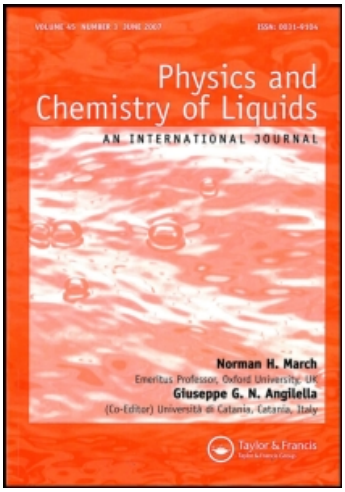

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Sound Velocities and Isentropic Compressibilities of Binary Mixtures of 1,1,1-Trichloroethane with Ketones and Esters at 303.15 K

K. Sivakumar[a]; P. R. Naidu[b]
[a] Department of Chemistry, S. V. Arts College, Tirupati, Andhra Pradesh, India [b] S. K. University, Anantapur, Andhra Pradesh, India

To cite this Article Sivakumar, K. and Naidu, P. R.(1998) 'Sound Velocities and Isentropic Compressibilities of Binary Mixtures of 1,1,1-Trichloroethane with Ketones and Esters at 303.15 K', Physics and Chemistry of Liquids, 35: 4, 209 — 221
To link to this Article: DOI: 10.1080/00319109808030589
URL: http://dx.doi.org/10.1080/00319109808030589

Phys. Chem. Liq., 1998, Vol. 35, pp. 209–221
Reprints available directly from the publisher
Photocopying permitted by license only

SOUND VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF BINARY MIXTURES OF 1,1,1-TRICHLOROETHANE WITH KETONES AND ESTERS AT 303.15 K

K. SIVAKUMAR[a,*] and P. R. NAIDU[b]

[a]*Department of Chemistry, S. V. Arts College, Tirupati-517 507, Andhra Pradesh, India;*
[b]*S. K. University, Anantapur, Andhra Pradesh, India*

(Received 3 February 1997)

Sound velocities for Binary mixtures of 1,1,1-Trichloroethane (TCE) with methyl ethyl ketone, methyl isobutyl ketone, acetophenone, cyclohexanone, methyl acetate, ethyl acetate, *n*-propyl acetate and *n*-butyl acetate were determined at 303.15 K. Isentropic compressibilities (k_s) were computed from sound velocity and density data, derived from excess volume. The deviation in isentropic compressibility (K_s) exhibits negative values for mixtures of TCE with methyl ethyl ketone, methyl isobutyl ketone, acetophenone, cyclohexanone ethyl acetate, *n*-propyl acetate and *n*-butyl acetate. On the other hand, the quantity is positive over the entire range of composition for the mixtures of TCE with methyl acetate. The results are explained in terms of interactions between unlike molecules. Further, the experimental sound velocity data have been analysed in terms of free length theory (FLT) and collision factor theory (CFT).

Keywords: Isentropic compressibility; volume fraction; sound speed; binary mixtures

1. INTRODUCTION

Ultrasonic studies find extensive applications in characterising aspects of the physico-chemical behaviour of liquid mixtures such as molecular interactions, association, dissociation and complex formation. The sound velocities in binary liquid mixtures can be computed

*Author to whom correspondence should be addressed.

theoretically at different mole fractions from Jacobsons [1] free length theory (FLT) and also the collision factor theory (CFT) of schaaffs [2]. Both the theories have been successfully applied to binary liquid mixtures by many workers [3–8]. In the present investigation new experimental data for sound velocity in binary mixtures of 1,1,1-trichloroethane with methyl ethyl ketone, methyl isobutyl ketone, acetophenone, cyclohexanone, methyl acetate, ethyl acetate, *n*-propyl acetate and *n*-butyl acetate, at 303.15 K have been reported. Further, the experimental sound velocity data have been analysed in terms of FLT and CFT. The theoretical values are in satsifactory agreement with experimental values. The sound velocity data were also used to compute the isentropic compressibilities (k_s). The deviation in real isentropic compressibilities (K_s) from ideal behaviour are attributable to the existence of strong dipole-induced dipole and dipole–dipole interactions between unlike molecules.

