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Ultrasonic Studies of Binary Mixtures of Trichloroethylene and Tetrachloroethylene with some Aliphatic and Alicyclic Ketones at 303.15 K

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Ultrasonic sound velocities and densities were measured for the binary mixtures of trichloroethylene and tetrachloroethylene with some aliphatic and alicyclic ketones namely, methylethylketone, methylpropylketone, diethylketone, cyclopentanone, and cyclohexanone at 303.5 K. Isentropic compressibilities k_s and deviation in isentropic compressibility from ideal behaviour have been calculated from the results. All the mixtures formed by trichloroethylene and tetrachloroethylene with ketones at 303.15 K exhibit negative deviation from ideal behaviour over the entire range of composition.

1 INTRODUCTION

In continuation of earlier work on excess volumes, V^E , of binary mixtures of trichloroethylene + ketones,¹ and tetrachloroethylene + ketones,² sound velocities and isentropic compressibilities (k_s) of trichloroethylene and tetrachloroethylene with some aliphatic and alicyclic ketones at 303.15 are reported here.

2 EXPERIMENTAL

Apparatus

Ultrasonic sound velocities were measured with a single crystal interferometer working at a fixed frequency of 1 MHz and were accurate to $\pm 0.075\%$. 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 are computed from experimental excess volumes data reported previously,^{1,2} using the relation

$$\rho = \frac{X_A M_A + X_B M_B}{V + V^E} \quad (1)$$

X_A , X_B denote the mole fractions of the two components, and M_A and M_B stands for the molecular weights. V represents the ideal molar volume of the mixture. V^E denotes the excess molar volume.

Materials

Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. Trichloroethylene (BDH), methylpropylketone (Fluka), and cyclohexanone (BDH) were purified by standard method described by Riddick and Bunger.³ Methyleneethylketone (BDH) and diethylketone (BDH) were dried over potassium carbonate for 3 days, then boiled for 2 hours and distilled as reported in literature.⁴ Cyclopentanone (Fluka) was dried over anhydrous sodium sulphate for 2 days and then fractionally distilled. 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 $\pm 0.2^\circ\text{C}$. The densities of pure compounds were 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.^{3,5}

TABLE I

Boiling points and densities of the pure compound at 303.15 K

Compound	Boiling point K		Density, ρ g cm ⁻³	
	Expt.	Lit. ^{3,5}	Expt.	Lit. ^{3,5}
Trichloroethylene	360.20	360.34	1.45134	1.4514
Tetrachloroethylene	394.28	394.4	1.60634	1.60640
Methyleneethylketone	352.60	352.79	0.79448	0.79452
Methylpropylketone	373.40	373.55	0.79661	0.79656
Diethylketone	375.00	375.15	0.80460	0.80461
Cyclopentanone	403.70	403.80	0.93898	0.93902
Cyclohexanone	428.70	428.80	0.93760	0.93761

Results and Discussion

Isentropic compressibility (k_s) was derived from the expression

$$k_s = u^{-2} \rho^{-1} \quad (2)$$

where u and ρ denotes sound velocity and density respectively. The k_s values were accurate to $\pm 1 \text{ TPa}^{-1}$. The deviation in isentropic compressibility (K_s) has been calculated from the equation

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

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 volume fractions. Densities, sound velocities, isentropic compressibilities, deviations in isentropic compressibility for all the binary systems are listed in Tables II and III. The plots of K_s against volume fraction of trichloroethylene and tetrachloroethylene are presented in Figures 1 and 2. The experimental K_s values against volume fraction ϕ_1

