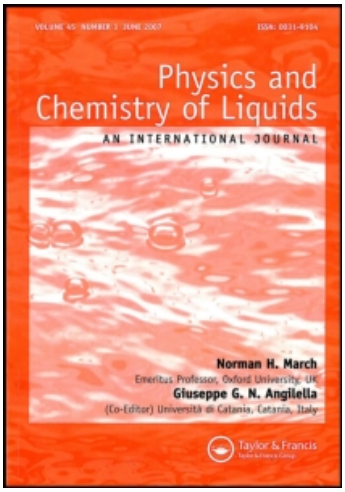

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Ultrasonic Studies of Binary Mixtures of Tetrachloroethylene with Branched Alcohols at 303.15 K

D. Venkatesulu[a]; P. Venkatesu[a]; M. V. Prabhakara Rao[a]
[a] Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, India

To cite this Article Venkatesulu, D. , Venkatesu, P. and Rao, M. V. Prabhakara(1996) 'Ultrasonic Studies of Binary Mixtures of Tetrachloroethylene with Branched Alcohols at 303.15 K', Physics and Chemistry of Liquids, 32: 2, 127 — 132
To link to this Article: DOI: 10.1080/00319109608030713
URL: http://dx.doi.org/10.1080/00319109608030713

Phys. Chem. Liq., 1996, Vol. 32, pp. 127–132
Reprints available directly from the publisher
Photocopying permitted by license only

ULTRASONIC STUDIES OF BINARY MIXTURES OF TETRACHLOROETHYLENE WITH BRANCHED ALCOHOLS AT 303.15 K

D. VENKATESULU, P. VENKATESU and M. V. PRABHAKARA RAO

Department of Chemistry, Sri Venkateswara University, Tirupati 517502, Andhra Pradesh, India

(Received 8 January 1996)

Ultrasonic sound velocities for the binary liquid mixtures of tetrachloroethylene with branched alcohols are measured at 303.15 K. The branched alcohols include 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butnaol, 2-butanol and 2-methyl-2-propanol. Further, isentropic compressibilities (K_s) and deviation in isentropic compressibilities (ΔK_s) have been computed from the sound velocity and density data. An inversion in the sign of ΔK_s from negative to positive was observed in all the binary mixtures formed by tetrachloroethylene with branched alcohols at 303.15 K. The ultrasonic sound velocities of these mixtures have been analyzed in terms of Free length theory (FLT). Collision factor theory (CFT) and Nomoto relation.

KEY WORDS: Binary mixtures, isentropic compressibilities, hydrogen bonding.

1 INTRODUCTION

In recent years there has been considerable advancement in the experimental investigation of the thermodynamic properties of liquid mixtures. Thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures of non-electrolytes. A Survey of literature showed that ultrasonic studies for binary mixtures, tetrachloroethylene with a homologous series of normal alcohols have been measured at 303.15 K[1]. However, no effort has been made to measure ultrasonic sound velocity of binary mixtures of tetrachloroethylene with branched alcohols. Hence we report here new sound velocities measurements for five binary mixtures of tetrachloroethylene with 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-butanol and 2-methyl-2-propanol at 303.15 K. The ultrasonic sound velocity of these mixtures have been analyzed in terms of Free length theory (FLT)[2-6], collision factor theory[2,6-9](CFT) and Nomoto relation[10]. The theoretical aspect has been already discussed in our earlier paper[11].

2 EXPERIMENTAL

All the chemicals used were of analytical grade. Tetrachloroethylene was purified by the method described by Venkatesulu *et al.*[12] The branched alcohols were further

purified by the methods described by Rao and Reddy[13]. The purity of the chemicals were checked by comparing the measured densities with those reported in literature[14,15]. The densities of all the components were measured by a bicapillary pycnometer with an accuracy of two parts in 10^5. The measured densities and those reported in literature are listed in Table 1.

Ultrasonic sould velocities were measured with single-crystal interferometer at a frequency of 4 MHz at 303.15 K and were accurate to $\pm 0.02\%$. All the measurements were made at a constant temperature employing a thermostat that could be maintained to ± 0.01 K.