2. EXPERIMENTAL

All the chemicals used were of Analytical grade and were purified by standard methods described in literature [9]. The purity of the samples were checked by comparing the measured densities with those reported in the literature [10]. The measured densities and the literature data are presented in Table I. Densities were determined with a bicapillary pyknometer with an accuracy of 2 parts in 10^5. Ultrasonic sound velocities of pure liquids and liquid mixtures were measured at 303.15 K with a single crystal interferometer at a frequency of 3 MHz and were accurate to ±0.15%. Densities of mixtures were computed from experimental excess volumes reported elsewhere [4] using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^0 + V^E} \tag{1}$$

where x_1, x_2 denote the mole fractions of the two components and M_1 and M_2 stand for the molecular weights, V^0 represents the ideal molar volume of the mixture and V^E denotes the excess molar volume.

TABLE I Densities of Pure Compounds

Compound	*Density (ρ) gcm^{-3}*	
	Experimental	*Literature*[10]
1,1,1-trichloroethane	1.32099	1.32096
Methyl isobutyl ketone	0.79127	0.79125
methyl ethyl ketone	0.79445	0.79452
acetophenone	1.01950	1.01947
cyclohexanone	0.93764	0.93761
methyl acetate	0.92079	0.92080
ethyl acetate	0.88850	0.88851
n-propyl acetate	0.87705	0.87716
n-butyl acetate	0.87134	0.87129

3. RESULTS AND DISCUSSION

The values of molar volume (V_m), 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), actual volume of the molecules per mole (B) of pure components are given in Table II. These data were taken from the literature [9–11] and the details of calculations are discussed earlier [12]. The sound velocity data predicted in terms of FLT and CFT are given along with the experimental results in columns 3 and 4 of Table III.

The results included in columns 2 and 4 of Table III showed that both FLT and CFT models gave satisfactory estimate of the sound velocity in all eight binary mixtures over entire range of composition.

Isentropic compressibilities (k_s) were calculated using the relation

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

where U and ρ are sound velocity and density respectively. The values of k_s are accurate to $\pm$ 2 TPa^{-1}. The deviation in K_s from ideal value, assumed to be additive interms of volume fraction, is estimated using the equation

$$K_s = k_s - \phi_1 k_{s1} - \phi_2 k_{s2} \tag{3}$$

where k_s, k_{s1} and k_{s2} are the isentropic compressibilities of the mixtures and the pure components respectively; ϕ_1 and ϕ_2 are the volume

TABLE II Calculated values of molar volume (V_m), molar volume at absolute zero (V_0), molar available volume (V_a), free length (L_f) surface area (Y), collision factor (S), average molecular radius (r), and actual volume of molecules per mole (B) of pure liquid components at 303.15 K

Component	V_m cm^3mol^{-1}	V_0 cm^3mol^{-1}	V_a cm^3mol^{-1}	L_f A°	Y cm^3mol^{-1}	S	r A°	B cm^3mol^{-1}
1,1,1-trichloro-ethane	100.9849	78.4642	22.5207	0.5828	77.2845	1.2666	2.6502	46.9392
methyl ethyl ketone	90.7546	70.6402	20.1144	0.6056	66.4280	1.6456	2.5188	40.2947
methyl isobutyl ketone	126.5871	100.8889	25.6982	0.6053	84.9106	1.6279	2.8617	56.8590
acetophenone	117.8519	100.2987	17.5532	0.4280	80.0243	1.8243	2.8593	58.9496
cyclohexanone	104.6768	85.9331	18.7437	0.4692	79.8964	1.7618	2.7348	51.5795
methyl acetate	80.4692	61.2076	19.2616	0.5804	66.3679	1.5679	2.4294	36.1582
ethyl acetate	99.1626	76.4662	22.6964	0.5972	76.0141	1.5375	2.6168	45.1869
n-propyl acetate	116.4385	91.5010	24.9375	0.5900	84.5389	1.5280	2.7836	54.3893
n-butyl acetate	133.3119	106.7253	26.5866	0.5807	91.5674	1.5228	2.9340	63.6888

TABLE III Experimental and predicted sound velocity data for the Binary Mixtures of 1,1,1-trichloroethane with ketones and esters at 303.15 K

