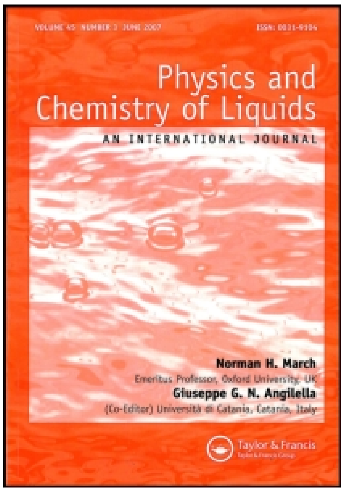

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Reddy, D. V. B. , Krishnaiah, A. and Ramanjaneyulu, K.(1989) 'Ultrasonic Velocities and Isentropic Compressibilities of Acetophenone with some Chloroethanes and Chloroethenes at 303.15 K', Physics and Chemistry of Liquids, 20: 4, 221 — 226

To link to this Article: DOI: 10.1080/00319108908028452

URL: http://dx.doi.org/10.1080/00319108908028452

Phys. Chem. Liq., 1989, Vol. 20, pp. 221–226
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ULTRASONIC VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF ACETOPHENONE WITH SOME CHLOROETHANES AND CHLOROETHENES AT 303.15 K

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(Received 9 November 1988)

Ultrasonic velocities (U) and densities (ρ) for binary liquid mixtures of acetophenone with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene were determined over the whole composition range at 303.15 K. Isentropic compressibilities (k_s) and deviation in isentropic compressibilities (K_s) were computed from experimental sound velocities and densities. The experimental data were used to explain the effect of successive chlorination and unsaturation on ethane molecules.

KEY WORDS: Ultrasonic velocities, Isentropic compressibilities.

INTRODUCTION

In continuation of our work, on the thermodynamic properties of binary mixtures consisting of chloroethanes and chloroethenes as one of the components[1–5], we report here new experimental data on sound velocities, isentropic compressibilities and deviations in isentropic compressibilities for the binary mixtures of acetophenone with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene. This investigations has been undertaken with a view to visualise the effect of successive chlorination and unsaturation of enthane molecule on deviations in isentropic compressibilities.

EXPERIMENTAL

Materials

Acetophenone (BDH) was kept over anhydrous calcium chloride for three days, filtered and fractionally distilled. 1,2-dichloroethane (BDH), 1,1,1-trichloroethane

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Table 1 Boiling points and densities of pure components at 303.15 K.

Components	Boiling point, K		Density, g cm^{-3}	
	Expt.	Lit.	Expt.	Lit.
Acetophenone	575.00	575.15	1.01941	1.01947
1,2-Dichloroethane	356.40	356.63	1.23828	1.23821
1,1,1-Trichloroethane	347.10	347.15	1.32092	1.32096
1,1,2,2-Tetrachloroethene	419.20	419.35	1.57857	1.57860
Trichloroethene	360.30	360.34	1.45136	1.45140
Tetrachloroethene	394.20	394.35	1.60635	1.60640

(Koch-Light) and 1,1,2,2-tetrachloroethane (Riedel) were purified by the methods described by Ramanjaneyulu *et al.*[6] Trichloroethene (BDH) and tetrachloroethene (BDH) were purified using the method described by Riddick and Bunger[7]. The measured densities and boiling points of the purified components are in good agreement with the literature data[7]. This data are given in Table 1.

Ultrasonic Velocity

Ultrasonic velocity was measured with a single crystal interferometer at a frequency of 2 MHz, and was accurate to ± 0.015%[8]. All measurements were made at constant temperature by circulating water around the cell from a U-10 thermostat, maintained at 303.15 ± 0.01 K. Densities of mixtures were computed from the measured excess volume data reported elsewhere[9] using trhe relation

$$\rho = \frac{xM_1 + (1 - x)M_2}{V^0 + V^E} \tag{1}$$

where "x" denotes mole fraction of acetophenone. V^0 and V^E stand for ideal molar volume and excess molar volume respectively. M_1 and M_2 represent molecular weights.

Isentropic Compressibility

Isentropic compressibility was calculated from the relation

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

Where U and ρ denote sound velocity and density. The quantity K_s was computed using the relation

$$K_s = k_s - \phi k_{s,1} - (1 - \phi)k_{s,2} \tag{3}$$

Where k_s, $k_{s,1}$ and $k_{s,2}$ are the isentropic compressibilities of the mixtures and the pure components and ϕ denote volume fraction of acetophenone. K_s represents the deviation from ideal behaviour.

