

## Excess volumes of isomeric butanols with di-*n*-butyl ether<sup>†</sup>

K R PATIL, GOPAL PATHAK and S D PRADHAN\*

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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**Abstract.** The excess volumes of four isomeric butanols with di-*n*-butyl ether were determined at 30°C. The isomeric effect was distinctly observed in the excess volume profiles. 1-Butanol and 2-methyl-1-propanol systems exhibited negative excess volumes throughout the concentration range. The 2-butanol system had positive excess volumes up to 0.9 mol fraction of alcohol after which it became negative, while the 2-methyl-2-propanol system exhibited positive excess volumes throughout the concentration range.

**Keywords.** Excess volume: binary mixtures: isomeric effect: butanol-ether systems.

### 1. Introduction

In continuation of our studies on structural effect and effect of functional groups on the excess thermodynamic properties of associated liquids (Pradhan 1979, 1981; Pathak *et al* 1987; Pathak and Pradhan 1988), we report here the excess volume studies on four isomeric butanols with di-*n*-butyl ether.

### 2. Experimental

#### 2.1 Materials

1-Butanol, 2-methyl-1-propanol, 2-butanol, 2-methyl-2-propanol, cyclohexane (AR grade) were further purified by fractional distillation. Benzene (AR grade) was purified with conc. sulphuric acid and then fractionally distilled. Di-*n*-butyl ether (Fluka AG) was used as such without further purification. All the compounds were analysed by GLC (Varian 3600) and found to be >99% pure.

#### 2.2 Apparatus and procedure

All the compounds were dried with freshly activated molecular sieves. Binary mixtures were made by taking weighed quantities of the two compounds.

Densities were determined by vibrating tube densimeter type A, Anton Paar (DMA

<sup>†</sup>NCL Communication No. 4678

\*For correspondence

602/60), using the differential arrangement. One of the cells was filled with distilled water and the other with sample mixture. Temperatures of cells were kept constant to  $\pm 0.005^\circ\text{C}$ . The densities are accurate to  $\pm 5 \times 10^{-6} \text{g/cm}^3$ . Densities of the benzene-cyclohexane system were determined at  $25^\circ$  while that of the alcohol-butyl ether systems were determined at  $30^\circ\text{C}$ .

### 3. Results and discussion

The apparatus and the procedure were standardized by determining the excess volumes of the benzene-cyclohexane system. The data from the present work were compared with those calculated by the least squares equation of the standard data of Kumaran and McGlashan (1977). Both sets of data are given in table 1. The standard deviation of the results of the present work is  $= 0.002 \text{cm}^3/\text{mol}$ .

The excess volume data for 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol systems with di-*n*-butyl ether are reported in table 2.

The data were fitted in by the least squares method to the equation

$$V^E = x_1 x_2 \sum_{i=0}^3 A_i (x_1 - x_2)^i.$$

The least squares parameters along with the standard deviations are given in table 3. The excess volumes ( $V^E$ ) as functions of the mole fractions of the alcohols are shown in figure 1.

**Table 1.** Excess volume of cyclohexane with benzene at  $25^\circ\text{C}$ .

$x_1$ Mole fraction cyclohexane	$V^E$ (ml/mol) (Present data)	$V^E$ (ml/mol) (Calculated)*
0.0000	—	—
0.0520	0.1206	0.1258
0.1029	0.2285	0.2316
0.1416	0.3099	0.3104
0.1876	0.3870	0.3897
0.2529	0.4805	0.4841
0.3107	0.5537	0.5500
0.3431	0.5858	0.5798
0.4015	0.6233	0.6202
0.4247	0.6325	0.6315
0.5184	0.6552	0.6496
0.5752	0.6417	0.6388
0.6254	0.6159	0.6153
0.6738	0.5793	0.5800
0.7534	0.4977	0.4945
0.8185	0.4054	0.3985
0.8678	0.3185	0.3097
0.9094	0.2254	0.2236
1.0000	—	—

