

Excess thermodynamic properties of isomeric butanols with *n*-heptane at 55° C*

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Abstract. The excess free energy, enthalpy and entropy of mixing of isomeric butanols with *n*-heptane determined at 55° C were found to be positive due to the breaking of hydrogen bonds. In the case of *n*-butanol the excess entropy was negative beyond the concentration range $x_2 > 0.4$. The data on excess free energy and enthalpy of mixing could be well represented by the Redlich-Kister equation. An attempt to calculate excess enthalpy from temperature dependence of excess free energy for iso and sec-butanol systems has been made. The results are discussed in the light of the idealised model.

Keywords. Isomeric butanols-*n*-heptane ; binary mixtures ; enthalpy of mixing ; free energy entropy of mixing, hydrogen bonds.

1. Introduction

In continuation of our earlier studies (Anil Kumar *et al* 1979 and Anil Kumar and Katti 1980) undertaken on thermodynamic properties of binary mixtures of non-electrolytes, it was thought worthwhile to study the enthalpy and free energy of mixing of four isomeric butanols with *n*-heptane. Literature survey revealed that some scattered work has been carried out for the above systems (Savini *et al* 1965; Brown *et al* 1969; Huong *et al* 1975).

In this paper we present the experimental results of a systematic study on excess free energy, enthalpy and entropy of mixing of *n*, iso, sec and tert-butanols with *n*-heptane at 55° C in order to understand the intermolecular interactions and the effect of branching off the alkyl chain on excess properties of the above systems. The excess enthalpy obtained calorimetrically for iso- and sec-butanol systems have been compared with those obtained from free energy of mixing at various temperatures.

2. Materials and apparatus

The compounds used in the present investigation and the methods of their purifications have already been given earlier (Anil Kumar *et al* 1979).

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The excess free energies of mixing were calculated from isothermal vapour liquid equilibrium data obtained from modified Jones Colburn Still (Ammer *et al* 1956) the details of which are given elsewhere (Duttachoudhury 1976). The uncertainty in temperature of 0.1°C caused the uncertainty in pressure of 0.2 mm . The vapour and liquid samples were analysed by a calibrated pycnometer. The mole fractions were accurate to within 0.0009 .

The excess enthalpy measurements were conducted using a twin type calorimeter similar to that of Adcock and McGlashan (1954), the details of which are given elsewhere (Pathak *et al* 1970 and Duttachoudhury and Mathur 1976).

In order to minimise the heat losses, the inner bath was covered with an insulated lid. The calorimeter was immersed in the constant temperature water-bath so that only the tubes for taking out the leads and steel rods were out of the thermostat. The temperature inside the calorimeter was constant to within $\pm 0.01^\circ\text{C}$ for 2 hr. The temperatures of outer and inner baths were maintained constant at $55 \pm 0.01^\circ\text{C}$. The accuracy in H^E data was found to be within $\pm 2\%$.

3. Results and discussion

The calculated values of G^E from vapour liquid equilibrium data have been plotted in figure 1 as a function of mole fraction x_1 of *n*-heptane.

