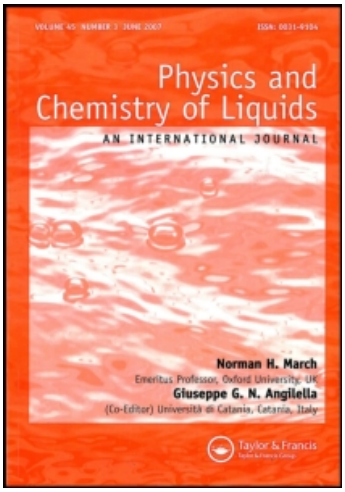

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Excess Volume, Speed of Sound and Isentropic Compressibilities of 1,2-Dichloroethane, 1,1,1-Trichloroethane 1,1,2,2-Tetrachloroethane with Methanol at 303.15 K

R. Vijayakumar[ab]; M. Anand Rao[ab]; M. Venkateshwara Rao[ab]
[a] Dept. of Chemistry, Osmania University, Hyderabad, A.P, India [b] College of Technology, Osmania University, Hyderabad, India

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EXCESS VOLUME, SPEED OF SOUND AND ISENTROPIC COMPRESSIBILITIES OF 1,2-DICHLOROETHANE, 1,1,1-TRICHLOROETHANE 1,1,2,2-TETRACHLOROETHANE WITH METHANOL AT 303.15 K

R. VIJAYAKUMAR, M. ANAND RAO* and M. VENKATESHWARA RAO

**Dept. of Chemistry, Osmania University, Hyderabad-500007, (A.P) India*
College of Technology, Osmania University, Hyderabad-500007, (A.P) India

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Excess volumes and speed of sound for the binary mixtures of 1,2-dichloroethane; 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane with methanol have been measured at 303.15 K. Excess volumes for the mixtures of 1, 2 dichloroethane and 1,1,1-trichloroethane with methanol are found to be positive whereas they are negative for 1,1,2,2-tetrachloroethane. The experimental speed of sound for these mixtures are found to be in good agreement with theoretical values. The speed of sound and excess volumes were used to calculate isentropic compressibilities.

KEY WORDS: Binary mixtures, excess volume, speed of sound, isentropic compressibilities.

1 INTRODUCTION

Speed of sound have been used to understand liquid structure. While indicating specific interactions between molecules they also enable the calculation of degree of intermolecular interactions, molecular freepath and isentropic compressibilities. Few measurements of the speed of sound in mixtures with halohydrocarbons have been made inspite of their significant intermolecular attraction due to σ and π electron acceptance. Speed of sound for liquid mixtures of fluorohydrocarbons and monochloro acetic acid in aqueous ethanol were studied earlier[1,2]. The speed of sound in binary liquid mixtures of methanol with 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane have been measured along with excess volumes in the present study.

2 EXPERIMENTAL

Molar excess volumes V_m^E were measured using the batch dialatometer described by Rao and Naidu[3]. The mixing cell contained two bulbs of different volumes that were contacted through a U-tube having mercury to seperate the two components. One end of the first bulb was fitted with a capillary outlet and the opposite end of the second

Table 1 Comparison of refractive indices (n_D) at 298.15 K and densities (ρ) at 303.15 K of pure components

Component	n_D		ρ/g-Cm^{-3}	
	Lit (4)	*Expt*	*Lit* (4, 5)	*Expt*
Methanol	1.32652	1.32498	0.78186	0.78184
1, 2-dichloroethane	1.44210	1.44106	1.24637	1.24682
1, 1, 1-trichloroethane	1.43590	1.44380	1.32990	1.32530
1, 1, 2, 2-tetrachloroethane	1.49140	1.49260	1.58666	1.58628

bulb was closed with a ground glass stopper. Five dilatometers of this type were used to cover the composition range. The composition of each mixture was determined directly by mass with corrections for buoyancy. The speed of sound was measured with a single crystal interferometer at a frequency of 2 MHz and the results were accurate to ± 0.15, isentropic compressibilities were calculated from densities "ρ" and the speed of sound determined at 303.15 K. The density was calculated from the molar excess volume V_m^E using the relation,

$$\rho = (x_1 M_1 + x_2 M_2)/(V_m + V_m^E)$$

where X_i is the mole fraction and M_i the molecular weight of component i. All measurements were made at a constant temperature using a thermostat that could be maintained to ± 0.01 K.

