixtures of tetrachloroethylene + n-alcohols at 303.15 K.

x_1	ϕ_1	ρ g · cm^{-3}	U_{exp} m sec^{-1}	k_s TPa^{-1}	K_s TPa^{-1}	U_{theo} (F.L.T) m sec^{-1}	U_{theo} (C.F.T) m sec^{-1}
			Tetrachloroethylene + 1-propanol				
0.0000	0.0000	0.79596	1190.5	886.4	—	1190.5	1190.5
0.0745	0.0989	0.87301	1169.4	837.7	−18.8	1159.5	1183.8
0.1715	0.2202	0.98215	1143.7	778.4	−41.5	1119.4	1174.5
0.2408	0.3019	1.04927	1132.6	742.9	−52.3	1100.8	1166.5
0.3219	0.3929	1.12004	1124.6	705.9	−61.8	1085.2	1155.9
0.4260	0.5073	1.21529	1105.7	673.0	−60.2	1066.5	1140.2
0.5014	0.5783	1.26531	1095.0	659.1	−52.7	1060.8	1128.8
0.6011	0.6726	1.34590	1077.7	639.7	−43.6	1049.3	1111.8
0.6901	0.7522	1.41055	1062.6	627.9	−31.3	1042.6	1095.5
0.7698	0.8021	1.44679	1054.2	621.9	−22.2	1044.8	1080.1
0.8601	0.8934	1.52053	1040.4	607.6	−9.0	1035.8	1061.9
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1032.1
			Tetrachloroethylene + 1-butanol				
0.0000	0.0000	0.80201	1223.4	833.1	—	1223.4	1223.4
0.0802	0.0886	0.87929	1197.4	793.2	−17.8	1186.3	1210.4
0.1801	0.1966	0.96077	1175.8	752.8	−31.4	1156.3	1193.6
0.2523	0.2732	1.03004	1157.2	725.0	−40.1	1131.8	1180.9
0.3499	0.3748	1.10528	1142.0	693.7	−46.2	1112.1	1162.8
0.4418	0.4705	1.18152	1127.6	665.7	−50.3	1093.5	1146.4
0.5414	0.5553	1.25210	1111.1	646.9	−48.1	1081.1	1127.3
0.6303	0.6551	1.33109	1092.9	629.0	−41.2	1064.9	1109.8
0.7217	0.7424	1.40534	1075.9	614.7	−33.8	1052.9	1091.2
0.7977	0.8146	1.45931	1064.2	605.1	−25.4	1046.8	1075.5
0.8811	0.8919	1.52354	1049.5	595.9	−15.3	1038.8	1057.8
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1232.1
			Tetrachloroethylene + 1-pentanol				
0.0000	0.0000	0.80755	1257.1	783.6	—	1257.1	1257.1
0.1023	0.0970	0.88621	1225.8	751.0	−13.2	1215.2	1235.2
0.1765	0.1682	0.94223	1206.8	728.7	−21.4	1191.1	1218.1
0.2655	0.2543	1.01167	1188.8	699.4	−33.5	1164.3	1199.3
0.3425	0.3295	1.07165	1173.5	677.6	−40.4	1143.9	1182.2
0.4419	0.4275	1.15004	1153.2	653.8	−44.6	1120.4	1160.0
0.5407	0.5262	1.22831	1128.7	639.1	−39.7	1100.1	1137.8
0.6299	0.6162	1.30054	1107.3	627.1	−33.8	1083.5	1117.5
0.7105	0.6983	1.36642	1089.0	617.1	−27.3	1070.0	1099.1
0.8002	0.7907	1.44140	1066.6	609.8	−16.3	1056.1	1078.5
0.9020	0.8967	1.52414	1044.2	601.7	−3.2	1043.4	1054.9
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1032.1

TABLE II (*continued*)