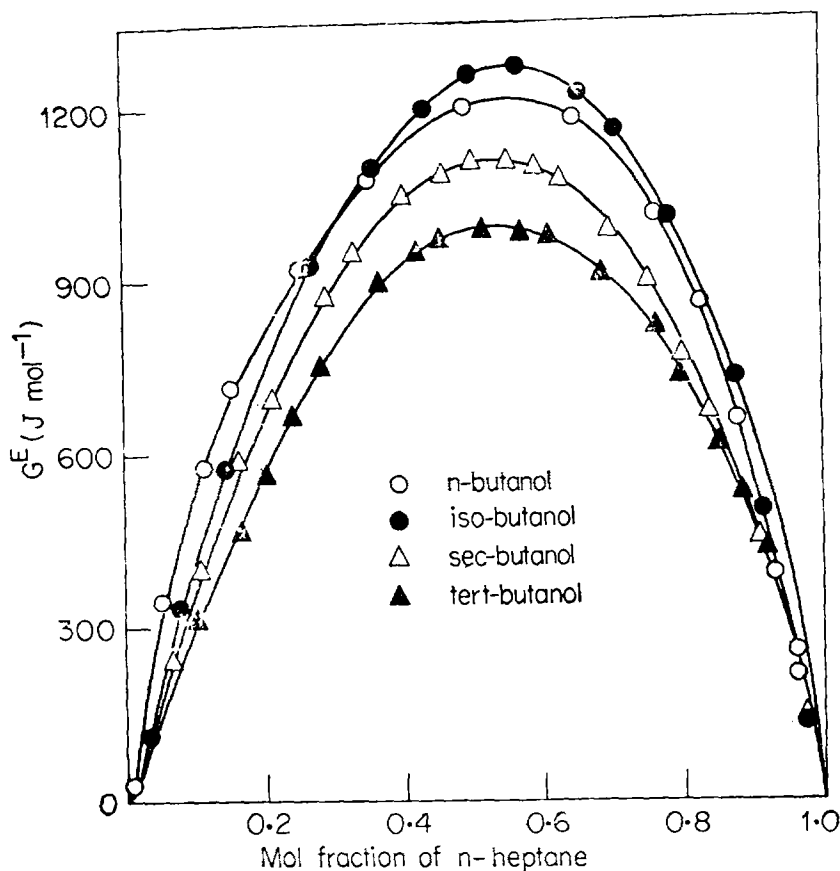


Figure 1. H^E vs x_1 (mole fraction of *n* heptane) plots for *n* heptane isomeric butanols systems at 55°C .

Since the experimental values of the second virial coefficients for all the compounds were not available in the literature at 55° C, they were calculated by using Pitzer-curl equation (Pitzer and Curl 1957) and are listed in table 1 along with the molar volumes. The liquid phase activity coefficients γ_1 and γ_2 were calculated by the usual formulae given elsewhere (Duttachoudhury 1976). The accuracy of thermodynamic data was checked by the Herrington thermodynamic consistency test (Herrington 1947) and the data were found to be consistently better than 2% for all systems. The mixtures were found to form azeotropes at 0.86, 0.78, 0.70 and 0.45 mole fractions of *n*-heptane. Curves of G^E vs x_1 have been fitted with Redlich Kister equation of the form

$$G^E = RT \left[x_1 (1 - x_1) \sum_{n=1}^3 A_n (1 - 2x_1)^{n-1} \right], \quad (1)$$

where x_1 is the mole fraction of *n*-heptane in liquid phase. The values of coefficients A_n along with this standard deviation σ are given in table 2.

Table 1. Second virial coefficients B and molar volume V^L of isomeric butanols and *n*-heptane at 55°

Compound	Second virial coefficient B ($-\text{cm}^3 \text{ mole}^{-1}$)	Molar volume V^L (ml mole^{-1})
<i>n</i> butanol	1368	94.78
iso-butanol	1277	95.56
sec-butanol	1149	94.94
tert-butanol	946	98.87
<i>n</i> -heptane	1366	153.28

Table 2. Coefficients along with standard deviation for relation between G and x_1 of *n*-heptane at 55° C.

System	A_1	A_2	A_3	$J^\sigma \text{ mole}^{-1}$
<i>n</i> butanol	4812	-324.5	2021	26.7
iso-butanol	5051	-1040	-860.2	19.9
sec-butanol	4440	-549.3	-399.1	12.5
tert-butanol	3956	-891.6	-585.7	23.7

The enthalpy of mixing of all the four systems have been measured throughout the concentration range and are presented in table 3. The plots of H^E vs x_2 are shown in figure 2. The H^E data can be well represented by the $\sum_{n=0}^2 A_n (2x_2 - 1)^n$ expression

$$H^E = x_2 (1 - x_2) \sum_{n=0}^2 A_n (2x_2 - 1)^n, \quad (2)$$

where x_2 is the mole fraction of butanol. The values of A_n along with the standard deviation σ are given in table 4.

The values of excess entropies of mixing TS^E at 55° have been calculated at various mole fractions at known intervals by the expression $G^E = H^E - TS^E$.

G^E is positive throughout the concentration range. It is clear from figure 1 that the values of G^E decreases from *n* to tertbutanol. This trend of free energy change is similar to the results obtained by Brown *et al* (1969) who explained this phenomena qualitatively by calculating the hydroxyl group contribution N_h on the basis of the idealised model. Thus it is clear that there is a pronounced effect of the isomers of butanols on G^E .

