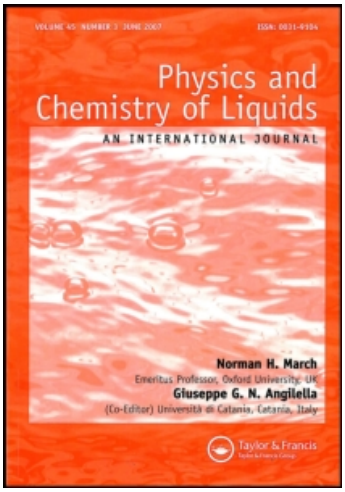

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Volumetric Behaviour of an Isomeric and Branched Alcohols with 1,2-Dichloroethane

K. Ram Babu[a]; J. Govindappa[a]; P. Venkateswarlu[a]; G. K. Raman[a]
[a] Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupati-2, India

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VOLUMETRIC BEHAVIOUR OF AN ISOMERIC AND BRANCHED ALCOHOLS WITH 1,2-DICHLOROETHANE

K. RAM BABU, J. GOVINDAPPA, P. VENKATESWARLU and G. K. RAMAN

Department of Chemistry, College of Engineering, Sri Venkateswara University Tirupati-2, India.

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Excess volumes (V^E) for the binary mixtures of 1,2-Dichloroethane with *i*-propanol, *i*-butanol, secbutanol, tert-butanol, *i*-pentanol, *i*-hexanol and cyclohexanol have been determined at 303.15 K, by dilatometric method over the entire range of composition. Values of V^E are positive over the whole mole fraction range studied. Results are explained in terms of break up of hydrogen bonds, interstitial accommodation of 1,2-dichloroethane in alcohol aggregates and possible hydrogen bond interaction of the type Cl···H—O between unlike molecules.

KEY WORDS: Hydrogen bonds, excess volumes.

1 INTRODUCTION

A survey of the literature has shown that many attempts have been made to measure the excess volumes for the mixtures of 1,2-dichloroethane with *n*-alkanes[1], *n*-alcohols[2], ketones[3], aromatic hydrocarbons[4] and acids[5]. But no attempt has been made to measure the excess volumes of dichloroethane with iso and branched alcohols. Hence we measured excess volumes for the mixtures of dichloroethane with *i*-propanol, *i*-butanol, sec-butanol, tert-butanol, *i*-pentanol, *i*-hexanol and cyclohexanol at 303.15 K.

2 EXPERIMENTAL

Excess volumes as a function of composition were measured directly by dilatometric method described by Rao and Naidu[6]. The experimental method was previously checked[7] for the test system benzene with cyclohexane and the results obtained showed a standard deviation of ± 0.003 cm^3 mol^{-1}. The dilatometers with different capacities were used to cover the entire range of molc fraction. Measurements were made using thermostatic bath controlled with in ± 0.001 K.

All materials were purified by the methods described by Riddick and Bunger[8]. 1,2-dichloroethane (BDH), washed with dilute potassium hydroxide and water, dried over an hydrous calcium chloride and fractionally distilled. All alcohols were dried by

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

Component	*Boiling point*		*Densities (ρ)*	
	Present work	*Literature*	*Present work*	*Literature*
1,2-dichloroethane	356.55	356.63	1.23832	1.23834
1-propanol	355.35	355.55	0.77691	0.77690
1-butanol	381.05	381.13	0.79439	0.79437
Sec.butanol	372.60	372.54	0.79895	0.79888
Tert-butanol	355.50	355.41	0.77570	0.77653
i-pentanol	403.75	403.65	0.80177	0.80179
i-hexanol	419.50	419.71	0.81873	0.81869
Cyclohexanol	434.20	434.35	0.94160	0.94155

refluxing with fused calcium oxide and fractionally distilled. The purity of the samples were checked by comparing the measured densities of the compounds with those reported in the literature[9]. Densities were determined using a bi-capillary type pyknometer which offered an accuracy of 2 parts in 10^5. The measured density and boiling points of the pure components are reported in table 1 along with literature.

3 RESULTS AND DISCUSSION

The experimental excess volumes of the seven binary mixtures are given in Table 2 and also graphically represented in Figure 1. The dependence of V^E on composition may be expressed by an empirical equation of the form

$$V^E/(\mathrm{cm^3 mol^{-1}}) = x_1 x_2 \left[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 \right] \quad (1)$$

Where a_0, a_1 and a_2 are adjustable parameters and x_1 is the mole fraction of dichloroethane. The values of the parameters obtained by the least square method are included in Table 3 along with standard deviation $\sigma(V^E)$.

The curves included in Figure 1 show that V^E is positive over the entire range of composition for the seven binary liquid mixtures. This values may be attributed the following factors (i) The addition of chloroethane to the associated alcohols may cause the break-up of alcohol aggregates into monomers leading to an increase in interspecies between the molecules in the mixtures compared with the pure components. (ii) Interstitial accommodation of dichloroethane in hydrogen bonded aggregates of alcohols and (iii) possible hydrogen bond interactions of the type Cl $\cdots$ H—O between unlike molecules. While the first factor contributes to the expansion of volume, the remaining factors may lead to contraction in volume. The actual value of V^E would be depend up on the balance between the two opposing contributions.