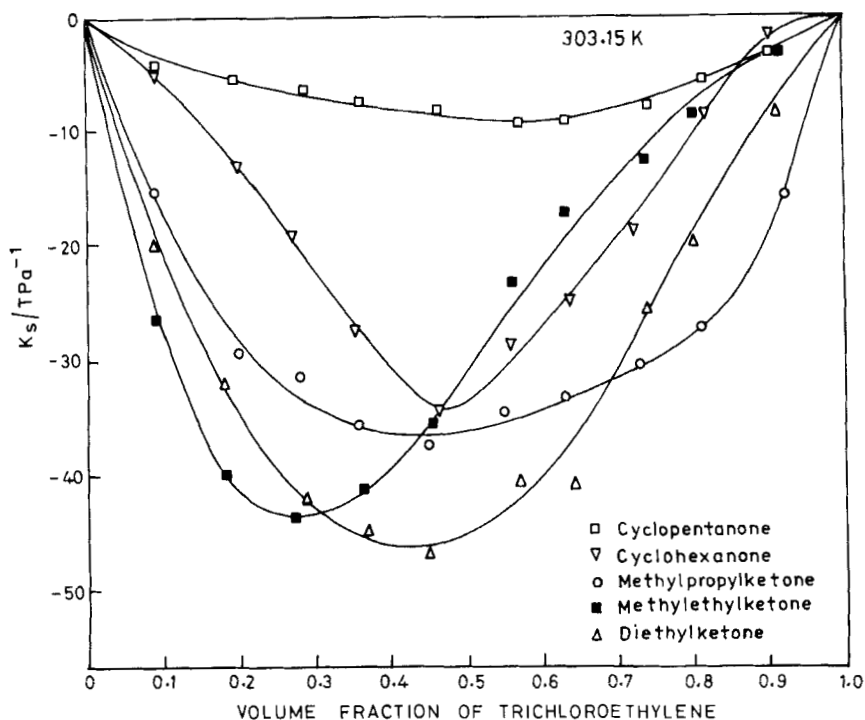


FIGURE 1 Parameter K_s versus volume fraction curves for trichloroethylene with ketones at 303.15 K.

TABLE II

Volume fraction ϕ_1 of trichloroethylene, density ρ , sound velocity u , isentropic compressibility K_s , from Eq. (2) and K_s , from Eq. (3) for trichloroethylene + ketones at 303.15 K

ϕ_1	ρ g cm ⁻³	U m sec ⁻¹	k_s TPa ⁻¹	K_s Tpa ⁻¹
Trichloroethylene + diethylketone				
0.0000	0.80460	1196.6	868.0	—
0.0871	0.87359	1173.8	830.8	-19.9
0.1823	0.92973	1159.7	799.8	-32.1
0.2911	0.99978	1141.0	768.3	-42.0
0.3669	1.05238	1125.4	750.2	-45.1
0.4505	1.11314	1107.7	732.1	-46.7
0.5710	1.18289	1087.7	714.6	-40.3
0.6404	1.22953	1054.0	732.1	-40.6
0.7389	1.28653	1056.7	696.1	-25.5
0.8008	1.32140	1047.4	689.8	-19.6
0.9117	1.40528	1023.9	678.8	-8.6
1.0000	1.45134	1014.2	669.9	—
Trichloroethylene + methylethylketone				
0.0000	0.79448	1171.1	917.8	—
0.0881	0.86329	1154.2	869.5	-26.5
0.1823	0.92453	1139.8	832.6	-40.0
0.2719	0.97930	1124.9	806.9	-43.5
0.3616	1.04414	1102.9	787.3	-40.9
0.4555	1.10568	1084.2	769.4	-35.5
0.5601	1.17027	1063.3	755.8	-23.2
0.6309	1.21281	1052.5	744.3	-17.1
0.7299	1.26997	1042.5	724.5	-12.4
0.8016	1.31938	1032.8	710.6	-8.5
0.9197	1.39592	1020.3	688.1	-3.2
1.0000	1.45134	1014.2	669.9	—
Trichloroethylene + methylpropylketone				
0.0000	0.79661	1200.3	871.3	—
0.0902	0.86071	1177.7	837.7	-15.4
0.2010	0.93182	1157.3	801.3	-29.5
0.2814	0.98198	1140.4	783.0	-31.6
0.3618	1.04454	1120.3	762.8	-35.6
0.4519	1.10937	1101.4	743.1	-37.2
0.5505	1.16829	1085.8	726.0	-34.4
0.6339	1.22270	1072.7	710.7	-32.9
0.7314	1.28935	1057.5	693.6	-30.4
0.8111	1.32997	1050.9	680.0	-27.1
0.9204	1.40178	1031.7	670.2	-15.7
1.0000	1.45134	1014.2	669.9	—
Trichloroethylene + cyclohexanone				
0.0000	0.93760	1388.4	553.3	—
0.0881	0.99354	1342.1	558.8	-4.8
0.2019	1.04592	1302.7	563.4	-13.4
0.2716	1.08257	1277.6	565.9	-19.1