Mole fraction of *1,1,1-trichloroethane* (x_1)	U_{exp} *m/sec*	U_{FLT} *m/sec*	U_{CFT} *m/sec*
	1,1,1-trichloroethane + methyl ethyl ketone		
0.0750	1153	1142	1153
0.1409	1144	1220	1139
0.2074	1131	1100	1125
0.3411	1102	1064	1096
0.4345	1081	1042	1075
0.5381	1064	1024	1052
0.5901	1047	1009	1039
0.7246	1016	984	1008
0.8014	994	971	990
0.8706	975	960	973
	1,1,1-trichloroethane + methyl isobutyl ketone		
0.0750	1164	1152	1153
0.1693	1153	1127	1131
0.2442	1143	1108	1114
0.3744	1116	1076	1085
0.4137	1112	1067	1076
0.5053	1093	1046	1055
0.6398	1062	1016	1024
0.7421	1034	994	995
0.8221	1099	978	983
0.9119	976	959	962
	1,1,1-trichloroethane + acetophenone		
0.0751	1435	1409	1420
0.1649	1393	1352	1372
0.2621	1338	1293	1321
0.3448	1289	1246	1277
0.4653	1222	1181	1234
0.5746	1164	1126	1158
0.6623	1111	1084	1113
0.7423	1070	1048	1071
0.8792	1001	990	1003
0.9324	976	968	976
	1,1,1-trichloroethane + cyclohexanone		
0.0602	1360	1353	1361
0.1658	1309	1283	1312
0.2075	1290	1281	1293
0.2938	1253	1226	1254
0.4304	1193	1161	1192
0.5018	1165	1129	1160
0.6485	1093	1068	1095
0.7499	1048	1028	1050
0.8137	1011	973	1022
0.9120	979	971	980

TABLE III (Continued)

Mole fraction of 1,1,1-trichloroethane (x_1)	U_{exp} *m/sec*	U_{FLT} *m/sec*	U_{CFT} *m/sec*
	1,1,1-trichloroethane + methyl acetate		
0.0502	1114	1118	1119
0.1321	1086	1095	1105
0.2064	1065	1076	1092
0.3523	1026	1044	1066
0.4512	1005	1024	1048
0.5261	990	1011	1034
0.6128	976	995	1017
0.7251	962	986	996
0.8357	952	963	974
0.9156	943	953	962
	1,1,1-trichloroethane + ethyl acetate		
0.1251	1092	1091	1099
0.2053	1074	1074	1085
0.3543	1045	1044	1058
0.4023	1036	1035	1050
0.5163	1015	1014	1030
0.6514	993	992	1005
0.7521	978	977	987
0.8024	970	969	978
0.8553	962	962	968
0.9251	953	952	956
	1,1,1-trichloroethane + *n*-propyl acetate		
0.0481	1133	1131	1132
0.1021	1123	1118	1122
0.2333	1099	1089	1095
0.3214	1083	1069	1078
0.4026	1069	1053	1062
0.4826	1055	1037	1045
0.6325	1025	1008	1015
0.7512	1001	986	992
0.8011	990	977	982
0.9261	963	955	957
	1,1,1-trichloroethane + *n*-butyl acetate		
0.0750	1151	1147	1147
0.1251	1144	1135	1136
0.2063	1130	1116	1119
0.3102	1111	1093	1096
0.4732	1076	1057	1060
0.5502	1061	1040	1042
0.6525	1036	1017	1020
0.7021	1024	1006	1009
0.8511	986	974	975
0.9027	973	963	964

fractions of the components. Experimental data for U, k_s and K_s at 303.15 K are included in Table IV. The K_s values against volume fraction ϕ_1 are also graphically presented in Figures 1 and 2. However, the deviation in isentropic compressibility for the mixture ethyl acetate is of the experimental error and hence it is not graphically represented in Figure 2. The dependence of K_s on volume fraction is expressed by the empirical equation

