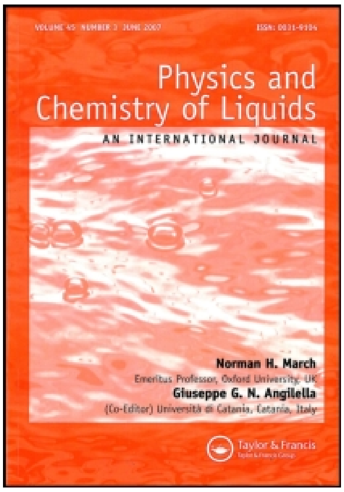

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EXCESS VOLUMES OF AN ALCOHOL WITH 1-BROMOBUTANE AT 303.15 K

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Excess volumes (V^E) for the binary mixtures of 1-bromobutane with *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *n*-pentanol, *i*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol have been determined at 303.15 K. V^E is almost positive over the entire range of composition in all nine systems studied. The experimental results are explained in terms of depolymerisation of hydrogen bonded alcohol aggregates, decrease in dipolar association and weak hydrogen-bonding interaction of the type Br---H—O between unlike molecules.

KEY WORDS: Hydrogen bonding, dipolar association.

1 INTRODUCTION

Thermodynamic properties have been extensive applications in characterising the aspects of physico-chemical behaviour of liquid mixtures such as molecular association, deassociation and complex formation. A survey of the literature has shown that many attempts have been made to measure excess volumes for the mixture of halo-substituted alkane (chloro and bromo alkane) with alcohols[1–4], alkanes[5–7], Ketones[8–10], aromatic hydrocarbons[11,12] and acids[13,14]. But no attempt has been made to study the excess volumes for the binary mixtures of *n*-alcohols and iso-alcohols. Hence we measured the excess volumes of bromobutane with *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *n*-pentanol, *i*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol at 303.15 K. Results are ascribed to interactions between unlike molecules.

2 EXPERIMENTAL

Excess volumes as a function of composition were measured directly by the dilatometric method[15,16]. The experimental method was previously checked[17] for the test system cyclohexane + benzene and the results obtained showed a standard deviation of $\pm 0.003\ \mathrm{cm^3\ mol^{-1}}$. Four dilatometers with different capacities were used to cover the entire mole-fraction range.

All alcohols except *n*-heptanol were dried by refluxing with fused calcium oxide and distilling from it. Heptanol (Koch-Light Lab. Ltd., England) was used without further

Table 1 Densities of pure components at 303.15 K

Component	*Density* (ρ)/g cm^3 mol^{-1}	
	Present work	*Literature*
1-Bromobutane	1.26130	1.26120
n-propanol	0.79574	0.79600
Iso-propanol	0.77691	0.77690
n-butanol	0.80215	0.80206
Iso-butanol	0.79439	0.79437
n-pentanol	0.80759	0.80764
Iso-pentanol	0.80177	0.80179
n-hexanol	0.81195	0.81201
n-heptanol	0.81573	0.81570
n-octanol	0.82188	0.82192

purification. Bromobutane were refluxed with concentrated sulphuric acid washed several times with water, dried over two portions of calcium chloride and finally fractioned. The purity of the samples were checked by comparing the measured densities with those reported in the literature[18,19]. Densities were determined using a bicapillary type pycno-meter with an accuracy of 2 parts in 10^5. The data are given in Table 1.

3 RESULTS AND DISCUSSION

The experimental excess volumes for the binary mixtures of bromobutane with alcohols at 303.15 K are presented in Table 2 and also graphically represented in Figures 1 and 2. The dependence of V^E on composition may be expressed by an empirical equation of the form

$$V^E/\mathrm{cm^3\,mol^{-1}} = X_1X_2[a_0 + a_1(X_1 - X_2) + a_2(X_1 - X_2)^2] \tag{1}$$

where a_0, a_1 and a_2 are adjustable parameters and X_1 is the mole-fraction of bromobutane. 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 $\sigma(V^E)$ were obtained using the equation

$$\sigma(V^E) = \left[\frac{\sum(V^E_{\mathrm{cal.}} - V^E_{\mathrm{exptl.}})^2}{n - p}\right]^{1/2} \tag{2}$$

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

The curves included in Figures 1 and 2 show that V^E is almost positive over entire range of composition for the mixtures of bromobutane with *n*-alcohols and iso-alcohols. The positive values of V^E are decreased with increasing the chain length of alcohol (C_3 to C_8). Excess volumes for the six binary mixtures (+*n*-alcohols) fall in order

n-propanol > *n*-butanol > *n*-pentanol > *n*-hexanol > *n*-heptanol and > *n*-octanol

Table 2 Excess volumes, V^E (cm^3 mol^{-1}) of 1-Bromo Butane with alcohols at 303.15 K (X_1 is mole fraction of 1-Bromo Butane)