x_1	ϕ^1	ρ g · cm^{-3}	U_{exp} m sec^{-1}	k_s TPa^{-1}	K_s TPa^{-1}	U_{theo} (F.L.T) m sec^{-1}	U_{theo} (C.F.T) m sec^{-1}
Tetrachloroethylene + 1-hexanol							
0.0000	0.0000	0.81195	1284.7	746.2	—	1284.7	1284.7
0.1139	0.0952	0.88823	1251.9	718.3	−12.5	1243.2	1256.2
0.2096	0.1783	0.95421	1221.7	702.2	−27.2	1212.1	1232.2
0.2815	0.2427	1.00531	1216.6	672.1	−34.8	1190.4	1214.1
0.3900	0.3434	1.09023	1189.7	648.1	−42.5	1157.5	1186.8
0.4921	0.4422	1.16374	1169.2	628.6	−46.1	1134.1	1161.1
0.5718	0.5598	1.25703	1135.5	616.9	−38.6	1101.9	1140.5
0.6618	0.6155	1.30129	1122.4	610.0	−36.6	1095.4	1118.1
0.7703	0.7328	1.39477	1089.5	604.0	−23.6	1073.1	1090.6
0.8419	0.8133	1.45793	1068.8	600.4	−14.2	1059.7	1072.4
0.9319	0.9180	1.54166	1043.3	595.9	−1.7	1043.4	1049.4
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1032.1
Tetrachloroethylene + 1-heptanol							
0.0000	0.0000	0.81572	1310.2	714.1	—	1310.2	1310.2
0.1204	0.0902	0.88731	1276.0	692.2	−10.2	1268.5	1276.6
0.2218	0.1711	0.95123	1253.3	669.3	−22.6	1235.7	1248.3
0.3066	0.2425	1.01004	1231.1	653.2	−29.4	1208.2	1224.7
0.4104	0.3268	1.07502	1212.6	632.6	−39.1	1131.4	1198.3
0.4912	0.4114	1.14113	1189.7	619.1	−41.6	1156.6	1173.3
0.5945	0.5149	1.22304	1163.9	603.5	−43.8	1128.9	1144.5
0.6609	0.5853	1.27905	1142.1	599.4	−38.8	1111.6	1126.1
0.7707	0.7088	1.38012	1104.7	593.7	−28.5	1083.1	1095.6
0.8305	0.7801	1.43485	1087.3	589.5	−23.4	1069.6	1078.9
0.9215	0.8947	1.52399	1056.7	587.6	−10.4	1049.2	1053.8
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1032.1
Tetrachloroethylene + 1-octanol							
0.0000	0.0000	0.82188	1330.0	686.9	—	1330.9	1330.9
0.1311	0.0893	0.89233	1299.1	664.0	−13.7	1287.8	1291.7
0.2300	0.1626	0.98451	1255.4	644.5	−25.7	1234.0	1262.2
0.3211	0.2351	1.01305	1249.9	631.9	−30.9	1224.2	1234.9
0.4019	0.3039	1.06172	1232.0	620.5	−35.3	1202.9	1210.8
0.5102	0.4037	1.14214	1199.7	608.3	−37.2	1169.4	1178.5
0.5919	0.4852	1.20310	1173.9	603.1	−34.1	1146.9	1154.1
0.6905	0.5918	1.28704	1137.1	600.9	−25.3	1118.4	1124.6
0.7911	0.7111	1.38054	1099.1	599.6	−14.4	1089.9	1094.5
0.8398	0.7731	1.43109	1078.8	600.4	−7.3	1075.5	1079.9
0.9510	0.9265	1.55092	1042.3	593.5	+1.6	1044.8	1046.7
1.0000	1.0000	1.60634	1032.1	584.4	—	1032.1	1032.1

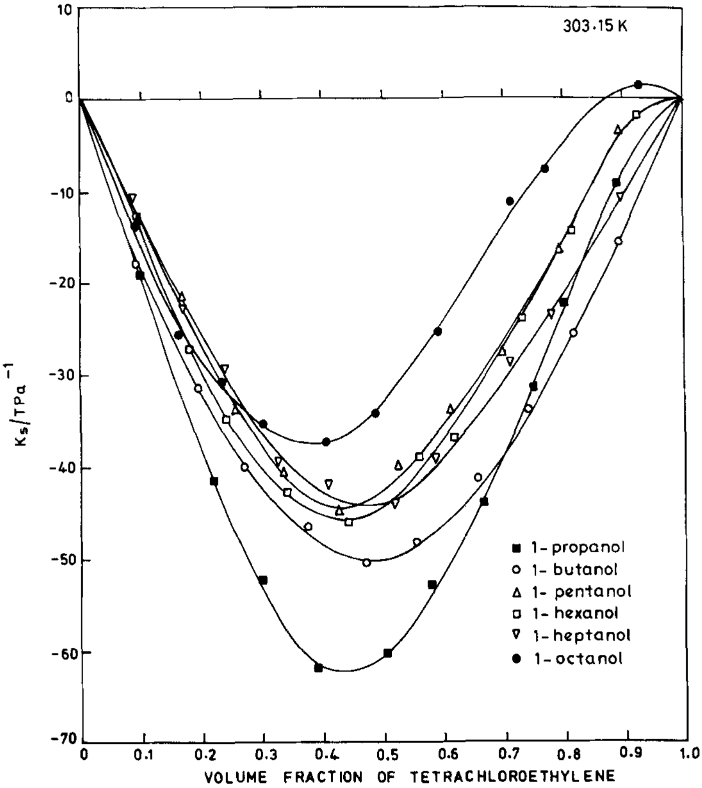

FIGURE 1 Parameter K_s values versus volume fraction curves for tetrachloroethylene with *n*-alcohols at 303.15 K.

