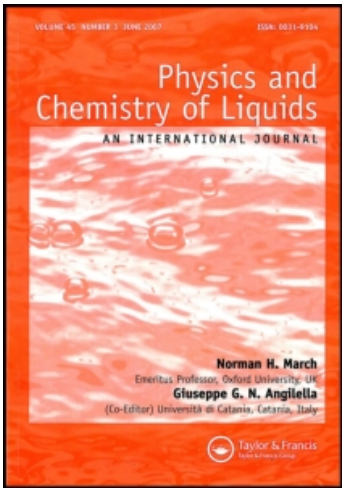

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Excess Volumes and Isentropic Compressibilities of 1,2-Dichloroethane with Ketones

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Experimental data for the excess volume and the sound velocity in binary mixtures of 1,2-dichloroethane with methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl iso-butyl ketone, cyclopentanone, cyclohexanone and 2-methyl cyclohexanone are reported at 303.15 K. All the systems exhibited small V^E and ΔK_s values.

1 INTRODUCTION

Excess thermodynamic properties and isentropic compressibilities have extensive applications in characterising the aspects of physico-chemical behaviour of liquid mixtures such as molecular association, deassociation and complex formation. Reddy and Naidu[1,2] studied the molecular interactions of some alcohols in methyl ethyl ketone and iso-butyl methyl ketone. Kehiaian and Grolier[3] have analysed the properties of binary mixtures containing ketones in terms of quasi-chemical group contribution model. Doan-Nguyen *et al.*[4] have studied the binaries of chloroalkane with alkane and alcohol. Grolier and Benson[5] have investigated the binary systems containing ketones. Handa and Benson[6,7] have attempted to study the molecular interactions in binary liquid mixtures containing chloroalkane as common component. Choudary *et al.*[8–12] have studied extensively the binary mixtures containing chloroalkane as common component. Krishnaiah and Naidu[13] have also investigated the binary mixtures containing chloroalkane as common component. Dharmaraju *et al.*[14] have reported the excess volumes and isentropic compressibilities of ketones in acetonitrile. However no attempt has been made to study the interactions between 1,2-dichloro-

ethane and ketones. Hence, we measured the excess volumes and isentropic compressibilities for the mixtures 1,2-dichloroethane with ketones which exhibit dipole–dipole interaction in pure state. The ketones include methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl iso-butyl ketone, cyclopentanone, cyclohexanone and 3-methyl cyclohexanone.

2 EXPERIMENTAL

The ketones were purified by the methods described by Riddick and Bunger.[15] 1,2-Dichloroethane was purified by the method described earlier.[8] The purity of the samples was checked by comparing the measured densities of the components with those reported in literature.[16] The density data of pure components are given in Table I.

TABLE I

Density of the pure components at 303.15 K

Component	ρ/g cm^{-3}	
	Present work	Literature
1,2-Dichloroethane	1.23832	1.23831
Methyl ethyl ketone	0.79445	0.79452
Diethyl ketone	0.80455	0.80461
Methyl propyl ketone	0.79660	0.79656
Methyl iso-butyl ketone	0.78221*	0.78230*
Cyclopentanone	0.93898	0.93902
Cyclohexanone	0.93757	0.93761
2-Methyl cyclohexanone	0.91625	0.91632

* Density at 313.15 K.

Excess volumes were measured using the dilatometer described by Rao and Naidu.[17] The mixing cell contained two bulbs of different capacities which were connected through a *U*-tube having mercury to separate the two components. One end of the bulb was fitted with a capillary (1 mm id) and the other end of the second bulb was fixed with ground glass stopper.

Isentropic compressibilities were computed from the density and sound speed data, density being computed from the measured excess volume data. The following relation was employed for computing density

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

where x, M and V_m denote the mole fraction, molecular weight and molar volume of the mixture respectively. V^E denotes the excess molar volome. The ultrasonic speed was measured with a single crystal interferometer at fre-

quency of 2 MHz and the data were accurate to $\pm 0.15\%$. All the measurements were made at a constant temperature employing a thermostat that could be maintained to ± 0.01 K.

3 RESULTS AND DISCUSSION

The experimental excess volumes for the seven binary mixtures are given in Table II. Isentropic compressibilities were calculated using the relation

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

TABLE II

Values of V^E for the binary mixtures of 1,2-dichloroethane with ketones at 303.15 K