TABLE II (continued)

ϕ_1	ρ g cm ⁻³	U m sec ⁻¹	k_s TPa ⁻¹	K_s TPa ⁻¹
0.3512	1.12950	1249.6	567.1	-27.2
0.4593	1.18784	1212.6	572.5	-34.4
0.5554	1.23107	1173.9	589.5	-28.6
0.6378	1.27050	1142.4	603.1	-24.6
0.7219	1.31151	1109.7	619.2	-18.3
0.8105	1.36409	1070.7	639.5	-8.3
0.8997	1.41276	1038.4	656.5	-1.7
1.0000	1.45134	1014.2	669.9	—
Trichloroethylene + cyclopentanone				
0.0000	0.93898	1373.1	564.9	—
0.0912	0.99778	1325.9	570.1	-4.4
0.1947	1.04959	1281.9	579.8	-5.5
0.2882	1.08654	1250.1	588.9	-6.3
0.3615	1.12397	1222.5	595.3	-7.6
0.4612	1.18250	1182.1	605.2	-8.1
0.5703	1.24117	1144.0	615.6	-9.2
0.6336	1.26985	1124.8	622.4	-9.0
0.7409	1.33005	1088.1	635.0	-7.7
0.8156	1.36668	1065.1	645.0	-5.5
0.9002	1.40985	1039.6	656.3	-3.1
1.0000	1.45134	1014.2	669.0	—

TABLE III

Volume fraction ϕ_1 of tetrachloroethylene, density ρ , sound velocity u , isentropic compressibility k_s from Eq. (2) and K_s from Eq. (3) for tetrachloroethylene + ketones at 303.15 K

ϕ_1	ρ g cm ⁻³	U m sec ⁻¹	k_s TPa ⁻¹	K_s TPa ⁻¹
Tetrachloroethylene + diethylketone				
0.0000	0.80460	1196.6	868.0	—
0.0902	0.88414	1179.3	813.3	-29.1
0.2019	0.97623	1161.6	759.2	-51.6
0.2913	1.04114	1152.2	723.5	-61.9
0.3666	1.10258	1140.6	697.2	-66.8
0.4518	1.17717	1125.9	670.1	-69.8
0.5505	1.25535	1110.2	646.3	-65.6
0.6418	1.32919	1092.0	630.9	-55.1
0.7299	1.39709	1078.2	615.7	-45.3
0.8107	1.46403	1062.6	604.9	-33.2
0.9117	1.54107	1043.9	595.5	-13.9
1.0000	1.60634	1032.1	584.4	—
Tetrachloroethylene + methylethylketone				
0.0000	0.79448	1171.1	917.8	—
0.0851	0.86401	1158.9	861.8	-27.6

(continued over page)

TABLE III (continued)