X_1	V^E	X_1	V^E
1-Bromobutane + *n*-propanol		1-Bromobutane + Iso-propanol	
0.0800	−0.007	0.1119	0.122
0.1783	0.018	0.1966	0.200
0.3801	0.134	0.2584	0.248
0.4496	0.167	0.4103	0.329
0.5853	0.209	0.4818	0.349
0.6225	0.210	0.5357	0.358
0.7093	0.202	0.6792	0.337
0.8307	0.143	0.8301	0.237
1-Bromobutane + *n*-butanol			
0.1005	−0.011		
0.2252	0.032		
0.2494	0.047		
0.2968	0.073		
0.4513	0.151		
0.6491	0.199		
0.7497	0.183		
0.8395	0.140		
1-Bromobutane + Iso-butanol		1-Bromobutane + *n*-pentanol	
0.1123	0.045	0.0636	−0.017
0.2176	0.081	0.2102	0.027
0.2807	0.092	0.3310	0.098
0.4649	0.149	0.4424	0.156
0.4946	0.156	0.4954	0.176
0.6492	0.182	0.7005	0.189
0.7239	0.184	0.7593	0.168
0.8570	0.145	0.8815	0.100
1-Bromobutane + Iso-pentanol			
0.1559	0.020		
0.2333	0.051		
0.3385	0.106		
0.5154	0.169		
0.6715	0.172		
0.6859	0.167		
0.7661	0.143		
0.8852	0.077		
1-Bromobutane + *n*-hexanol		1-Bromobutane + *n*-heptanol	
0.1747	−0.028	0.2241	0.040
0.2400	0.007	0.3653	0.103
0.3706	0.085	0.4458	0.134
0.4725	0.136	0.4825	0.146
0.5605	0.167	0.6312	0.168
0.7173	0.173	0.7404	0.158
0.7775	0.152	0.8018	0.139
0.8585	0.114	0.8827	0.095
1-Bromobutane + *n*-octanol			
0.1226	0.004		
0.2729	0.060		
0.4271	0.130		
0.5289	0.165		
0.6132	0.178		
0.7431	0.171		
0.8101	0.150		
0.9423	0.062		

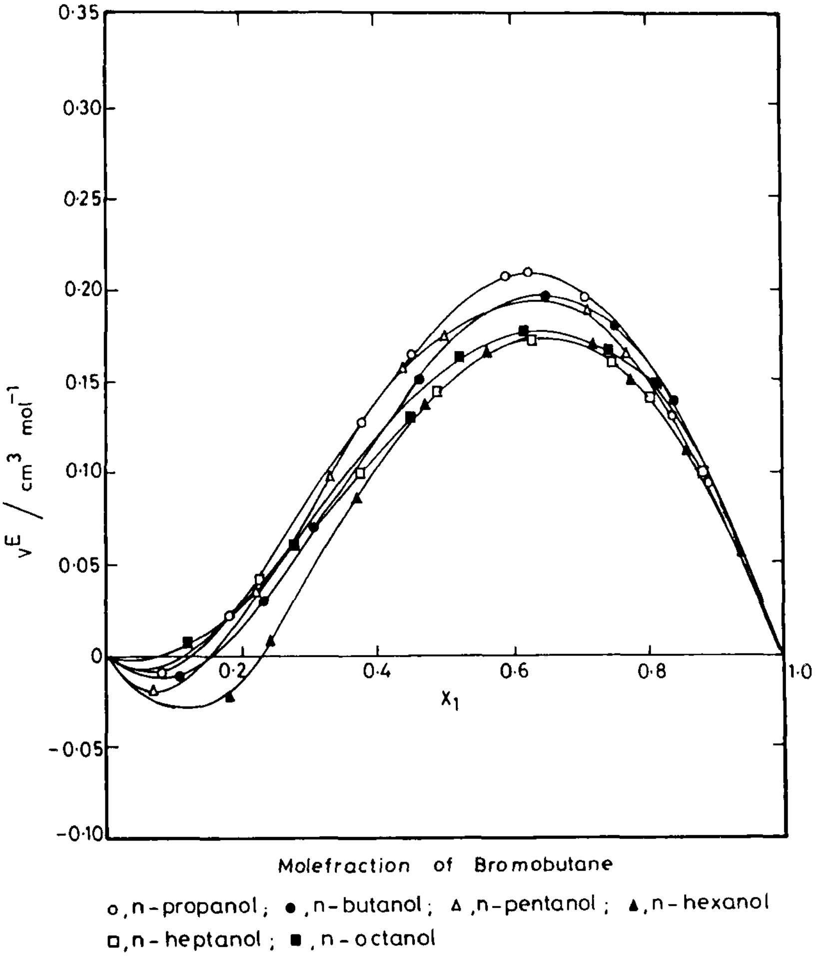

Figure 1 Mole fraction (X_1) of 1-bromobutane against excess volumes (V^E) for the systems of bromobutane with *n*-alcohols at 303.15 K. ○—*n*-propanol, ●—*n*-butanol, △—*n*-pentanol, ▲—*n*-hexanol, □—*n*-heptanol, ■—*n*-octanol.