X_1	V^E cm^3 mol^{-1}	X_1	V^E cm^3 mol^{-1}
1,2-dichloroethane + methyl ethyl ketone		1,2-dichloroethane + diethyl ketone	
0.1647	−0.032	0.1756	−0.031
0.2435	−0.040	0.2917	−0.028
0.2855	−0.040	0.3301	−0.026
0.4175	−0.033	0.4505	−0.018
0.5206	−0.029	0.5543	−0.014
0.6286	−0.019	0.6609	0.005
0.7124	−0.010	0.7619	0.014
0.9003	−0.003	0.9045	0.006
1,2-dichloroethane + methyl propyl ketone		1,2-dichloroethane + methyl iso-butyl ketone	
0.1878	−0.016	0.2031	0.030
0.2682	0.003	0.2351	0.033
0.3699	0.016	0.3067	0.042
0.4595	0.025	0.3474	0.050
0.5765	0.036	0.4991	0.063
0.6902	0.043	0.6271	0.067
0.8159	0.034	0.7861	0.070
0.9113	0.026	0.9196	0.055
1,2-dichloroethane + cyclopentanone		1,2-dichloroethane + cyclohexanone	
0.1835	0.000	0.1927	0.020
0.2060	0.010	0.2044	0.021
0.3035	0.019	0.2988	0.026
0.4090	0.026	0.4644	0.042
0.5220	0.032	0.5777	0.052
0.6512	0.042	0.6569	0.054
0.7211	0.041	0.7680	0.048
0.8786	0.020	0.8827	0.042

(continued)

TABLE II (*continued*)

X_1	V^E cm^3 mol^{-1}
1,2-dichloroethane + 2-methyl cyclohexanone	
0.1440	−0.020
0.2434	−0.010
0.3372	0.008
0.4293	0.023
0.5463	0.040
0.6020	0.050
0.7977	0.058
0.8967	0.045

where u and ρ denote the sound velocity and density. The values of K_s are accurate to ± 2 TPa^{-1}. The deviation in isentropic compressibility from the ideal value assumed to be additive in terms of volume fraction is estimated using the equation

$$\Delta K_s = K_s - (\phi_1 K_{s1} + \phi_2 K_{s2}) \tag{3}$$

where K_s, K_{s1} and K_{s2} are isentropic compressibilities of mixture and pure components respectively. ϕ_1 and ϕ_2 are the volume fractions of the component. The experimental data for density, sound velocity, isentropic compressibility and ΔK_s are included in Table III.

TABLE III

Volume factors (ϕ_1), densities (ρ), sound velocities (u), and the deviation in isentropic compressibilities (ΔK_s) of binary liquid mixtures of 1,2-dichloroethane with ketones at 303.15 K

ϕ_1	ρ (g cm^{-3})	u (m sec^{-1})	K_s	ΔK_s (TPa^{-1})
1,2-dichloroethane + methyl ethyl ketone				
0.0000	0.79445	1170.0	920	0
0.1479	0.86041	1166.5	854	−17
0.2208	0.89291	1164.5	826	−20
0.2603	0.91038	1162.5	813	−20
0.3869	0.96654	1160.0	769	−21
0.4888	1.01174	1159.5	735	−21
0.5984	1.06029	1158.0	703	−17
0.6856	1.09889	1159.0	678	−12
0.8883	1.18875	1167.5	617	−5
1.0000	1.23829	1175.0	585	0

(*continued*)

TABLE III (*continued*)

ϕ_1	ρ (g cm^{-3})	u (m sec^{-1})	K_s	ΔK_s (TPa^{-1})
	1,2-dichloroethane + diethyl ketone			
0.0000	0.80455	1197.0	867	0
0.1361	0.86541	1188.0	818	−11
0.2351	0.90675	1181.0	791	−10
0.2689	0.92139	1171.5	751	−9
0.3797	0.96940	1171.5	752	−8
0.4814	1.01352	1167.5	724	−7
0.5927	1.06156	1165.0	694	−6
0.7049	1.11012	1165.0	664	−3
0.8761	1.18446	1167.0	620	0
1.0000	1.23829	1175.0	585	0
	1,2-dichloroethane + methyl propyl ketone			
0.0000	0.79660	1200.0	872	0
0.1460	0.86120	1183.0	830	0
0.2131	0.89068	1176.0	812	1
0.3026	0.93009	1171.0	784	1
0.3859	0.96678	1169.5	756	5
0.5015	1.01771	1163.5	725	3
0.6222	1.07088	1165.0	688	3
0.7661	1.13453	1163.5	651	1
0.8836	1.18651	1167.5	618	0
1.0000	1.23829	1175.0	585	0
	1,2-dichloroethane + methyl iso-butyl ketone			
0.0000	0.79125	1169.0	925	0
0.1386	0.85299	1168.0	859	−19
0.1625	0.86367	1166.0	852	−18
0.2183	0.88857	1161.0	835	−16
0.2515	0.90329	1158.5	825	−15
0.3862	0.96326	1154.0	780	−14
0.5150	1.02076	1153.0	734	−13
0.6988	1.10279	1157.0	677	−10
0.8784	1.18306	1164.5	623	−3
1.0000	1.23829	1175.0	585	0
	1,2-dichloroethane + cyclopentanone			
0.0000	0.93898	1374.0	564	0
0.1670	0.98896	1339.0	564	−4
0.1879	0.99509	1333.0	566	−2
0.2799	1.02249	1311.0	569	−1
0.3817	1.05291	1281.5	578	6
0.4935	1.08627	1262.0	578	4
0.6248	1.12538	1238.5	579	2
0.6976	1.14720	1225.0	581	2
0.8659	1.19785	1196.0	584	2
1.0000	1.23829	1175.0	585	0