RESULTS AND DISCUSSION

The experimental values for density (ρ), sound velocity (U), isentropic compressibility (k_s) and the deviation in isentropic compressibility (K_s) are given in Table 2 as a function of volume fraction (ϕ) of acetophenone. The variation of K_s with ϕ are graphically illustrated in Figure 1. The dependence of K_s on volume fraction is expressed by an empirical equation of the form

$$K_s = \phi(1 - \phi)[a_0 + a_1(2\phi - 1) + a_2(2\phi - 1)^2] \tag{4}$$

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

Table 2 Volume fraction (ϕ), density (ρ), sound velocity (u), Isentropic compressibility (k_s) and Deviation in Isentropic compressibility (K_s) at 303.15 K.

ϕ	ρ	u	k_s	K_s
	$g\,cm^{-3}$	$m\,s^{-1}$	TPa^{-1}	TPa^{-1}
	Acetophenone + 1,2-dichloroethane			
0.0000	1.23828	1173.3	586.6	0.0
0.1464	1.20555	1203.2	573.0	4.7
0.2586	1.18071	1229.3	560.5	6.2
0.4149	1.14656	1269.9	540.8	6.0
0.4952	1.12891	1292.4	530.3	5.5
0.5974	1.10667	1346.7	516.9	4.9
0.6773	1.08931	1346.7	506.2	4.1
0.7558	1.07223	1372.1	495.4	3.1
0.8061	1.06133	1388.7	488.6	2.6
0.8618	1.04927	1407.8	480.8	1.8
0.9126	1.03830	1425.6	473.9	1.2
1.0000	1.01941	1457.4	461.8	0.0
	Acetophenone + 1,1,1-trichloroethane			
0.0000	1.32092	942.6	852.1	0.0
0.0953	1.29395	985.8	795.2	−19.7
0.1667	1.27335	1018.7	756.7	−30.3
0.2521	1.24823	1058.1	715.6	−38.1
0.3466	1.22004	1102.5	674.3	−42.5
0.4708	1.18262	1163.9	624.2	−44.1
0.5928	1.14557	1226.9	579.9	−40.8
0.6639	1.12352	1265.4	555.7	−37.3
0.7456	1.09872	1312.9	528.0	−33.1
0.8091	1.07905	1348.3	509.8	−26.5
0.8748	1.05866	1386.2	491.6	−19.1
1.0000	1.01941	1457.4	461.8	0.0

(*continued*)

Table 2 (*continued*)

ϕ	$\frac{\rho}{g\,cm^{-3}}$	$\frac{u}{m\,s^{-1}}$	$\frac{k_s}{TPa^{-1}}$	$\frac{K_s}{TPa^{-1}}$
	Acetophenone + 1,1,2,2 – tetrachloroethane			
0.0000	1.57857	1133.1	493.4	0.0
0.1351	1.50380	1163.1	491.5	2.4
0.2161	1.45874	1182.7	490.1	3.5
0.2537	1.43779	1192.0	489.5	4.1
0.3545	1.38154	1218.9	487.2	5.0
0.4237	1.34284	1238.7	485.3	5.3
0.5573	1.26804	1281.0	480.6	4.8
0.6475	1.21744	1312.2	477.0	4.1
0.7409	1.16505	1347.0	473.1	3.1
0.8567	1.09997	1393.6	468.1	1.8
0.9141	1.06771	1418.3	465.6	1.1
1.0000	1.01941	1457.4	461.8	0.0
	Acetophenon + trichloroethene			
0.0000	1.45136	1013.7	670.5	0.0
0.1270	1.39844	1057.8	639.1	−4.9
0.2553	1.34357	1106.9	607.4	−9.8
0.3958	1.28324	1164.9	574.3	−13.6
0.4484	1.26046	1187.8	562.3	−14.6
0.5282	1.22589	1223.2	545.2	−15.1
0.6038	1.19301	1257.0	530.5	−14.0
0.7416	1.13290	1321.5	505.4	−10.3
0.8191	1.09897	1359.6	492.3	−7.3
0.8681	1.07749	1385.1	483.7	−5.6
0.9399	1.04588	1423.5	471.8	−2.5
1.000	1.01941	1457.4	461.8	0.0
	Acetophenone + tetrachloroethene			
0.0000	1.60635	1027.8	589.3	0.0
0.1128	1.53956	1062.6	575.2	0.3
0.1600	1.51183	1077.5	569.7	0.8
0.2267	1.47280	1099.4	561.8	1.4
0.2999	1.43006	1124.4	553.1	2.0
0.3992	1.37206	1160.0	541.6	3.2
0.4911	1.31842	1195.5	530.7	4.0
0.5817	1.26542	1233.2	519.6	4.5
0.6825	1.20639	1278.8	506.9	4.6
0.7701	1.15492	1322.2	495.3	4.2
0.8966	1.08047	1391.4	478.1	3.1
1.0000	1.01941	1457.4	461.8	0.0

The values of K_s for the mixtures of acetophenone with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and tetrachloroethene are positive and negative for the systems of acetophenone with 1,1,1-trichloroethane and trichloroethene over the entire composition range. Values of K_s can be explained in terms of contributions made by the following factors: (i) change in free lengths defined by Jacobson[10] and (ii) Orientation of molecules in mixtures. The non-ideality in density has a tendency to oppose the effect of non-ideality in free lengths. The experimentally observed