The values of V^E for the binary mixtures of bromobutane with *i*-alcohols are fall in order

i-propanol > *i*-butanol and > *i*-pentanol

The observed V^E values may be explained qualitatively by postulating following factors (1) depolymerisation of hydrogen bonded alcohol aggregates (2) decrease in dipolar association of the components (3) interstial accommodation of bromobutane in hydrogen bonded alcohol aggregates and (4) weak hydrogen bonding interaction of the type Br---H—O between unlike molecules as well as difference in size and shape. While the first two factors lead to expansion in volume, the factors (3) and (4) contribute to contraction. The actual value of V^E will depend upon the balance

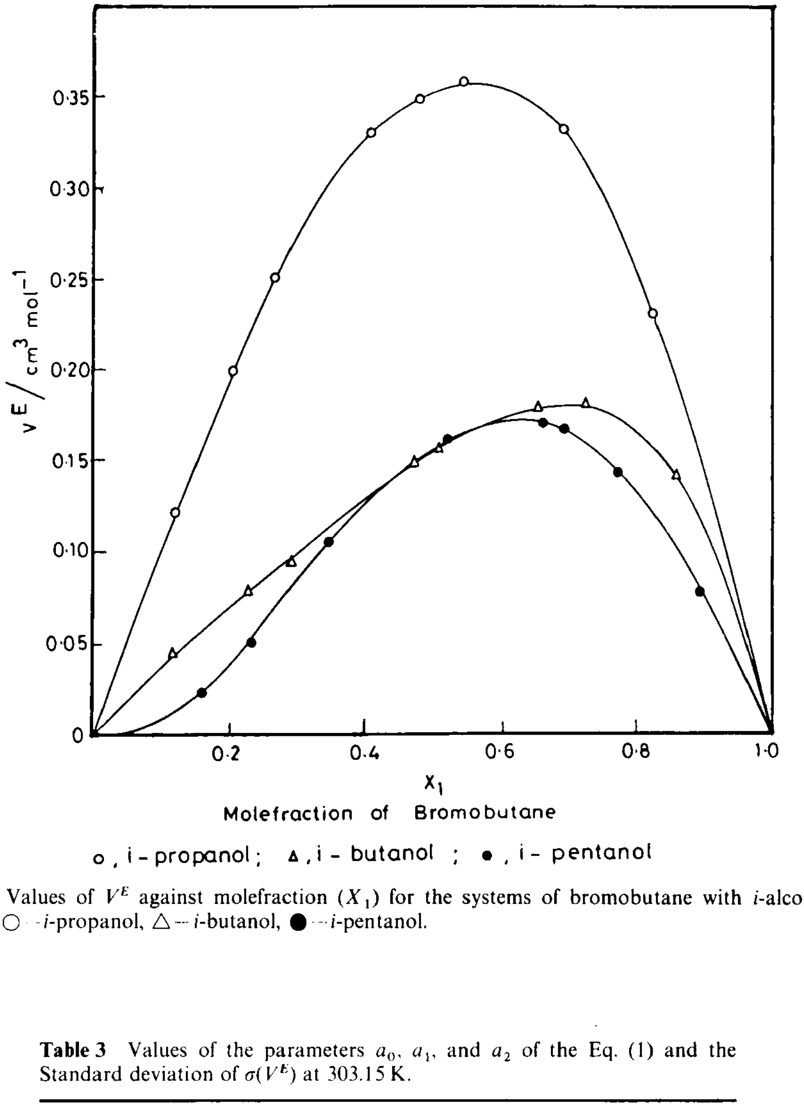

Figure 2 Values of V^E against molefraction (X_1) for the systems of bromobutane with *i*-alcohols at 303.15 K. ○ -*i*-propanol, △—*i*-butanol, ● —*i*-pentanol.

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	a_0	a_1	a_2	$\sigma(V^E)$
	$cm^3\ mol^{-6}$			
1-Bromobutane + *n*-propanol	0.747	0.687	−0.394	±0.003
1-Bromobutane + Iso-propanol	1.420	0.320	0.093	±0.002
1-Bromobutane + *n*-Butanol	0.693	0.735	−0.343	±0.002
1-Bromobutane + Iso-Butanol	0.624	0.507	0.376	±0.003
1-Bromobutane + *n*-Pentanol	0.714	0.680	−0.511	±0.002
1-Bromobutane + Iso-Pentanol	0.666	0.458	−0.425	±0.002
1-Bromobutane + *n*-Hexanol	0.595	0.833	−0.530	±0.004
1-Bromobutane + *n*-Heptanol	0.601	0.558	−0.191	±0.002
1-Bromobutane + *n*-octanol	0.615	0.667	−0.107	±0.003

between two opposing sets of contributions. The experimental V^E values for the mixtures suggest that factors (1) and (2) are dominant in all the nine systems studied.

The lower positive values of V^E for *n*-propanol, *n*-butanol and *n*-pentanol than *i*-propanol, *i*-butanol and *i*-pentanol may be due to steric hindrance of braching alkyl groups.

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