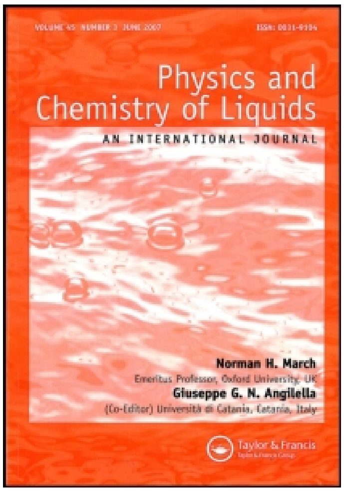

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S. Renuka Kumari[a]; K. Rambabu[a]; P. Venkateswarlu[a]; G. K. Raman[a]
[a] Physico-Chemical Laboratories, Department of Chemistry, College of Engineering, S. V. University, Tirupati, India

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MOLECULAR INTERACTIONS IN BINARY LIQUID MIXTURES CONTAINING 1,2-DIBROMOETHANE

S. RENUKA KUMARI, K. RAMBABU, P. VENKATESWARLU and G. K. RAMAN

Physico-Chemical Laboratories, Department of Chemistry,
College of Engineering, S. V. University,
Tirupati-517502, India

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Excess volumes (V^E) have been determined at 303.15 K for the binary systems of 1,2- dibromoethane with iso-propanol, iso-butanol, iso-pentanol, sec-butanol, tert-butanol and cyclohexanol. V^E is positive over the whole range of composition, indicating the dissociation of dimers and higher polymers of branched alcohols on dilution.

KEY WORDS: Hydrogen bonding, depolymerisation.

1 INTRODUCTION

A survey of the literature has shown that many attempts have been made to measure excess volumes for mixtures of haloalkanes with 1-alkanols[1–3], 1-alkanes[4], aromatic hydrocarbons[5,6], Ketones[7,8] and acid[9,10]. But no attempt has been made to measure the excess volumes of branched alkanols with 1,2-dibromoethane. Alcohols are self associated in the pure state through intermolecular hydrogen bonding. Dilution of such liquids with polar solvents like haloalkanes is expected to bring about dissociation of dimers and polymers of alcohols and formation of intermolecular hydrogen bonds between unlike-molecules. With a view to study the effect of these, hydrogenbond interactions between unlike molecules on V^E we have measured excess volumes for the systems 1,2-dibromoethane with iso-propanol, iso-butanol, iso-pentanol, sec-butanol, tert-butanol and cyclohexanol at 303.15 K.

2 EXPERIMENTAL

Excess volumes were measured with the dilatometer described by Rao and Naidu[11]. 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 i.d.) and the other end of the second bulb was fixed with a ground-glass stopper. The V^E values were accurate to ± 0.003 cm^3

Table 1 Densities of Pure Components at 303.15 K.

Component	*Density* (ρ)/*g Cm.*^{3} *mol*$^{-1}$	
	Present work	*Literature*
1,2-dibromoethane	2.15967	2.15970
Iso-propanol	0.77691	0.77690
Iso-butanol	0.79439	0.79437
Iso-pentanol	0.80177	0.80179
Sec-butanol	0.79896	0.79896
Tert-butanol	0.77623	0.77620
Cyclo hexanol	0.94160	0.94155

Table 2 Excess Volumes, V^E(cm^3 mol^{-1}) of 1,2-dibromoethane with branched alcohols at 303.15 K (X_1 is molefraction of 1,2-dibromoethane).