Isentropic compressibilities (K_s) were calculated from the measured ultrasonic velocities (U) and density (ρ) values using the relation,

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

The densities of binary mixtures were obtained from excess volumes using the relation:

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

where x_1, x_2 denote the mole fractions and M_1, M_2 are molar masses of components 1 and 2 respectively. V is the molar volume and V^E the excess volume of the mixture.

The deviation in isentropic compressibilities (ΔK_s) were evaluated from the equation,

$$\Delta K_s = K_s - \phi_1 K_{s_1} - \phi_2 K_{s_2} \tag{3}$$

where K_s, K_{s_1} and K_{s_2} are the isentropic compressibilities of the mixture and the pure components respectively. ϕ_1 and ϕ_2 are volume fractions of the components.

3 RESULTS AND DISCUSSION

The values of molar volume (V), molar volume at absolute zero (V_0), available volume (V_a), free length (L_f), surface area (Y), collision factor (S), average radius of the molecules (r_m) and molar sound velocity (R) of the pure components are listed in

Table 1 Densities of pure components at 303.15 K.

Compound	*Density g/cm³*	
	Expt.	*Lit.*
Tetrachloroethylene	1.60636	1.60640
2-Propanol	0.77686	0.77690
2-Methyl-1-propanol	0.79434	0.79437
3-Methyl-1-butanol	0.80174	0.80179
2-Butanol	0.79891	0.79895
2-Methyl-2-propanol	0.77616	0.77620

Table 2. The experimental data for the five binary systems are reported in Table 3 along with theoretical sound velocities. The variation of ΔK_s with volume fraction of tetrachloroethylene is graphically presented in Figure 1. The dependence of ΔK_s on

Table 2 Molar volume (V), molar volume at absolute zero (V_0), available volume (V_a), free length (L_f), surface area (Y), collision factor (S), molecular radius (r_m) and molecular sound velocity (R) of the pure components at 303.15 K.

Component	V	V_0	V_a	L_f	Y	S	r_m/o_A	R
		$cm^3\ mol^{-1}$						
Tetrachloro-ethylene	103.236	84.415	18.821	0.4843	77.72	1.3331	2.7014	1041.9
2-Propanol	77.358	58.924	18.434	0.6358	57.99	1.6431	2.3590	804.8
2-Methyl-1-propanol	93.313	73.268	20.045	0.6041	66.36	1.6579	2.5373	983.8
3-Methyl-1-butanol	109.947	88.078	21.869	0.5776	75.72	1.6695	2.7097	1174.8
2-Butanol	92.779	72.245	20.534	0.5911	69.48	1.6690	2.5428	984.4
2-Methyl-2-propanol	95.498	72.604	22.894	0.6488	70.57	1.5862	2.5437	987.0