All the materials were purified by methods described by Riddick *et al*[4]. Methanol spectroscopy grade S.D fine chem was purified by distilling through a 30 plate bubble-cap column. The middle fraction was refractioned through dry carbondioxide. 1,2-dichloro-ethane AR grade S.D fine chem was washed with dilute KOH solution and water, dried over anhydrous calcium chloride and fractionally distilled. 1,1,1-trichloroethane (Merk) was washed with concentrated hydrochloric acid, then with 10% sodium chloride solution, dried over calcium chloride and finally distilled twice. The middle fraction of the second distillation was collected. 1,1,2,2-tetrachloroethane (AR grade S.D fine chem) was shaken with concentrated sulphuric acid for 10 min at 80 to 90 °C. The operation was repeated until the acid developed no more colour. The chloroalkane was then washed with water, steam distilled and dried over potassium carbonate and finally fractionated.

The purification of the samples was checked by comparing the measured refractive indices and densities of the compounds with those reported in the literature (Table 1). Densities were determined using a bicapillary type pykonmeter which offered an accuracy of 2 parts in 10^5. The differences between the experimental refractive indices and densities of pure substrates and the literature data fall within the experimental error.

3 RESULTS AND DISCUSSION

The excess molar volumes for binary mixtures of 1,2-dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane with methanol at 303.15 K are given in

Table 2 and are also graphically represented in Figure 1. The values of V_m^E are well represented by the following emperical equation

$$V_m^E = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (1)$$

In Eq. 1 x_1 refers to the mole fraction of the chloroethanes x_2 refers to the mole fraction of methanol and A_0, A_1 and A_2 are characteristic constants of a system at a given temperature. The values of constants A_0, A_1, and A_2 along with standard deviation σV_m^E are given in Table 3.

The values of the quantity K_s^E which refers to the deviation of the experimental values of K_s for various mixtures from the volume fraction are also given in Table 2, and have been fitted by the least square to the following equation

$$K_s^E = \phi_1 \phi_2 [B_0 + B_1(\phi_1 - \phi_2) + B_2(\phi_1 - \phi_2)] \quad (2)$$

In Eq. (2) ϕ_1 refers to the volume fraction of chloroethane and ϕ_2 refers to volume fraction of methanol. B_0, B_1 and B_2 are constants characteristic of a system at a given temperature. The values of constants B_0, B_1 and B_2 along with standard deviation $\sigma(K_s^E)$ are given in Table 4.

The excess volumes for mixtures of the chloroethanes (1,2-dichloroethane; 1,1,1-trichloroethane) with methanol are positive over the whole composition at 303.15 K.

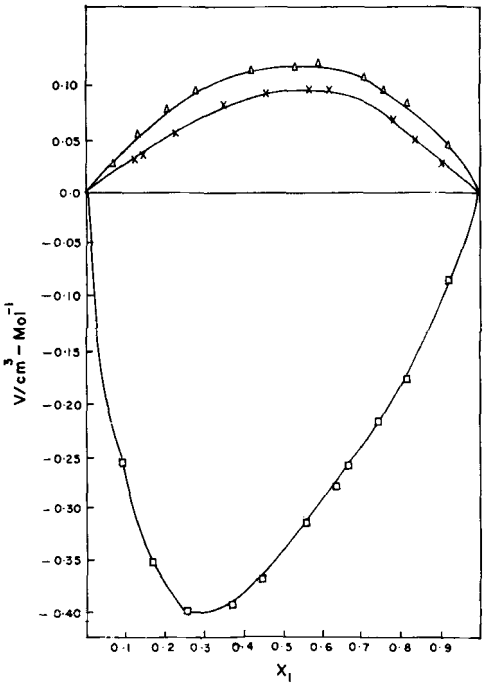

Figure 1 Excess molar volumes V^E of (Δ) (x) 1,2-dichloroethane + $(1-x)$ methanol, (×) (x) 1,1,1-trichloroethane + $(1-x)$ methanol, (□) (x) 1,1,2,2-tetrachloroethane + $(1-x)$ methanol at 303.15 K.