X_1	V^E	X_1	V^E
1,2-dibromoethane + iso-propanol		1,2-dibromomethane + iso-butanol	
0.1134	0.132	0.1354	0.144
0.2176	0.233	0.1724	0.179
0.2851	0.293	0.2976	0.290
0.3045	0.308	0.3793	0.348
0.4236	0.392	0.5304	0.410
0.4794	0.421	0.5558	0.414
0.6257	0.462	0.6960	0.389
0.8307	0.353	0.8904	0.204
0.8903	0.262		
1,2-dibromoethane + Sec-butanol		1,2-dibromoethane + tert-butanol	
0.1499	0.261	0.1315	0.164
0.2573	0.397	0.2778	0.328
0.2984	0.438	0.3338	0.377
0.4356	0.528	0.4930	0.482
0.5195	0.550	0.5424	0.497
0.5630	0.548	0.5988	0.499
0.6709	0.511	0.7585	0.417
0.8913	0.252	0.8709	0.279
1,2-dibromoethane + iso-pentanol		1,2-dibromoethane + cyclohexanol	
0.1561	0.165	0.1238	0.198
0.2399	0.229	0.2219	0.296
0.3869	0.305	0.3322	0.375
0.4093	0.311	0.4262	0.403
0.5074	0.324	0.5219	0.404
0.6492	0.295	0.6420	0.365
0.8237	0.185	0.7506	0.293
0.8974	0.119	0.8060	0.242
		0.8949	0.144

mol^{-1}. 1,2-dibromoethane (BDH) was washed with concentrated sulphuric acid, sodium carbonate solution, and water, dried over calcium chloride, and fractionally distilled. All alcohols were dried by refluxing with fused calcium oxide and distilling from it. The purity of the samples were checked by comparing the measured densities with those reported in the literature[12,13]. Densities were determined using a bicapillary type pycnometer with an accuracy of 2 parts in 10^5. The data are given in Table 1.

3 RESULTS AND DISCUSSION

The experimental V^E data for the mixtures of 1,2-dibromoethane with branched alcohols are given in Table 2 and graphically represented in Figures 1 and 2. The dependence of V^E on composition may be expressed by an empirical equation of the form

$$V^E/\mathrm{Cm}^3\ \mathrm{mol}^{-1} = X_1 X_2[a_0 + a_1(X_1 - X_2) + a_2(X_1 - X_2)^2] \qquad (1)$$

Where a_0, a_1 and a_2 are adjustable parameters and X_1 is the molefraction of 1,2-dibromoethane. The values of parameters obtained by the least squares method are included in Table 3 along with standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$

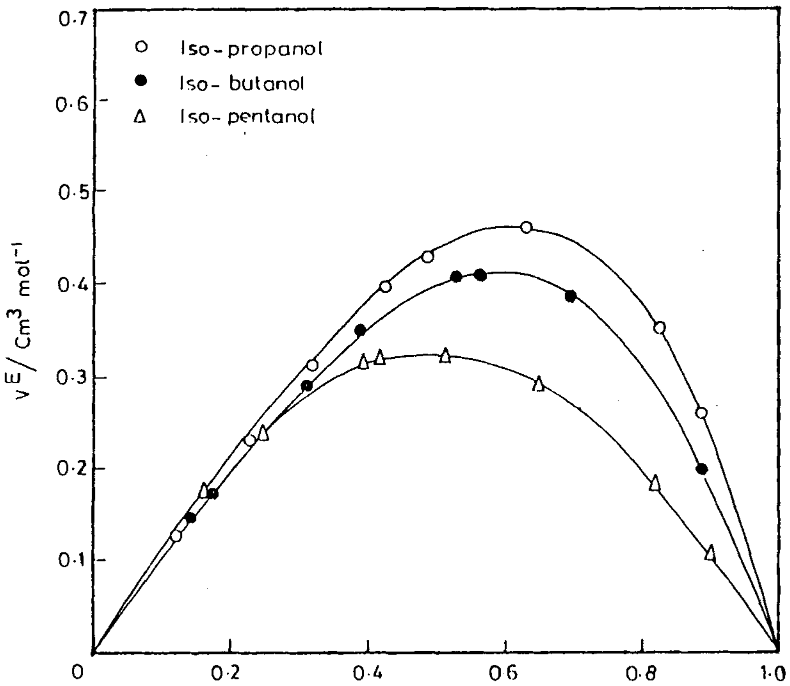

Figure 1 Mole fraction of 1,2-dibromoethane.