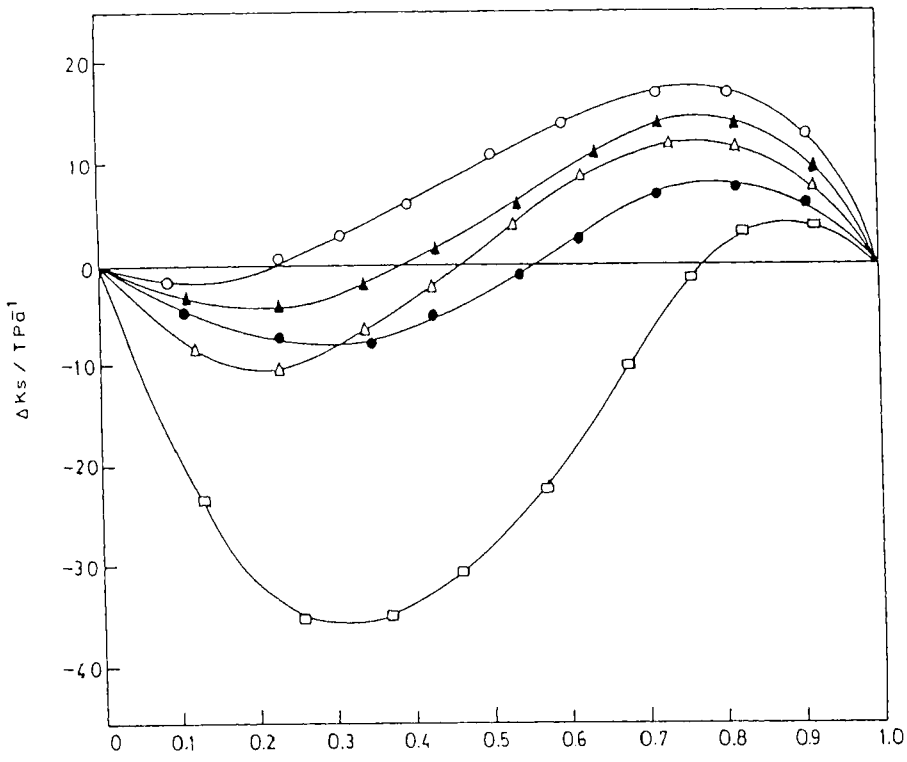

Figure 1 Deviation in isentropic compressibilities (ΔK_s) for Tetrachloroethylene + 2-Propanol (□), + 2-Methyl-1-Propanol (Δ), + 3-Methyl-1-butanol (0), + 2-butanol (Δ) and + 2-Methyl-2-propanol (●).

Table 3 Mole fraction (x_1) and volume fraction (ϕ_1) of tetrachloroethylene, ρ, U, K_s, ΔK_s predicted sound velocities (U) from various models for the binary mixtures of tetrachloroethylene with branched alcohols at 303.15 K.

x_1	ϕ_1	ρ/ g cm^{-3}	U_{exp}/ ms^{-1}	K_s/ Tpa^{-1}	ΔK_s/ Tpa^{-1}	$U_{theoretical}$/ms^{-1}		
						FLT	*CFT*	*Nomoto*
			Tetrachloroethylene + 2-Propanol					
0.0000	0.0000	0.77686	1126.0	1015.3	–	1126.0	1126.0	1126.0
0.1028	0.1326	0.88645	1098.0	935.7	−23.1	1088.7	1122.5	1112.7
0.2072	0.2586	0.99049	1077.2	870.1	−35.0	1062.9	1117.1	1110.1
0.3070	0.3716	1.08371	1059.2	822.5	−34.4	1046.3	1110.1	1088.9
0.3926	0.4631	1.15918	1046.4	787.9	−30.0	1036.6	1103.1	1079.9
0.5027	0.5743	1.25069	1033.6	748.4	−22.1	1028.5	1092.6	1069.0
0.6105	0.6766	1.33487	1022.4	716.7	−10.2	1024.3	1080.7	1059.0
0.6982	0.7554	1.39992	1016.0	692.0	−1.4	1023.2	1070.2	1051.4
0.7882	0.8324	1.46391	1014.8	663.3	2.8	1023.4	1058.5	1044.0
0.8976	0.9213	1.53864	1018.8	626.2	3.6	1025.2	1043.2	1035.5
1.0000	1.0000	1.60636	1028.0	589.1	–	1028.0	1028.0	1028.0
			Tetrachloroethylene + 2-Methyl-1-propanol					
0.0000	0.0000	0.79434	1172.0	916.5	–	1172.0	1172.0	1172.0
0.1124	0.1229	0.89387	1135.2	868.1	−8.2	1133.9	1159.0	1153.6
0.2157	0.2333	0.98316	1107.2	829.7	−10.4	1106.9	1146.2	1137.2
0.3156	0.3379	1.06759	1082.4	799.5	−6.4	1086.5	1133.3	1121.9
0.4057	0.4303	1.14215	1064.0	773.4	−2.2	1071.8	1121.0	1108.4
0.5099	0.5351	1.22664	1046.0	745.1	3.8	1058.2	1106.2	1093.3
0.5996	0.6236	1.29801	1033.6	721.1	8.8	1049.4	1092.9	1080.7
0.7145	0.7347	1.38784	1023.2	688.2	12.2	1040.4	1075.2	1065.0
0.8032	0.8187	2.45623	1020.0	660.0	11.5	1035.2	1061.0	1053.3
0.9080	0.9161	1.53632	1020.8	624.7	8.1	1030.7	1043.7	1039.6
1.0000	1.0000	1.60636	1028.0	589.1	–	1028.0	1028.0	1028.0
			Tetrachloroethylene + 3-Methyl-1-butanol					
0.0000	0.0000	0.80174	1220.0	838.0	–	1220.0	1220.0	1220.0
0.0975	0.0921	0.87571	1184.8	813.5	−1.6	1186.5	1202.1	1201.3
0.2467	0.2352	0.99053	1137.6	780.1	0.6	1144.0	1174.4	1172.8
0.3283	0.3146	1.05414	1115.2	762.8	3.1	1124.6	1159.1	1157.2
0.4163	0.4011	1.12338	1093.6	744.3	6.1	1106.2	1142.5	1140.3
0.5256	0.5099	1.21041	1069.6	722.2	11.1	1086.2	1121.5	1119.3
0.6182	0.6032	1.28511	1052.8	702.1	14.2	1071.9	1103.6	1101.5
0.7334	0.7209	1.37948	1036.0	675.4	16.8	1056.1	1081.1	1079.4
0.8214	0.8120	1.45287	1026.8	652.8	16.9	1045.5	1063.8	1062.4
0.9161	0.9111	1.53340	1022.0	624.4	13.2	1035.7	1044.9	1044.2
1.0000	1.0000	1.60636	1028.0	589.1	–	1028.0	1028.0	1028.0
			Tetrachloroethylene + 2-Butanol					
0.0000	0.0000	0.79891	1194.4	877.4	–	1194.4	1194.4	1194.4
0.1024	0.1127	0.88881	1156.0	841.9	−3.0	1156.0	1180.0	1174.8
0.2130	0.2315	0.98373	1122.4	806.9	−3.8	1123.6	1163.7	1154.4
0.3172	0.3408	1.07110	1096.0	777.2	−2.0	1099.3	1147.7	1135.8
0.4016	0.4275	1.14046	1077.2	755.7	1.6	1083.6	1134.2	1121.2
0.5142	0.5408	1.23112	1056.8	727.3	5.8	1066.6	1115.7	1102.4
0.6125	0.6376	1.30870	1041.6	704.3	10.7	1054.8	1099.0	1086.4
0.7018	0.7237	1.37810	1030.8	682.9	14.1	1046.4	1083.3	1072.3
0.8032	0.8196	1.45601	1024.0	655.0	13.9	1038.6	1065.0	1056.8
0.9108	0.9191	1.53816	1022.4	622.0	9.6	1032.0	1045.0	1040.8
1.0000	1.0000	1.60636	1028.0	589.1	–	1028.0	1028.0	1028.0