The parameters a_k determined by the method of least squares analysis are given in Table IV along with the standard deviation $\sigma(K_s)$. The results in Table III show that sound velocities calculated in terms of FLT and CFT are in good agreement with the experimental data. However, a close examination of the data shows that the divergence between the FLT sound velocities and the experimental results decreases from 1-propanol to 1-hexanol. The divergence between the CFT sound velocities and the experimental data, on the other hand, increases from 1-propanol to 1-hexanol.

Values of K_s are negative in all the mixtures over the entire range of composition except for the mixture formed by tetrachloroethylene + 1-octanol for which an inversion in the sign of K_s is observed over part of concentration of tetrachloroethylene. K_s is maximum over the range

TABLE IV

Parameters of Eq. (13) and standard deviation $\sigma(K_s)$ of experimental values for the binary mixtures of tetrachloroethylene with *n*-alcohols at 303.15 K.

	a_0	a_1	a_2	$\sigma(K_s)$
Compound		TPa^{-}		
Tetrachloroethylene + 1-propanol	−240.9310	78.0752	140.7529	1
Tetrachloroethylene + 1-butanol	−193.8867	31.9759	12.5900	1
Tetrachloroethylene + 1-pentanol	−170.8268	67.6527	122.3839	1
Tetrachloroethylene + 1-hexanol	−179.5643	73.4316	128.5557	1
Tetrachloroethylene + 1-heptanol	−176.3756	19.4827	90.3477	2
Tetrachloroethylene + 1-octanol	−131.6212	118.5493	74.5098	1

0.5 volume fraction of tetrachloroethylene. This may be explained as follows: In solutions, rich in alcohols, the tetrachloroethylene molecules get interstitial accommodation in alcohol aggregates. This factor will mitigate the effect of depolymerization of alcohol aggregates. According to Foort and Moore,[19] the difference in the boiling points of two components is a rough measure of strength of interaction between molecules. The data given in Table V and Figure 2 show that the boiling point difference between the two components is roughly proportional to K_s (for equimolar composition). Further the negative values of K_s in the binaries fall in the order:

1-propanol > 1-butanol > 1-pentanol ≈ 1-hexanol ≈ 1-heptanol > 1-octanol

This order shows that increase in chain length of the alcohol decreases the deviation in isentropic compressibility.

TABLE V

Δ(bp) (*n*-alcohols-tetrachloroethylene) and $K_s(\phi_1 \approx 0.5)$ calculated from Eq. (12) at 303.15 K.

Compound	Boiling point (K)	bp bp(Alcohols-tetrachloethylene)	$K_s(\phi_1 \approx 0.5)$ TPa^{-1}
Tetrachloroethylene	394.28	—	—
1-Propanol	370.25	−24	−60
1-Butanol	390.75	−4	−50
1-Pentanol	411.0	17	−45
1-Hexanol	430.88	37	−41
1-Heptanol	449.00	55	−40
1-Octanol	467.45	73	−33

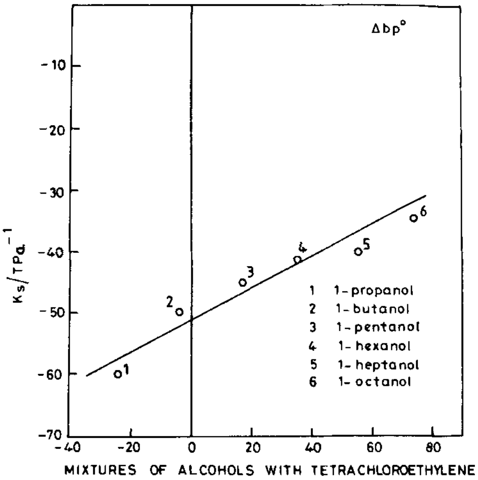

FIGURE 2 Parameter Δ(bp) versus $K_s(\phi_1 \approx 0.5)$ curves for tetrachloroethylene with *n*-alcohols at 303.15 K.

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