

Volume change on mixing of isomeric butanols with normal heptane*

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Abstract. Volume changes on mixing of isomeric butanols with *n*-heptane have been determined at 25° C and that of tertbutanol at 26° C. All the four systems show a positive excess volume throughout concentration range. The excess volumes have been found to vary in the order of tert > sec > iso > *n*-butanols. The order of the excess volume has been attributed to breaking of hydrogen bonds of associated species of alcohol by dilution with *n*-heptane and more random distribution of *n*-heptane molecules.

Keywords. Volume change; excess volumes; binary systems; butanols-heptane.

1. Introduction

In continuation of the work from our laboratory on excess thermodynamic properties like excess volume, free energy and heats of mixing of various systems, attempts are being made to study isomeric butanols and *n*-heptane binary systems. Excess volumes of the binary systems of alkanol with alkane have been widely studied (Stavely and Spice 1952; Van Ness *et al* 1967; Brown *et al* 1969; Diaz Pena and Cheda 1970; Ruel 1973; Marsh and Burfitt 1975; Gupta *et al* 1976; Treszczanowicz and Benson 1977) and the data obtained have been used to compare them with theory.

In this paper our results on the volume changes in the mixing of binary mixtures of *n*, iso, sec. and tertiary butanols with *n*-heptane at 25° C are reported with a view to investigate the nature of interactions between different isomeric butanols with *n*-heptane and the effect of branching of alkyl chain of butanols on breaking the hydrogen bonds.

2. Materials

n-Butanol (BDH pure grade), iso-butanol (BDH LR grade), sec.-butanol (Renal Budapest) and tertiary butanol (Baeyer German Product) were used. The butanols were refluxed over NaOH pellets and thereafter fractionally distilled using 1 m

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long column packed with glass helices with a reflux ratio of 1 : 30. The constant boiling middle fractions were again fractionally distilled in the same manner. All butanols were refluxed over anhydrous CaO before use.

n-Heptane, a product of Reachim Standard, U.S.S.R., was purified in the same manner over P_2O_5 . The butanols and *n*-heptane were stored over molecular sieve type 4A before use. The purity of the compounds was found to be more than 99.5%.

Densities of pure components were measured at 25° C and those of tert-butanol at 26° C. The densities of pure components are listed in table 1 along with the values from literature for ready comparison.

3. Apparatus

The volume change on mixing was calculated from density measurements of the binary mixtures of weighed quantity of butanols and *n*-heptane. The densities were determined by using a Lipkin type two-arm pycnometer having a capillary bore of 0.5 mm I.D. and the normal volume of 34.06 ml. The temperature of the thermostat was maintained within $\pm 0.01^\circ\text{C}$ by means of a toluene regulator and an electronic relay.

The uncertainty involved in the measurement of volume and mass of liquid were 10^{-4} ml and 10^{-4} g respectively. Each of them introduces an error of 4×10^{-4} units of density and hence the maximum combined effect is 8×10^{-6} g/ml in the measurement of density.

The overall working of the experimental set-up was standardised by studying the volume change on mixing of benzene and *n*-heptane system at 25° C. The results obtained by us for this system agreed fairly well (figure 1) with those reported by Brown and Ewald (1951) and Jain *et al* (1968).

4. Results and discussion

The results of the volume change on mixing of *n*, iso, sec. and tertiary butanols with *n*-heptane are presented in table 2. The excess volume V^E has been fitted by the least square method into a series equation of the type

$$V^E = Ax + Bx^2 + Cx^3 + Dx^4,$$

Table 1. Densities of pure components at 25° C.

Component	d_{observed}	$d_{\text{literature}}$
<i>n</i> -Butanol	0.80570	0.80570 ^a
iso-Butanol	0.79790	0.79780 ^b
sec. Butanol	0.80223	0.80260 ^b
tert-Butanol (26° C)	0.77987	..
<i>n</i> -Heptane	0.67950	0.67951 ^b

^aTimmermans (1950).