Table 3 (*Contd.*)

x_1	ϕ_1	ρ/ g cm^{-3}	U_{exp}/ ms^{-1}	K_s/ Tpa^{-1}	ΔK_s/ Tpa^{-1}	$U_{theoretical}$/ms^{-1}		
						FLT	*CFT*	*Nomoto*
			Tetrachloroethylene + 2-Methyl-2-propanol					
0.0000	0.0000	0.77616	1104.0	1057.1	-	1104.0	1104.0	1104.0
0.1027	0.1101	0.86536	1074.4	1001.1	−4.5	1075.8	1098.8	1095.4
0.2143	0.2277	0.96132	1050.0	943.5	−7.0	1053.6	1092.5	1086.4
0.3299	0.3474	1.05954	1031.6	886.9	−7.6	1037.2	1085.1	1077.2
0.4102	0.4292	1.12696	1021.1	850.9	−5.3	1029.3	1079.5	1070.9
0.5188	0.5382	1.21705	1010.8	804.2	−1.0	1022.3	1071.4	1062.7
0.6036	0.6221	1.28655	1005.6	768.6	2.6	1019.3	1064.6	1056.3
0.7072	0.7231	1.37055	1002.8	725.6	6.9	1018.5	1055.9	1048.7
0.8124	0.8240	1.45519	1006.0	679.0	7.5	1020.1	1046.4	1041.1
0.9075	0.9138	1.53158	1014.0	635.0	5.6	1023.2	1037.3	1034.4
1.0000	1.0000	1.60636	1028.0	589.1	-	1028.0	1028.0	1028.0

volume fraction has been expressed by the polynomial,

$$\Delta K_s = \phi_1 \phi_2 [b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \tag{4}$$

where b_0, b_1 and b_2 are the parameters obtained by the method of least squares and are given in Table 4 along with standard deviation $\sigma(\Delta K_s)$.