\*Kumaran and McGlashan (1977)

**Table 2.** Excess volumes of isomeric butanol (1) and di-*n*-butyl ether (2) systems at 30 °C.

<i>x</i>	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	<i>x</i>	$V^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )
<i>1-Butanol–di-n-butyl ether</i>			
0.0218	-0.024	0.5204	-0.227
0.0621	-0.076	0.5751	-0.226
0.0812	-0.088	0.7364	-0.183
0.1065	-0.101	0.8101	-0.144
0.2031	-0.160	0.9025	-0.070
0.2968	-0.192	0.9519	-0.035
0.4174	-0.220		
<i>2-Methyl-1-propanol–di-n-butyl ether</i>			
0.0507	-0.032	0.4987	-0.151
0.1009	-0.066	0.5462	-0.149
0.1433	-0.081	0.6015	-0.147
0.1929	-0.108	0.6626	-0.142
0.2779	-0.124	0.7105	-0.131
0.3343	-0.134	0.7906	-0.109
0.3879	-0.142	0.8357	-0.095
0.4500	-0.149	0.9248	-0.057
<i>2-Butanol–di-n-butyl ether</i>			
0.0199	0.005	0.5034	0.135
0.0523	0.031	0.6040	0.112
0.0748	0.036	0.6677	0.094
0.1007	0.054	0.6924	0.083
0.1924	0.086	0.7983	0.038
0.3016	0.121	0.8729	0.010
0.3801	0.132	0.9534	-0.008
<i>2-Methyl-2-propanol–di-n-butyl ether</i>			
0.0314	0.049	0.4740	0.392
0.0508	0.077	0.5487	0.403
0.0769	0.111	0.6232	0.396
0.1776	0.228	0.6868	0.367
0.2480	0.293	0.7821	0.300
0.3180	0.339	0.8608	0.219
0.4002	0.372	0.9424	0.106

**Table 3.** Redlich–Kister parameters for excess volumes of isomeric butanol-di-*n*-butyl ether systems at 30 °C.

System	<i>A</i> <sub>0</sub> (ml/mol)	<i>A</i> <sub>1</sub> (ml/mol)	<i>A</i> <sub>2</sub> (ml/mol)	<i>A</i> <sub>3</sub> (ml/mol)	Standard deviation
1-Butanol + di- <i>n</i> -butyl ether	-0.92261	-0.05331	-0.06923	0.35499	0.0038
2-Methyl-1-propanol + di- <i>n</i> -butyl ether	-0.59635	0.01964	-0.20662	-0.12151	0.0027
2-Butanol + di- <i>n</i> -butyl ether	0.56039	-0.27786	-0.47929	-0.07161	0.0049
2-Methyl-2-propanol + di- <i>n</i> -butyl ether	1.59865	0.19006	0.21155	0.00752	0.0029