^bRiddick and Bunger (1970)

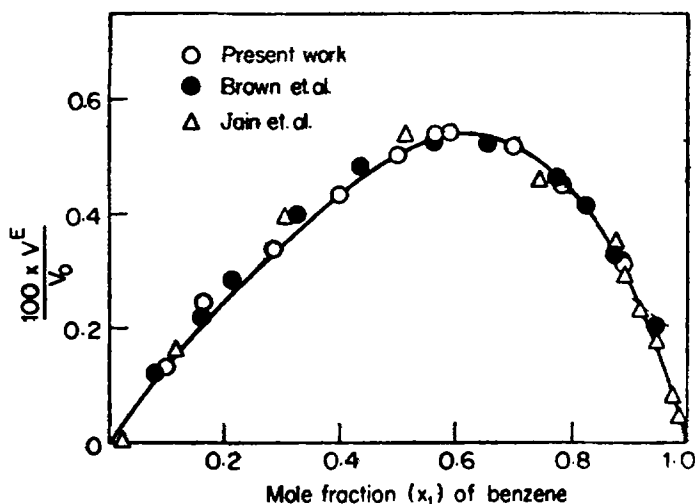


Figure 1. $100 V^E / V_{ideal}$ versus x_1 plot for benzene (1)-*n*-heptane (2) system at 25° C.

where A , B , C and D are constants and x is the mole fraction of butanol. The values of the constants were calculated by Honeywell-400 computer and are tabulated in table 3.

Treszczanowicz and Benson (1977) also studied the *n*-butanol and *n*-heptane system at the same temperature V^E vs a function of x_1 , the mole fraction of *n*-butanol, is plotted in figure 2 along with their data and it is found that their results agree with our data.

The excess volumes as a function of the mole fraction of alcohols for all four systems have been plotted in figure 3. The V^E is positive throughout the entire concentration range for all the four systems. It is well established that the aliphatic alcohols undergo self-association through hydrogen bonding and these species are broken on dilution with a non-polar solvent. The positive excess volume change on mixing is, therefore, attributed to the dissociation of associated species of alcohol by dilution with *n*-heptane.

The branching of the alkyl chain of alcohol has a considerable effect on the volume change on mixing as shown in figure 3. The change in magnitude and symmetry is observed among the curves with the branching of alcohols. The maximum shifts towards the higher mole fraction of the alcohol as the substitution of the methyl group shifts towards α -carbon atom. Thus the maximum volume change on mixing for *n*, iso, sec. and tertiary butanols are obtained nearly at 0.275, 0.348, 0.40 and 0.55 mole fractions of the respective alcohols. Brown *et al* (1969) obtained the maxima at nearly the same mole fractions of alcohols in case of isomeric butanols with benzene. The V^E vs x_1 curves suggest the probable stoichiometry of the interactions. The maxima at 0.275 mole fraction of *n*-butanol in the first system indicate that *n*-butanol probably has tetrameric association in pure liquid state, while the maximum V^E at 0.55 mole fraction of tert-butanol indicates the possibility of the predominance of dimeric species in pure liquid state. It may be noted that higher polymeric species decrease as the substitution of the methyl group approaches the α -carbon atom. This is consistent with the obser-

Table 2. Volume change on mixing of isomeric butanols-*n*-heptane at 25° C.

Sl. No.	x_1 mole fraction of alcohol	d_M	V^E ml/mole	Sl. No.	x_1 mole fraction of alcohol	d_M	V^E ml/mole
<i>n</i> -Butanol				<i>sec.</i> -Butanol			
1.	0.0255	0.68109	0.0933	1.	0.0501	0.68270	0.1543
2.	0.0506	0.68294	0.1401	2.	0.1035	0.68637	0.2845
3.	0.0755	0.68482	0.1712	3.	0.1502	0.68986	0.3717
4.	0.1063	0.68730	0.1890	4.	0.2024	0.69408	0.4409
5.	0.1508	0.69105	0.2086	5.	0.3000	0.70261	0.5357
6.	0.2110	0.69637	0.2255	6.	0.4025	0.71272	0.5704
7.	0.2751	0.70241	0.2369	7.	0.5037	0.72389	0.5452
8.	0.3420	0.70907	0.2357	8.	0.5974	0.73570	0.4611
9.	0.4005	0.71542	0.2143	9.	0.6953	0.74919	0.3726
10.	0.4999	0.72692	0.1822	10.	0.8015	0.76556	0.2576
11.	0.5998	0.73955	0.1437	11.	0.8505	0.77390	0.1943
12.	0.6746	0.75000	0.1061	12.	0.8976	0.78232	0.1254
13.	0.7449	0.76045	0.0733				
14.	0.7999	0.76920	0.0509				
15.	0.8482	0.77730	0.0345				
16.	0.9010	0.78665	0.0188				
17.	0.9502	0.79581	0.0145				
<i>iso</i> -Butanol				<i>tert</i> -Butanol (at 26° C)			
1.	0.0510	0.68267	0.1441	1.	0.0294	0.67982	0.1795
2.	0.1059	0.68662	0.2313	2.	0.0523	0.68085	0.2920
3.	0.1504	0.69004	0.2801	3.	0.1018	0.68360	0.4172
4.	0.2516	0.69841	0.3461	4.	0.1504	0.68644	0.5400
5.	0.3483	0.70735	0.3713	5.	0.2503	0.69294	0.7185
6.	0.4509	0.71790	0.3522	6.	0.3467	0.69980	0.8635
7.	0.5464	0.72870	0.3103	7.	0.4515	0.70820	0.9711
8.	0.6410	0.74057	0.2545	8.	0.5508	0.71710	1.0195
9.	0.7498	0.75567	0.1780	9.	0.6517	0.72762	0.9961
10.	0.8528	0.77162	0.1094	10.	0.7503	0.73946	0.8648
11.	0.9502	0.78863	0.0361	11.	0.8246	0.74985	0.6704
				12.	0.8509	0.75373	0.5999
				13.	0.8972	0.76110	0.4413
				14.	0.9499	0.77023	0.2119