ϕ_1	ρ g cm ⁻³	u m sec ⁻¹	k_s TPa ⁻¹	K_s TPa ⁻¹
0.1923	0.95889	1140.6	801.6	-52.1
0.2779	1.03105	1126.9	763.8	-61.3
0.3665	1.11145	1110.4	729.7	-65.9
0.4505	1.17205	1100.5	704.5	-63.1
0.5614	1.26091	1086.2	672.2	-58.4
0.6689	1.34570	1073.4	645.0	-49.8
0.7211	1.38012	1070.2	632.2	-45.2
0.8002	1.45413	1056.9	615.6	-35.4
0.9213	1.55420	1041.6	593.0	-17.7
1.0000	1.60634	1032.1	584.4	—
Tetrachloroethylene + methylpropylketone				
0.0000	0.79661	1200.3	871.3	—
0.0902	0.87491	1174.9	827.9	-17.5
0.1903	0.96006	1149.3	788.5	-28.2
0.2844	1.03892	1126.8	758.1	-31.6
0.3513	1.09028	1116.5	735.8	-34.7
0.4419	1.16278	1099.0	712.0	-32.5
0.5782	1.27948	1076.3	674.7	-30.7
0.6311	1.31200	1073.4	661.5	-28.7
0.7409	1.40271	1060.4	634.0	-24.7
0.8111	1.46833	1050.9	616.7	-21.9
0.9116	1.54742	1042.9	594.1	-15.7
1.0000	1.60634	1032.1	584.4	—
Tetrachloroethylene + cyclohexanone				
0.0000	0.93760	1388.4	553.3	—
0.0924	1.00556	1346.6	548.4	-7.8
0.2112	1.08444	1301.7	544.2	-15.7
0.2713	1.12407	1281.0	542.1	-19.6
0.3605	1.18209	1250.9	540.6	-23.9
0.4500	1.24771	1218.1	540.2	-27.1
0.5619	1.32408	1172.6	549.3	-21.5
0.6398	1.37503	1142.9	556.8	-16.4
0.7288	1.43570	1111.2	564.1	-11.9
0.8081	1.48516	1084.3	572.7	-5.7
0.9312	1.57053	1046.7	581.2	-1.1
1.0000	1.60634	1032.1	584.4	—
Tetrachloroethylene + cyclopentanone				
0.0000	0.93898	1373.1	564.9	—
0.0862	1.00583	1329.7	562.3	-4.3
0.1829	1.07291	1291.3	559.0	-9.5
0.2711	1.12986	1260.5	557.0	-13.2
0.3660	1.19605	1224.1	557.9	-14.1
0.4617	1.25051	1194.5	560.5	-13.4
0.5665	1.32719	1155.7	564.1	-11.8
0.6309	1.37059	1134.7	566.7	-10.5
0.7305	1.43480	1102.7	573.2	-9.1
0.8155	1.49237	1077.7	576.9	-6.9
0.9214	1.56602	1051.6	577.4	-3.3
1.0000	1.60634	1032.1	584.4	—