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

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

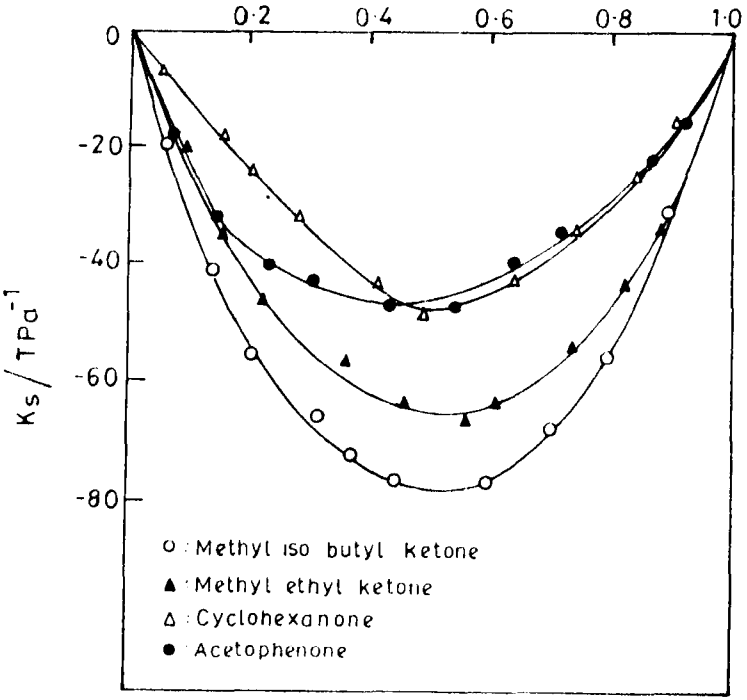

FIGURE 1 Volume fraction of 1,1,1-Trichloroethane.

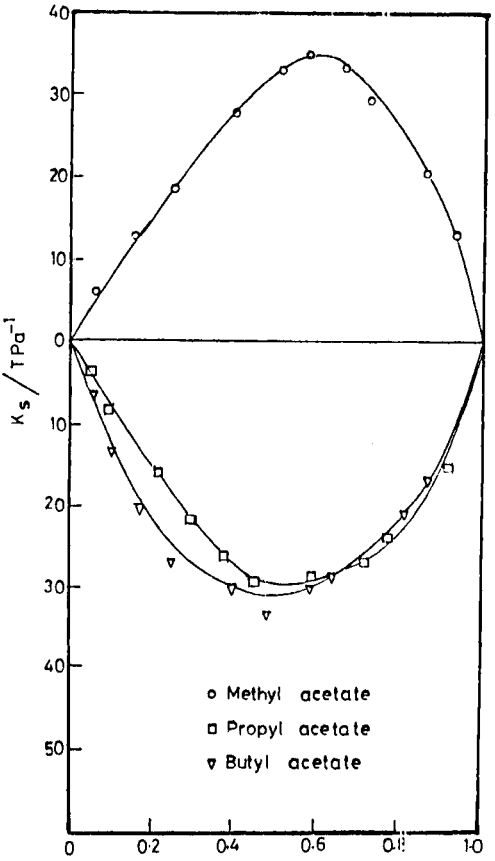

FIGURE 2 Volume fraction 1,1,1 Trichloroethane.

The values of K_s may be interpreted in terms of two opposing effects viz. (i) loss of mutual dipolar association and difference in size and shape of unlike components molecules, and (ii) dipole-induced dipole and dipole–dipole interactions. The former effect contributes to an increase in free lengths of component mixtures described by Jacobson. This leads to negative deviation in sound velocity and positive deviation in isentropic compressibility. The latter effect, on the other hand contributes to positive deviation in sound speed and negative deviation in isentropic compressibility. The sign and magnitude of the

TABLE IV Volume fraction ϕ_1 of 1,1,1-trichloroethane,density ρ, sound velocity U, isentropic compressibility k_s and deviation isentropic compressibility K_s for 1,1,1-trichloroethane with ketones (or) esters at 303.15 K