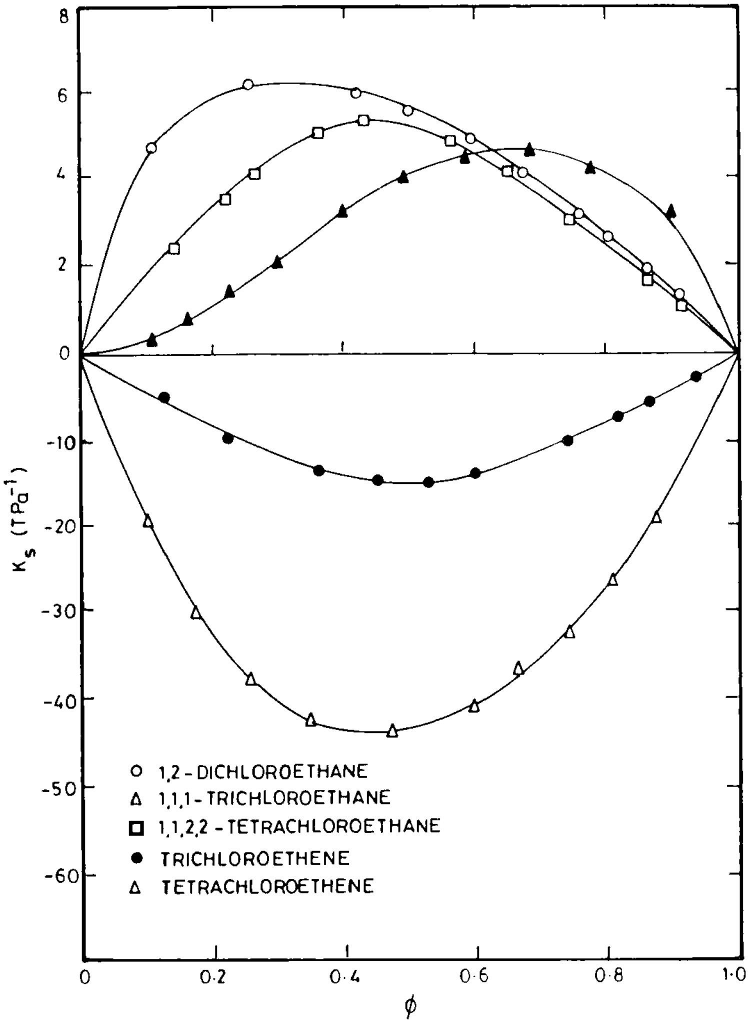

Figure 1 Deviation in isentropic compressibility (K_s) vs. volume fraction (ϕ) of acetophenone with chloroethanes and chloroethenes at 303.15 K.

deviations will be the net result of these two opposing effects. The algebraic values of K_s for acetophenone with chlorethanes fall in the order—

1,2-dichloroethane > 1,1,2,2-tetrachloroethane > 1,1,1-trichloroethane.

The above order shows that the presence of hydrogen bonding may not be possible in these systems, since the interactions are maximum in the system, acetophenone + 1,1,1-trichloroethane though 1,1,1-trichloroethane has no active hydrogens[11]. K_s values for the systems of acetophenone with chloroethanes is explained by taking the following factors into consideration: (i) double bond character of chloroethenes,

Table 3 Values of the parameters, a_0, a_1 and a_2 in Eq. 7 and the standard deviation, $\sigma(K_s)$ at 303.15 K.

System	a_0	a_1	a_2	$\sigma(K_s)$
		TPa^{-1}		
Acetophenone + 1,2-dichloroethane	23.024	−15.472	8.028	0.1
Acetophenone + 1,1,1-trichloroethane	−174.071	32.071	−44.556	0.5
Acetophenone + 1,1,2,2-tetrachloroethane	20.268	−4.405	−4.813	0.2
Acetophenone + trichloroethene	−58.923	−2.582	23.148	0.2
Acetophenone + tetrachloroethene	15.439	17.260	4.313	0.3

(ii) shielding of ethylenic double bond by chlorine atoms and (iii) partial saturation of the electron accepting nature of chlorine atoms by π-electrons of the ethylenic double bond. The algebraic values of K_s of acetophenone with chloroethenes fall in the order—

Tetrachloroethene > Trichloroethene

The negative K_s in the system, acetophenone + trichloroethene may be attributed to the π–π interactions between the unlike molecules. But the electrons of trichloroethene do not involve fully due to the partial shielding by chlorine atoms. The positive K_s in the system, acetophenone + tetrachloroethene may be due to the breaking of dipole-dipole interactions of C=O[12]. The π-electrons of tetrachloroethene may not participate in the interactions, since it is completely shielded by four chlorine atoms[13].

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