All the four systems exhibit endothermic heats of mixing throughout the concentration range. The high endothermic enthalpy of mixing may be attributed

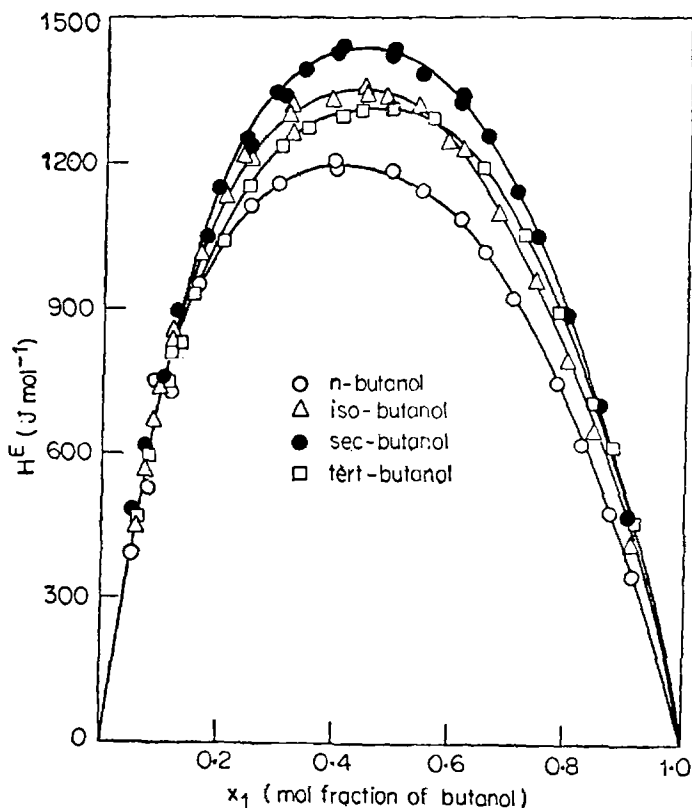


Figure 2. H^E vs x_1 (mole fraction of butanol) plots for isomers of butanols *n*-heptane systems at 55° C.

Table 3. Heats of mixing of isomeric butanols-*n*-heptane system at 55° C.

x_1 Mole fraction of butanol	H^E (J/mole)	H^E/x_1x_2 (kJ/mole)	x_1 Mole fraction of butanol	H^E (J/mole)	H^E/x_1x_2 (kJ/mole)
<i>n</i> -butanol			<i>iso</i> -butanol		
0.0489	394.9	8.492	0.0588	456.0	8.239
0.0820	527.9	7.013	0.0765	568.2	8.042
0.1094	737.7	7.572	0.0881	674.7	8.398
0.1182	809.0	7.762	0.1033	734.8	7.933
0.1667	948.8	6.830	0.1270	857.8	7.736
0.2030	1039.8	6.426	0.1276	840.0	7.546
0.2545	1121.8	5.912	0.1684	1015.2	7.249
0.3027	1160.5	5.498	0.2157	1136.8	6.719
0.3991	1202.0	5.012	0.2415	1215.4	6.634
0.4019	1211.9	5.041	0.2500	1212.9	6.469
0.4952	1188.1	4.752	0.3213	1302.2	5.971
0.5462	1143.0	4.611	0.3256	1268.1	5.775
0.6150	1088.2	4.595	0.3256	1322.7	6.623
0.6561	1027.8	4.555	0.3961	1345.5	5.624
0.7070	930.5	4.491	0.4493	1353.4	5.469
0.7871	749.9	4.475	0.4498	1361.9	5.503
0.8279	627.1	4.401	0.4840	1343.9	5.381
0.8750	481.9	4.406	0.5422	1319.8	5.317
0.9146	357.6	4.570	0.5918	1247.9	5.165
			0.6168	1235.9	5.228
			0.6798	1103.9	5.071
			0.7469	963.0	5.094
			0.8021	801.5	5.049
			0.8478	661.3	5.125
			0.9085	414.8	4.990
<i>Sec</i> -butanol			<i>Tert</i> -butanol		
0.0538	478.9	9.407	0.0585	471.0	8.552
0.0769	614.9	8.662	0.0807	596.1	8.034
0.1066	758.1	7.959	0.1020	706.0	7.708
0.1289	891.9	7.943	0.1122	752.8	7.552
0.1818	1053.9	7.085	0.1333	833.0	7.210
0.2000	1151.9	7.199	0.1584	937.0	7.028
0.2442	1254.9	6.799	0.2030	1040.0	6.427
0.2963	1349.8	6.473	0.2488	1158.0	6.195
0.3091	1346.9	6.307	0.3077	1245.9	5.848
0.3468	1399.8	6.179	0.3489	1283.0	5.647
0.4028	1433.8	5.960	0.4108	1304.8	5.390
0.4112	1445.8	5.971	0.4413	1323.9	5.369
0.4952	1441.8	5.768	0.4976	1319.8	5.279
0.4953	1430.8	5.723	0.5679	1304.8	5.317
0.5463	1395.6	5.630	0.6511	1196.5	5.267
0.6168	1349.8	5.711	0.7244	1064.0	5.329
0.6179	1334.9	5.654	0.7862	899.9	5.353
0.6611	1263.9	5.641	0.8478	713.9	5.533
0.7103	1152.1	5.598	0.8798	625.9	5.918
0.7458	1064.1	5.612	0.9143	462.0	5.896
0.8007	895.0	5.608			
0.8557	707.9	5.732			
0.9111	467.6	5.773			