Volume fraction (ϕ_1) of	ρ	U	k_s	K_s
1, 1, 1-trichloroethane	*g cm^{-3}*	*m/sec*	*Tpa^{-1}*	*Tpa^{-1}*
	1,1,1-trichloroethane + methyl ethyl ketone			
0.0000	0.79445	1169	921	–
0.0827	0.83822	1153	897	–18
0.1543	0.87608	1144	872	–38
0.2254	0.91364	1131	856	–50
0.3654	0.98755	1102	834	–62
0.4607	1.03793	1081	824	–66
0.5644	1.08104	1064	816	–67
0.6155	1.11954	1047	815	–64
0.7453	1.18785	1016	816	–54
0.8178	1.22592	994	825	–40
0.8821	1.25966	975	835	–26
1.0000	1.32099	942	853	–
	1,1,1-trichloroethane + methyl isobutyl ketone			
0.0000	0.79125	1172	920	–
0.0607	0.82355	1164	896	–19
0.1398	0.86558	1153	869	–41
0.2049	0.90012	1143	851	–55
	0.96285	1116	833	–65
0.3607	0.98248	1112	823	–72
0.4489	1.02956	1093	813	–76
0.5863	1.10233	1062	804	–76
0.6966	1.16076	1034	805	–68
0.7866	1.20840	1099	812	–55
0.8920	1.26408	976	830	–30
1.0000	1.32099	942	853	–
	1,1,1- trichloroethane + acetophenone			
0.0000	1.01950	1460	460	–
0.0650	1.03984	1435	467	–18
0.1447	1.06464	1393	484	–32
0.2333	1.09218	1338	511	–40
0.3107	1.11605	1289	539	–43
0.4271	1.15167	1222	581	–46
0.5364	1.18488	1164	623	–47
0.6269	1.21216	1111	668	–38
0.7126	1.23767	1070	706	–34
0.8618	1.28162	1001	778	–20
0.9219	1.29902	976	807	–15
0.0000	1.32099	942	853	–

TABLE IV (Continued)

Volume fraction (ϕ_1) *of* *1, 1, 1-trichloroethane*	ρ $g\ cm^{-3}$	U *m/sec*	k_s Tpa^{-1}	K_s Tpa^{-1}
	1,1,1- trichloroethane + cyclohexanone			
0.0000	0.93761	1389	553	–
0.0582	0.96082	1360	563	−7
0.1609	1.00171	1309	583	−18
0.2016	1.01803	1290	590	−23
0.2864	1.05161	1253	606	−32
0.4216	1.10467	1193	636	−43
0.4929	1.13230	1165	651	−49
0.6403	1.18896	1093	703	−42
0.7431	1.22772	1048	741	−34
0.8482	1.25186	1011	782	−25
0.9091	1.28871	979	810	−15
1.0000	1.32099	942	853	–
	1,1,1-trichloroethane + methyl acetate			
0.0000	0.92060	1133	846	–
0.0622	0.94504	1114	852	6
0.1602	0.98493	1086	860	13
0.2457	1.01780	1065	866	19
0.4050	1.01823	1026	877	28
0.5069	1.12192	1005	882	33
0.5811	1.15161	990	885	35
0.6639	1.18691	976	885	34
0.7668	1.20809	962	880	29
0.8635	1.26520	952	872	20
0.9308	1.29252	945	865	13
1.0000	1.32099	942	853	–
	1,1,1-trichloroethane + ethyl acetate			
0.0000	0.88851	1121	896	–
0.1271	0.94328	1092	889	−1
0.2083	0.97828	1074	886	−1
0.3585	1.04299	1045	878	−2
0.4067	1.06379	1036	876	−2
0.5198	1.11260	1015	872	−2
0.6555	1.17130	993	866	−2
0.7555	1.21459	978	861	−2
0.8053	1.23619	970	860	−1
0.8875	1.25886	962	858	−1
0.9263	1.28888	953	855	−1
1.0000	1.32099	942	853	–
	1,1,1-trichloroethane + *n*-propyl acetate			
0.0000	0.87705	1142	874	–
0.0419	0.89576	1133	870	−3
0.0897	0.91721	1123	864	−8

TABLE IV (Continued)

Volume fraction (ϕ_1) *of*	ρ	U	k_s	K_s
1, 1, 1-trichloroethane	*g cm* $^{-3}$	*m/sec*	*Tpa* $^{-1}$	*Tpa* $^{-1}$
0.2087	0.97028	1099	853	−17
0.2936	1.00807	1083	846	−22
0.3690	1.04151	1069	840	−26
0.4474	1.07635	1055	835	−30
0.5987	1.14358	1025	832	−27
0.7774	1.22267	990	833	−25
0.9157	1.28385	963	840	−15
1.0000	1.32099	942	853	–
	1,1,1-trichloroethane + *n*-butyl acetate			
0.0000	0.87134	1164	847	–
0.0578	0.89768	1151	841	−6
0.0976	0.91568	1144	834	−14
0.1644	0.94582	1130	828	−20
0.2540	0.98622	1111	821	−27
0.4047	1.05417	1076	819	−30
0.4808	1.08837	1061	816	−34
0.5870	1.13612	1036	820	−30
0.6408	1.16030	1024	822	−29
0.8123	1.127226	986	831	−21
0.8754	1.26555	973	835	−17
1.0000	1.32099	942	853	–

actual deviation depend on the relative strength or the two opposing effects. The experimental values of K_s, which are negative, except for the mixture methyl acetate point out that the latter effect dominates in all the mixtures. On the other hand, the former effect is dominant in the mixture of methyl acetate with TCE. The algebraic K_s values for ketones fall in the order:

methyl isobutyl ketone > methyl ethyl ketone > cyclohexanone > acetophenone and for esters the order is as follows:
methyl acetate > ethyl acetate > *n*-propyl acetate > *n*-butyl acetate