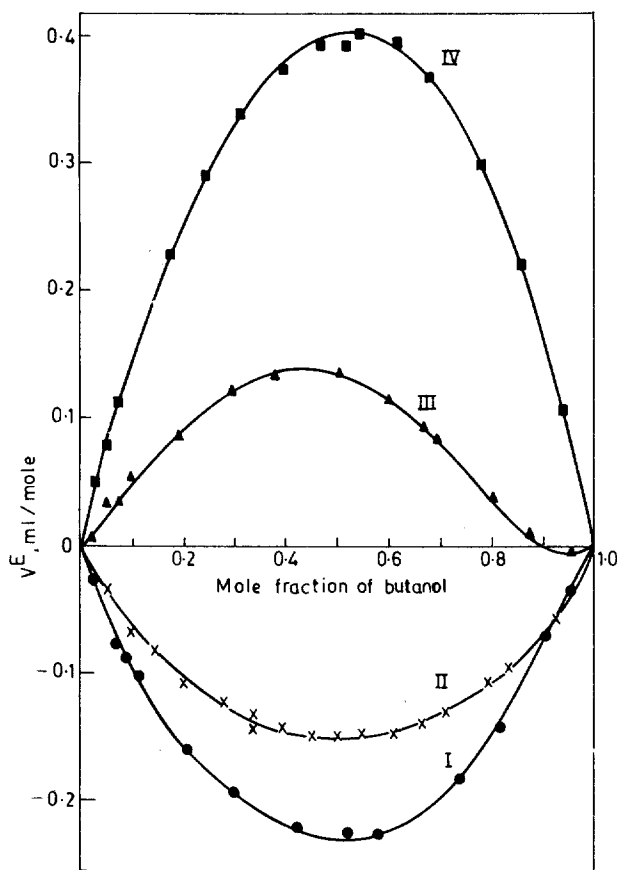


Figure 1.  $V^E$  vs  $x_1$  plots for isomeric butanol (1) and di-*n*-butyl (2) systems (I – 1-butanol, II – 2-methyl-1-propanol, III – 2-butanol, IV – 2-methyl-2-propanol).

There is a considerable effect of the structure of butanol molecules on the excess volumes. The 1-butanol and 2-methyl-1-propanol systems showed negative excess volumes throughout the concentration range. The negative excess volume of the former system was greater than that of the latter system,

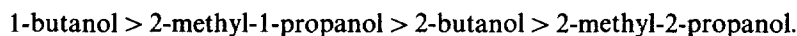
$$1\text{-butanol} > 2\text{-methyl-1-propanol}.$$

The 2-butanol system exhibited a positive excess volume upto nearly 0.89 mole fraction of alcohol. The  $V^E$  was negative between 0.9 to 1.0 mole fraction. The 2-methyl-2-propanol system exhibited positive excess volumes throughout the concentration range. Amongst these two systems the positive excess volumes increased in the order

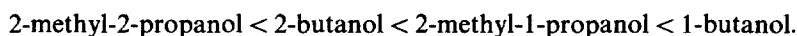
$$2\text{-methyl-2-propanol} > 2\text{-butanol}.$$

The enthalpies of mixing of these systems show strong endothermic behaviour indicating the breaking of H-bonded alcohol polymers. At the same time it is established by thermochemical cycle calculations that subsequently ether-alcohol

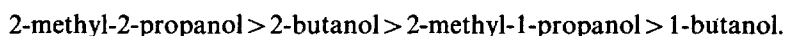
complex formation also takes place (Pathak and Pradhan 1988). Such complex formation is also established by IR spectroscopy (Murthy and Rao 1968). The breaking of H-bonds leads to liquid structure-breaking and positive excess volume, while H-bond formation leads to negative excess volume. The endothermic heats of mixing at 0.5 mole fraction for these systems vary as



This indicates that the degree of H-bonded complex formation between alcohol and ether molecules decrease in the same manner. The contribution of negative volume change to the net volume change, therefore, changes as below



The disruption of the orientational ordered structure of dibutyl ether molecules by alcohol molecules also contributes to excess volumes. 1-Butanol being a linear molecule will have a structure-oriented effect due to Van der Waals forces of attraction while 2-methyl-2-propanol being nearly spherical will have a significant structure-breaking effect. The disorder in the dibutyl ether liquid structure is therefore expected to vary as



It is therefore clear that both the steric hindrance in the formation of H-bonding between alcohol and ether molecules and the different degrees of disruption of dibutyl ether liquid structure due to the branching of the butyl alcohol chain contribute to the observed trend of excess volumes. The excess volumes of 1-butanol system are negative as the linearity of the butanol molecule favours both H-bond formation and orientational ordering. Both these factors are adversely affected as there is branching in the butyl chain and the effect increases as the branching approaches the  $\alpha$ -carbon atom. The excess volumes, therefore, become less negative for the 1-methyl-1propanol, positive for the 2-butanol and more positive for the 2-methyl-2-propanol systems.

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