Table 4. Coefficients along with standard deviation for the relation between H^E and x_2 of butanol at 55°C.

System	A_0	A_1	A_2	($J^\circ \text{ mole}^{-1}$)
<i>n</i> -butanol	4715	-1619	-2112	27.4
iso-butanol	5346	-1396	-1988	28.7
sec-butanol	5719	-1170	-2002	22.7
tert-butanol	5231	-933	-2361	21.0

Table 5. Comparison of H^E values obtained calorimetrically and obtained from temperature dependence of G^E for iso- and sec-butanol systems at 55°C.

Mole fraction of butanol	H^E experimental ($J \text{ mole}^{-1}$)	H^E calculated ($J \text{ mole}^{-1}$)	% deviation
iso-butanol system			
0.2500	1230	1176	4
0.3500	1338	1600	19
0.4000	1364	1600	17
0.4500	1362	1600	17
0.5000	1356	1692	25
0.6000	1250	1600	28
sec-butanol system			
0.3000	1344	1702	26
0.4000	1440	1466	2
0.5000	1434	1428	Zero
0.6000	1355	1600	18
0.7000	1181	1500	27
0.8000	900	1125	25

to the breaking of hydrogen bonds and the enthalpy of hydrogen bonds breaking (in the low concentration range) is in the order $n > \text{iso} > \text{sec} > \text{tert}$, which is also supported by enthalpies of association from IR studies of Geisler *et al* (1971).

The excess entropies of mixing were positive in all the isomeric forms of butanols except in *n*-butanol where an S-type curve was obtained. In *n*-butanol-*n*-heptane systems at high mole fractions of butanol ($x_2 > 0.4$) TS^E values were negative which may be due to high restriction on translational and orientational movements which reduce the hydrogen bond-breaking process and hence low

Table 6. Thermodynamic excess functions for equimolar mixture of isomeric butanols + *n*-heptane at 55° C.

System	G (J mole ⁻¹)	H^E (J mole ⁻¹)	TS^E (J mole ⁻¹)	H^E from temp. dependence of G^E
<i>n</i> -butanol	1216	1188	-28	..
iso-butanol	1262	1350	88	1692
sec-butanol	1120	1440	320	1428
tert-butanol	980	1320	340	..

entropy. The positive TS^E in the lower mole fractions region may be ascribed to the larger number of hydrogen bonds broken by means of which there is greater freedom in orientational and translational movements. This in turn facilitates an increase in entropy of the system. In branched butanols the positive excess entropies are obvious due to hydrogen bond breaking as discussed above.

The values of H^E have been calculated for iso and secbutanol systems by Gibbs Helmholtz equation making use of the present G^E values at 55° and the values at 65° and 75° from our earlier vapour liquid equilibrium data (Anil Kumar and Katti 1980) and have been given in table 5 for comparison. The H^E values could not be calculated for *n*-butanol system due to non-uniform change in G^E with temperature, whereas tert-butanol system did not exhibit any considerable change in G^E with temperature. Thermodynamic excess functions for these systems for equimolar mixture have been given in table 6.

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