The sign [6] of deviation in isentropic compressibility plays a vital role in the assesment of compactness due to molecular arrangement and the extent of molecular interactions in liquid mixtures and provides useful information about their structures. A negative deviation in isentropic compressibility is an indication of strong interactions in a liquid mixture. This is due to charge transfer,

TABLE V Least-square parameters and the standard deviation $\sigma(K_s)$ at 303.15 K

SYSTEM	a_0	a_1	a_2	$\sigma(K_s)$
		Tpa^{-1}		
1,1,1-trichloroethane + methyl ethyl ketone	−274.48	−0.46	30.55	2
1,1,1-trichloroethane + methyl isobutyl ketone	−311.02	6.88	−28.74	3
1,1,1-trichloroethane + acetophenone	−174.76	53.53	−92.60	2
1,1,1-trichloroethane + cyclohexanone	−181.15	−33.91	38.53	2
1,1,1-trichloroethane + methyl acetate	128.21	55.72	24.01	1
1,1,1-trichloroethane + *n*-propyl acetate	−118.72	−52.71	−23.44	2
1,1,1-trichloroethane + *n*-butyl acetate	−130.85	−5.96	−18.69	2

dipole-induced-dipole interactions, while a positive sign indicates weak interactions and is ascribed due to dispersion forces. An examination of results included in Table IV suggests that strong interactions exist between TCE with ketones and esters except for the system TCE + methyl acetate. On the other hand, weak interactions exist in TCE + methyl acetate.

Further, a comparision of deviation in isentropic compressibility (K_s) for the systems 1,1,1-trichloroethane with methyl ethyl ketone and ethyl acetate, where the non-common components differ only by their functional group suggests that the K_s values are relatively less in the mixtures of methyl ethyl ketone than in mixtures of ethyl acetate. This is due to high polarizability [9] value of methyl ethyl ketone than ethyl acetate. This observation is similar to that of Rajasekhar and Reddy [13] which was reported earlier.

References

[1] Jacobson, B. (1952). *Acta Chem. Scand* (Denmark) 1485; *J. Chem. Phys.* (USA), **20**, 927.
[2] Schaaffs, W. (1963). *Molecular Kustick* (Springer-Veriag, Berlin-Gothingen-Heidelberg), Ch XI & XII.
[3] Kaulgud, M. V. (1971). *Acustica*, **10**, 316.

[4] Venkateswarlu, P., Choudary, N. V., Krishnaiah, A. and Raman, G. K. (1986). *J. Phys. Chem. Liq.*, **15**, 203.
[5] Choudary, N. V. and NaiduP. R. (1982). *Chem. Sci.*, **89**, 59.
[6] Rai, R. D., Shukla, R. K., Shukla, A. K. and Pandey, J. D. (1989). *J. Chem. Thermodyn.*, **21**, 125.
[7] Mishra, R. L. and Pandey, J. D. (1917). *Indian J. Pure and Appl. Phys.*, **15**, 505.
[8] Seshadri, K. and Reddy, K. C. (1973) *Acustica*, **29**, 59; *J. Acoust Soc.* India, **4**, 1951.
[9] Riddick, J. A. and Bunger, W. B. (1970). *Organic solvents* (Wiley-Inter Science, New York).
[10] Timmenmans, J. (1950). *Physico-chemical Constants of pure Organic Compounds* (Essenier, Amstardam).
[11] John A. Dean (1987). *Hand Book of Organic Chemistry* (McGraw-Hill, New York).
[12] Dewan, R. K., Gupta, C. M. and Mehta, S. K. (1988). *Acustica*, **65**, 245.
[13] Rajasekhar, P. and Reddy,K. S. (1988). *J. Phys. Chem. Liq.*, **17**, 195.