Table 2 Speed of sound for the binary mixtures of chloroalkane with methanol at 303.15 K.

	(x) 1,2-dichloroethane + $(1-x)$methanol				(x) 1,1,1-trichloroethane + $(1-x)$methanol		
x	U ($m.s^{-1}$)	K_s	K_s^E (TPa^{-1})	x	U	K_s ($m.s^{-1}$)	K_s^E
0.1001	1094.0	960	−33.0	0.07526	1062.8	1016	−27
0.1429	1098.6	920	−39.0	0.1368	1052.6	968	−49
0.2292	1106.0	857	−42.0	0.2098	1042.4	926	−64
0.3496	1112.5	793	−34.0	0.2854	1031.0	898	−69
0.4659	1118.5	746	−22.0	0.4225	1009.5	871	−62
0.5693	1124.0	712	−12.0	0.5373	992.5	861	−49
0.6229	1128.0	695	−7.0	0.5919	985.0	858	−42
0.7816	1144.0	646	−0.5	0.7092	970.0	855	−27
0.8356	1152.0	632	1.0	0.7537	965.0	854	−22
0.9104	1162.0	611	−0.1	0.8192	958.0	854	−15
				0.9232	950.0	850	−7
	(x) 1,1,2,2-tetrachloroethane + $(1-x)$methanol						
0.0935	1088.1	874	−83				
0.1705	1093.8	783	−93				
0.2585	1094.4	721	−89				
0.3726	1095.0	654	−70				
0.4502	1096.0	625	−56				
0.5614	1102.0	588	−41				
0.6341	1103.0	571	-				
0.6709	1108.0	558	−28				
0.7521	1114.0	539	−20				
0.8155	1119.0	526	−14				
0.9514	1129.0	501	−3				

Table 3 Values of the parameters A_0, A_1 and A_2 in Eq. 1 the standard devation σV_m^E at 303.15 K.

Systems	A_0	A_1	A_2	σV_m^E
		Cm^3/mol		
(x) 1,2-dichloroethane + $(1-x)$ methanol	0.39295	0.04482	−0.12965	0.00260
(x) 1,1,1-trichloroethane + $(1-x)$ methanol	0.48365	0.07856	0.10466	0.0018
(x) 1,1,2,2-tetrachloroethane + $(1-x)$ methanol	−1.39681	0.97819	−1.00318	0.0025

Table 4 Values of the parameters B_0, B_1, B_2 of Eq. 2 and standard deviation σK_m^E at 303.15 K.

Systems	B_0	B_1	B_2	σK_δ^E
		$10^{12}\ Pa^{-1}$		
(x) 1,2-dichloroethane + $(1-x)$ methanol	−134.349	−154.725	−0.824	1.483
(x) 1,1,1-trichloroethane + $(1-x)$ methanol	−278.693	−25.420	−138.372	0.505
(x) 1,1,2,2-tetrachloroethane + $(1-x)$ methanol	−337.591	−236.670	83.57	0.797

However, the excess volumes are negative for 1,1,2,2-tetrachloroethane + methanol. The results may be explained in terms of relative strengths of two opposing effects: (1) expansion in volume due to the dissociation of self associated alcohols i.e depolymerisation of alcohol aggregates[6] and (2) contraction in volume due to the interstitial accommodation of halogenated alkanes in the aggregates of alcohols and weak hydrogen bond interaction (Cl $\cdots$ H $\cdots$ O) between unlike molecules. The experimental results suggest that the first factor is dominant in mixture of 1,2-dichloroethane and 1,1,1-trichloroethane with methanol whereas factor two becomes dominant in mixtures of methanol with 1,1,2,2-tetrachloroethane. These results further suggested that two opposing effects balance each other to varying degrees depending on the nature of the chloroalkane.

The values of K_s are given in Table 2. It has been observed that the excess compressibility becomes increasingly negative as the strength of interaction between unlike molecules increases. The values support the results obtained through excess volume data the compressibility is in the order; 1,1,1-trichloroethane > 1,2-dichloroethane > 1,1,2,2-tetrachloroethane. The greater the compressibility of the binary mixture, larger could be the volume occupied.

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