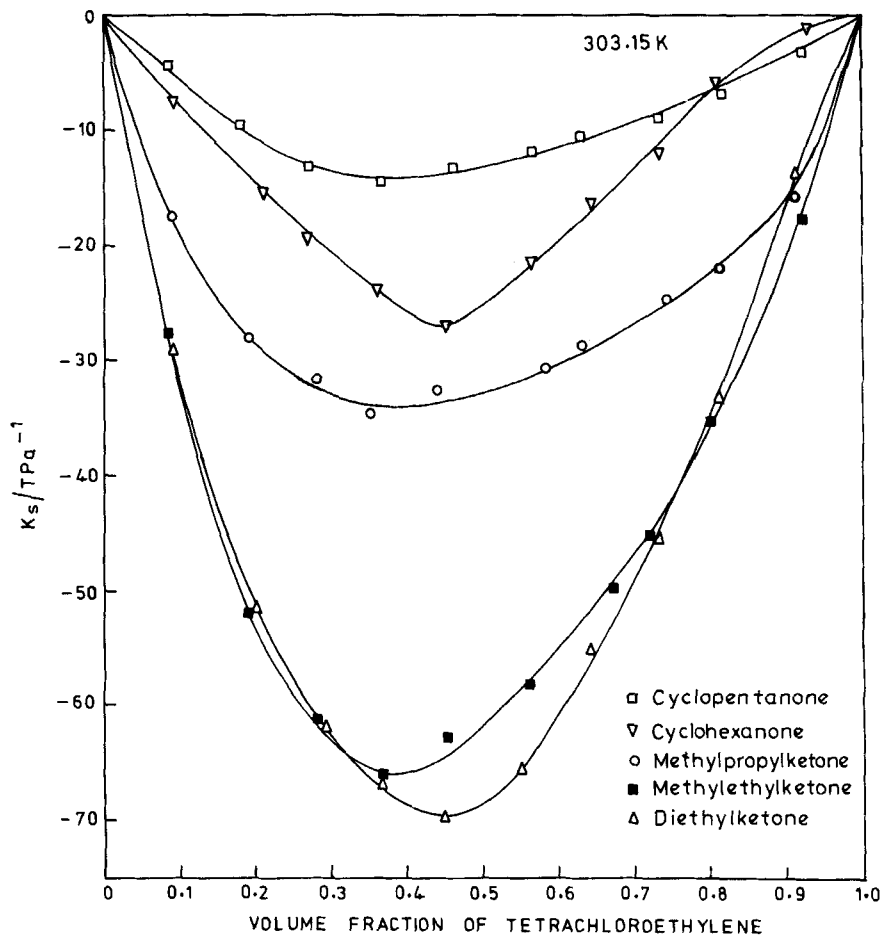


FIGURE 2 Parameter K_s versus volume fraction curves for tetrachloroethylene with ketones at 303.15 K.

may be represented by

$$K_s/\phi_1\phi_2 = a_0 + a_1(\phi_1 - \phi_2) + a_2(\phi_1 - \phi_2)^2 \quad (4)$$

where a_0 , a_1 , a_2 are adjustable parameters obtained by the method of least squares and are given in Table IV along with the standard deviation $\sigma(K_s)$. The K_s curves are negative over the entire range of composition for all of the systems formed by trichloroethylene with ketones. This could be due to existence of specific interaction between the dipole of the ketones and polarizable of trichloroethylene.

TABLE IV

Least square parameters in Eq. (4) and the standard deviation σ (TPa⁻¹) of K_s at 303.15 K

System	a_0	a_1	a_2	$\sigma(K_s)$
	TPa ⁻¹			
Trichloroethylene + methylethylketone	-119.5279	174.7749	-97.8379	2
Trichloroethylene + methylpropylketone	-142.2650	-2.9802	-87.4645	1
Trichloroethylene + diethylketone	-174.4509	81.5326	0.8963	1
Trichloroethylene + cyclopentanone	-33.7096	3.0128	-13.1836	1
Trichloroethylene + cyclohexanone	-124.0364	23.4827	134.7536	2
Tetrachloroethylene + methylethylketone	-256.2268	80.0246	-47.9458	2
Tetrachloroethylene + methylpropylketone	-124.7354	23.4517	-111.6879	1
Tetrachloroethylene + diethylketone	-269.5398	97.4790	7.0700	1
Tetrachloroethylene + cyclopentanone	-52.3289	11.9238	-2.8449	1
Tetrachloroethylene + cyclohexanone	-93.7049	43.9993	58.7886	1

The K_s curves for the mixtures of tetrachloroethylene with ketones are also negative over the whole composition range. This may be examined on the basis of the electron donating capacities of the carbonyl group of the ketones which induces dipole interaction between the dipole of the ketones and tetrachloroethylene. The negative values of K_s for all the binary systems with trichloroethylene and tetrachloroethylene fall in the following order:

Diethylketone > methylethylketone > methylpropylketone >
cyclohexanone > cyclopentanone

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