(*continued*)

TABLE III (*continued*)

ϕ_1	ρ (g cm^{-3})	u (m sec^{-1})	K_s	ΔK_s (TPa^{-1})
	1,2-dichloroethane + cyclohexanone			
0.0000	0.93757	1388.0	554	0
0.1541	0.98372	1347.0	560	1
0.1657	0.98718	1343.5	562	3
0.2455	1.01114	1321.5	566	4
0.3983	1.05687	1288.0	570	4
0.5108	1.09056	1259.5	578	8
0.5938	1.11544	1241.0	582	10
0.7165	1.15244	1216.5	586	10
0.8517	1.19310	1194.0	588	8
1.0000	1.23829	1175.0	585	0
	1,2-dichloroethane + 2-methyl cyclohexanone			
0.0000	0.91625	1346.0	602	0
0.0990	0.94828	1326.0	600	0
0.1736	0.97223	1309.0	600	1
0.2493	0.99646	1289.5	604	6
0.3293	1.02208	1264.5	612	16
0.4401	1.05755	1248.0	607	12
0.4968	1.07569	1240.0	605	11
0.7202	1.14736	1205.0	600	10
0.8500	1.18935	1189.0	595	8
1.0000	1.23829	1175.0	585	0

The values given in Table II shows that V^E exhibits small negative and positive values in systems of 1,2-dichloroethane with methyl ethyl ketone, diethyl ketone, methyl propyl ketone and 2-methyl cyclohexanone. The binary mixtures of 1,2-dichloroethane with methyl iso-butyl ketone, cyclopentanone and cyclohexanone result in small positive V^E values throughout the molefraction studied. As the experimental V^E values are very small we did not fit V^E into smoothing equation. The following factors influence V^E: (a) size difference, (b) deassociation of self associated chloroalkane[18] and ketones[10] and (c) dipole–induced–dipole interaction between ketoxy group and free electrons of chlorin atom of dichloroethane. The first two factors contribute to the positive excess volume while the last factor contributes to negative excess volume. The small experimental V^E values show that the two opposing factors compensate each other.

The results included in Table III show that ΔK_s is negative over volume fraction range studied in the systems 1,2-dichloroethane with methyl ethyl ketone, diethyl ketone, methyl iso-butyl ketone and is positive in the systems dichloroethane with methyl propyl ketone, cyclohexanone and 2-methyl cyclohexanone. The mixtures of dichloroethane and cyclopentanone exhibit

small negative and positive ΔK_s values. Finally it may be concluded from the above observations that the seven binary systems under investigation exhibit almost ideal behaviour.

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References

1. K. S. Reddy and P. R. Naidu, *J. Chem. Thermodyn.*, **10**, 2861 (1978).
2. K. S. Reddy and P. R. Naidu, *Aust. J. Chem.*, **32**, 687 (1979).
3. H. V. Kehiaian and J. P. E. Grolier, *Fluid Phase Equilibria*, **7**, 95 (1981).
4. T. H. Doan-Nguyen, J. H. Vera, and G. A. Ratcliff, *J. Chem. Eng. Data*, **23**, 219 (1978).
5. J. P. E. Grolier and G. C. Benson, *J. Chem. Eng. Data*, **20**, 243 (1975).
6. Y. P. Handa and G. C. Benson, *Fluid Phase Equilibria*, **4**, 261 (1980).
7. Y. P. Handa and G. C. Benson, *Fluid Phase Equilibria*, **4**, 277 (1980).
8. N. V. Choudary and P. R. Naidu, *Can. J. Chem.*, **59**, 2210 (1981).
9. N. V. Choudary, A. Krishnaiah, and P. R. Naidu, *J. Chem. Eng. Data*, **27**, 4 (1982).
10. N. V. Choudary, A. Krishnaiah, and J. C. Mouli, and P. R. Naidu, *J. Chem. Eng. Data*, (in press).
11. N. V. Choudary and P. R. Naidu, *Chemica Scripta*, **19**, 89 (1982).
12. N. V. Choudary, J. C. Mouli, and P. R. Naidu, *Acoustics Letters*, **6**, 56 (1982).
13. A. Krishnaiah and P. R. Naidu, *J. Chem. Eng. Data*, **25**, 135 (1980).
14. G. Dharmaraju, G. Narayanaswamy, and G. K. Raman, *J. Chem. Eng. Data*, (in Press).
15. J. A. Riddick and W. B. Bunger, *Organic Solvents*, Wiley Interscience, New York (1970).
16. J. Timmermans, "Physico-chemical constants of pure organic compounds," Elsevier Publishing Co., Amsterdam (1950).
17. M. V. P. Rao and P. R. Naidu, *Can. J. Chem.*, **52**, 788 (1976).
18. A. A. L. McClelian and S. W. Nicksic, *J. Phys. Chem.*, **69**, 446 (1965).