The analysis of the experimental and predicted sound velocities given in Table 3 indicate that the FLT, CFT and Nomoto models give a rough estimate of sound velocities in all binary mixtures and FLT satisfactorily estimates sound velocity when compared to CFT and Nomoto models.

An inversion in the sign of ΔK_s from negative to positive is observed in all the binary systems studied. ΔK_s is negative for the mixtures rich in alcohols and becomes positive with increase in the concentration of tetrachloroethylene. The values

Table 4 Least square parameters of Eqn. (4) and standard deviation, $\sigma(\Delta K_s)$ at 303.15 K.

Systems	b_0	b_1	b_2	$\sigma(\Delta K_s)$
	Tpa^{-1}			
Tetrachloroethylene + 2-Propanol	−109.40	160.98	42.41	1.0
Tetrachloroethylene + 2-Methyl-1-Propanol	7.07	114.88	2.03	0.5
Tetrachloroethylene + 3-Methyl-1-butanol	39.79	99.86	44.03	1.3
Tetrachloroethylene + 2-Butanol	17.16	95.16	44.45	0.04
Tetrachloroethylene + 2-Methyl-2-Propanol	−10.03	73.94	33.03	0.6

of ΔK_s can be explained in terms of contributions made by the following factor: (i) the break-up of hydrogen bonds in branched alcohols with tetrachloroethylene and (ii) the formation of new species acting as an adduct between the branched alcohols and tetrachloroethylene. The dissociation alcohol leads to an increase in ΔK_s and the formation of an adduct leads to a decrease in ΔK_s. The brief, the former and latter effects contribute to positive and negative deviation in isentropic compressibilities. The observed ΔK_s values are the resultant of the aforesaid effects along with the presence of double bond in tetrachloroethylene and steric hindrance exhibited by chlorine atoms on ethylenic double bond. The algebraic values of ΔK_s for the binary systems of tetrachloroethylene with branched fall in the following order: 3-methyl-1-butanol > 2-butanol > 2-methyl-1-propanol > 2-methyl-2-propanol > 2-propanol.

References

1. H. Iloukhani and M. V. P. Rao, *Phys. Chem. Liq.*, **15**, 137 (1985).
2. B. Jacobson, *Acta Chem Scand*, **5**, 1214 (1951); **6**, 1485 (1952) 1485; *J. Chem. Phys.*, **20**, 927 (1952).
3. M. V. Kaulgud, *Acustica*, **10**, 316 (1960); **25**, 14 (1971); *Indian J. Phys.*, **36**, 577 (1962); *Z. Phys. Chem.*, **36**, 365 (1936).
4. K. Seshadri, N. P. Rao and K. C. Reddy, *Z. Phys. Chem.*, **89**, 108 (1974).
5. K. Seshadri and K. C. Reddy, *Acustica*, **29**, 59 (1973); *J. Acoust. Soc. India*, **4**, 1951 (1973).
6. K. Ravindra Prasad and K. C. Reddy, *Acustica*, **39**, 3 (1977); *Proc. Indian. Acad. Sci. Set A.*, **82**, 217 (1975).
7. W. Schaaffs, Molekulara Kustik (Spinger Verlag, Berlin-Gottinger-Heidelberg) 1963, Chap XI and XII; *Z. Phys.*, **114**, 110 (1939); **115**, 69 (1940).
8. Nutch-Kuhnkies, *Acustica*, **15**, 383 (1963).
9. C. V. Chaturvedi and S. Pratap, *Acustica*, **42**, 260 (1979).
10. O. Nomoto, *J. Phys. Soc. Jpn.*, **13**, 1528 (1958); **11**, 1146 (1956).
11. P. Venkatesu, D. Venkatesulu and M. V. P. Rao, *Indian J. Pure and Appl. Phys.*, **31**, 818 (1993).
12. D. Venkatesulu, M. V. P. Rao and D. Veeranna, *Thermochimica Acta*, **242**, 33 (1994).
13. K. P. Rao and K. S. Reddy, *Thermochimica Acta*, **91**, 321 (1985).
14. J. A. Riddick and W. B. Bunger, Techniques of Chemistry, Wiley-Interscience, New York, 3rd Edn. (1986).
15. J. Timmermans, Physico-chemical constants of pure organic compounds, Elsevier, Amsterdam, (1950 & 1962).