vation that steric hindrance increases as we go from iso to sec. to tert-butanols.

The magnitude of the volume change on mixing increases in the following order:

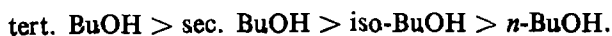


Table 3. The least square constants of the equation $V^E = Ax + Bx^2 + Cx^3 + Dx^4$ for the volume change on mixing of isomeric butanols with *n*-heptane at 25° C.

System	A	B	C	D	σ (standard deviation)
<i>n</i> -Butanol	0.08245	1.11984	-2.69571	1.43182	0.24×10^{-2}
iso-Butanol	0.06011	1.19341	-3.54737	1.56835	0.41×10^{-2}
sec-Butanol	0.01350	3.08509	-5.04582	1.95435	0.50×10^{-2}
tert-Butanol	0.14608	2.54242	-0.47393	-2.2264	0.83×10^{-2}

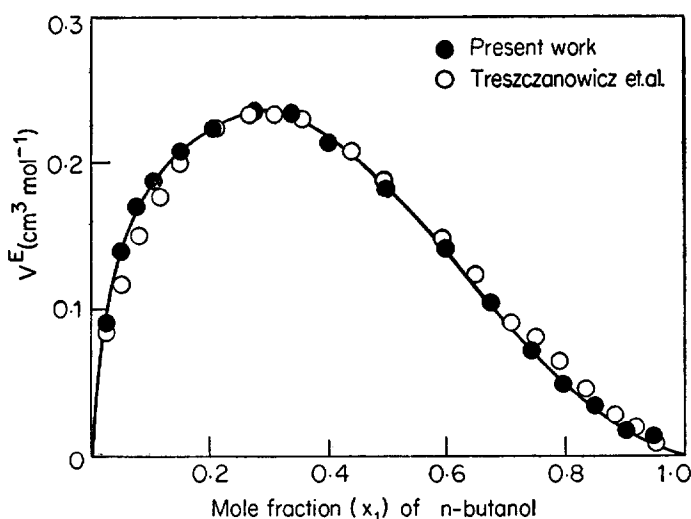


Figure 2. V^E versus x_1 plot for *n*-butanol(1)-*n*-heptane (2) systems at 25° C.

The above trend has also been observed in the case of isomeric butanols with benzene systems by Brown *et al* (1969). The trend of the excess volume observed in the present study agrees with that of enthalpies of isomeric butanols with *n*-hexane studied by Brown *et al* (1969).

Considering the fact that V^E in the case of tert-butanol system is 330% more than that of *n*-butanol system, the increase in V^E may not be entirely due to the number of hydrogen bonds breaking on dilution with *n*-heptane. It may be probable that the shape of the molecule also plays an important role. The *n*-butanol molecules are planned and elongated similar to those of *n*-heptane. The molecular alignment of these molecules on mixing is therefore likely to be ordered due to Van der Waal's forces. The molecules of tert-butanol, on the contrary, are bulky and spherical and the mixture with *n*-heptane molecules is likely to be more random. The spherical tert-butanol molecules may also destroy the ordered alignment of *n*-heptane molecules.