Table 2 Values of V^E for the binary mixtures of 1,2-dichloroethane with iso-alcohol at 303.15 K (x_1 is the mole fraction of 1,2-dichloroethane).

x_1	V^E	x_1	V^E
1,2-dichloroethane + *i*-propanol		1,2-dichloroethane + sec-butanol	
0.1365	0.176	0.1998	0.325
0.2423	0.294	0.3493	0.500
0.3348	0.385	0.4075	0.550
0.4257	0.441	0.4577	0.582
0.5486	0.478	0.6028	0.604
0.6724	0.448	0.6440	0.595
0.8114	0.326	0.7841	0.472
0.9090	0.180	0.8969	0.280
1,2-dichloroethane + *i*-butanol		1,2-dichloroethane + Tert-butanol	
0.1522	0.169	0.1428	0.388
0.2281	0.249	0.2978	0.636
0.3177	0.327	0.3840	0.709
0.4200	0.392	0.4823	0.750
0.5890	0.418	0.5920	0.735
0.6092	0.416	0.7174	0.634
0.7739	0.318	0.7645	0.573
0.8554	0.225	0.8510	0.420
1,2-dichloroethane + *i*-pentanol		1,2-dichloroethane + *i*-hexanol	
0.1944	0.176	0.2176	0.396
0.2785	0.231	0.3427	0.537
0.3264	0.259	0.4745	0.624
0.4260	0.325	0.5698	0.635
0.5249	0.336	0.6785	0.590
0.6371	0.356	0.6950	0.578
0.7935	0.306	0.7381	0.541
0.8936	0.203	0.9060	0.256
1,2-dichloroethane + Cyclohexanol			
0.1225	0.118		
0.2564	0.250		
0.3703	0.356		
0.5243	0.470		
0.6035	0.502		
0.7027	0.496		
0.7868	0.445		
0.8957	0.280		

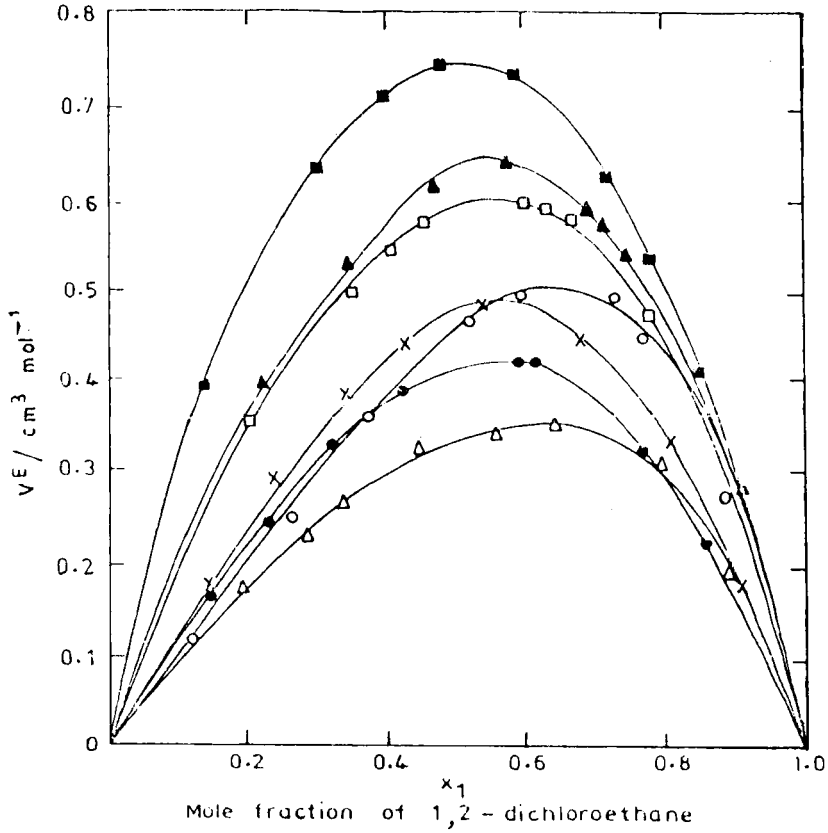

Figure 1 Values of V^E of 1,2-dichloroethane with Iso-alcohols at 303.15 K. (X_1 is the mole fraction of 1,2-dichloroethane). × = *i*-propanol, ● = *i*-butanol, △ = *i*-pentanol, ▲ = *i*-hexanol, □ = sec-butanol, ■ = tert-butanol, ○ = cyclohexanol.

Table 3 Values of parameters in equation (1) and the standard deviation (V^E) at 303.15 K.

System	a_0	a_1	a_2	σV^E
1,2-dichloroethane + *i*-propanol	1.885	0.461	−0.120	0.002
1,2-dichloroethane + *i*-butanol	1.674	0.368	−0.221	0.001
1,2-dichloroethane + Sec-Butanol	2.388	0.668	0.146	0.002
1,2-dichloroethane + Tert-Butanol	3.012	0.102	0.473	0.002
1,2-dichloroethane + *i*-pentanol	1.327	0.629	0.501	0.002
1,2-dichloroethane + *i*-hexanol	2.523	0.460	0.174	0.002
1,2-dichloroethane + Cyclohexanol	1.827	1.223	0.336	0.001

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