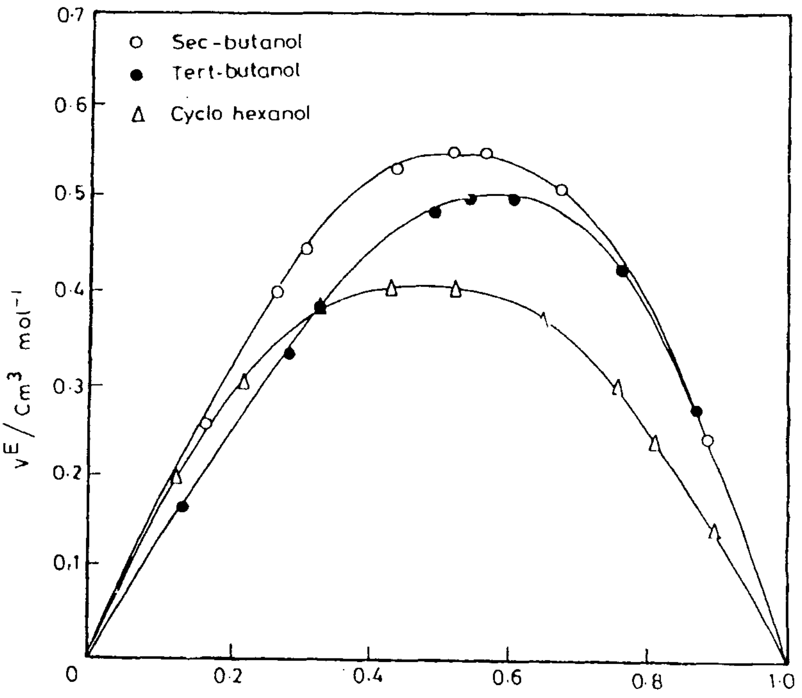

Figure 2 Mole fraction of 1,2-dibromoethane.

were obtained using the equation.

$$\sigma(V^E) = \left[\frac{(V^E\,\text{cal.} - V^E\,\text{exp}\,tl.)^2}{(n-p)}\right]^{1/2} \tag{2}$$

Where n is the number of experimental data and p is the number of parameters.

The data included in Table 2 and curves represented in Figures 1 and 2 show that V^E for all the systems under investigation are positive over the whole molefraction range. The following factors influence the excess volume: (a) depolymerisation of

Table 3 Values of the parameters a_0, a_1 and a_2 of the Eq. (1) and the standard deviation of $\sigma(V^E)$ at 303.15 K.

Systems *1,2-dibromoethane +*	a_0	a_1	a_2	$\sigma(V^E)$
	Cm³ mol⁻¹			
Iso-propanol	1.724	0.864	0.452	0.002
Iso-butanol	1.610	0.567	0.056	0.003
Sec-butanol	2.186	0.357	0.228	0.002
Tert-butanol	1.930	0.701	0.046	0.003
Iso-pentanol	1.292	0.027	−0.049	0.003
Cyclohexanol	1.623	−0.177	0.089	0.003

hydrogen bonded alcohol aggregates (b) the decrease in dipolar association of the components (c) interstitial accommodation of halo alkane in hydrogen bonded alcohol aggregates and (d) weak hydrogen bond interaction between unlike molecules. While the first two factors contribute to increase in excess volumes, the last two factors contribute to decrease in excess volumes. The reported positive excess volume pointed out that the factors influencing the expansion in volume are dominant over the factors influencing the contraction in volume. The decrease in excess volume of the binary mixtures is due to increase in chain length and consequent increase in dimerisation and decrease in the formation of higher polymers. This is in agreement with the fact that the strength of hydrogen bonding and hence association of alcohols decrease with increase in chain length.

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