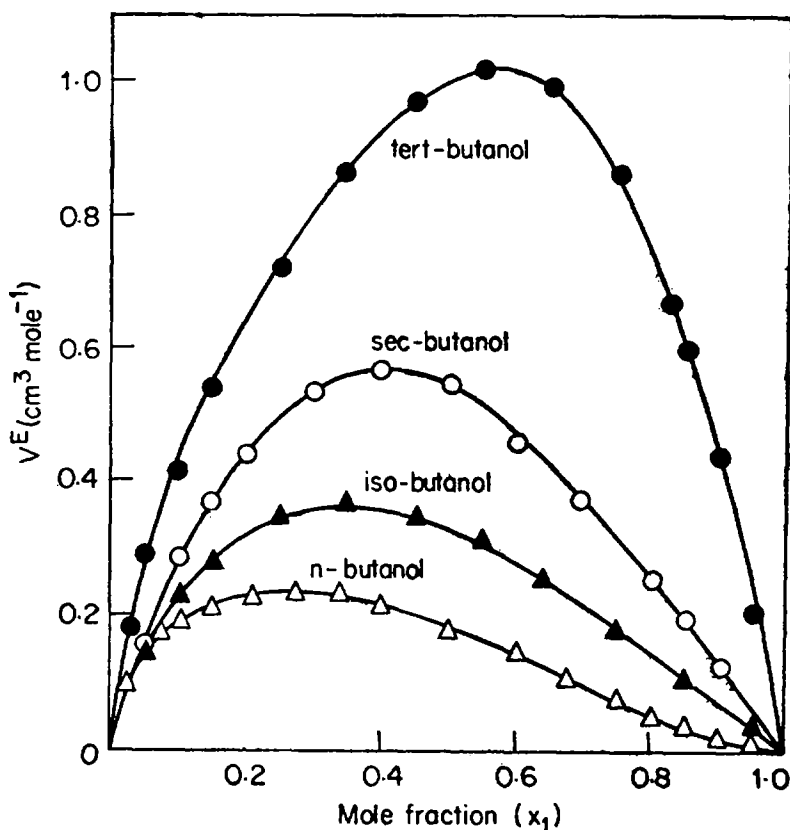


Figure 3. V^E versus x_1 plots for isomeric butanols (1) and *n*-heptane (2) systems at 25° C.

Table 4. Partial molar excess volume.

System	$x_1 \rightarrow 0$ ml/mole	$x_2 \rightarrow 0$ ml/mole
<i>n</i> -Butanol	6.0	0.2
iso-Butanol	3.7	0.7
sec-Butanol	3.4	1.0
tert-Butanol	7.2	4.1
<i>n</i> -Propanol ^a	8.0	1.13
iso-Propanol ^a	9.1	2.24

^aVan Ness *et al* (1967).

The values of V^E/x_1x_2 were plotted against x_1 for all the four systems and the extrapolated values at $x_1 = 0$ and $x_2 = 0$ are given in table 4. The value of partial molar excess volume \bar{V}^E for *n*-butanol is 6.0 ml/mele and is in good acree

ment with that obtained by Treszczanowicz and Benson (1977). The values given in table 4 follow the same trend as that of excess volume. The partial molar excess volume of *n*-heptane at infinite dilution for *n*-butanol system is 0.2 ml/mole and agrees with that reported by Treszczanowicz and Benson (1977) values.

The partial molar excess volume of *n*-heptane is affected by the structure and the shape of the alcohol molecules. In the case of *n*-butanol with straight alkyl chain, the value of V^E of *n*-heptane is 0.2 ml/mole, whereas in the case of isobutanol and sec. butanol the corresponding values are 0.7 and 1.0 ml/mole respectively. It may be noted that shifting the methyl substitution from β to α -carbon atom of alcohol makes a small change in symmetry accompanied by a small increase in \bar{V}^E , i.e. 0.3 ml/mole. The large value of \bar{V}^E in the case of tert-butanol, i.e. 4.1 ml/mole is believed to be due to presence of two methyl groups in α -carbon atom of alkyl chain.

A similar behaviour was also observed by Van Ness *et al* (1967) in the case of *n*- and iso-propanol with *n*-heptane. On comparison of the results obtained by Van Ness *et al* on partial molar excess volume tabulated in table 4, our analogy of more random distribution of *n*-heptane molecules due to mixing with spherical molecules seems to be reasonable.

From the above study it may be concluded that excess volumes mainly depend on hydrogen bond breaking on dilution and the structure and shape of alcohol molecules.

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