

EXCESS ENTHALPIES AND EXCESS VOLUMES OF MIXING FOR ISOMERIC BUTANOL–ACETONE SYSTEMS AT 303.15 K *

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ABSTRACT

The excess enthalpies and excess volumes of normal, iso, secondary and tertiary butanols with acetone were determined at 303.15 K by means of microcalorimetry and densimeter measurements respectively. Dissociation of self-associated alcohol species and alcohol–acetone complex formation takes place in solution. The positive excess properties are attributed to dominance of dissociation over formation. The enthalpies of complex formation were calculated by means of a thermochemical cycle. The isomeric structure of butanol has only a small effect on the enthalpies of complex formation but has a significant effect on the excess volumes, for which the trend is *t*-butanol > *s*-butanol > *i*-butanol > *n*-butanol.

INTRODUCTION

We continue our studies of hydrogen bond energies between different proton acceptor and donor groups and the effect of molecular structure on excess thermodynamic properties [1–5], presenting work on the excess enthalpies and excess volumes of mixing of isomeric butanols with acetone.

EXPERIMENTAL

N-butanol, *i*-butanol, *s*-butanol, *t*-butanol and acetone (all analytical reagent grade) were further purified by fractional distillation and dried over an activated molecular sieve.

The excess enthalpies were determined using a heat flux Calvet-type microcalorimeter (Setaram C-80). The calorimeter was calibrated by means of a Joules calibrator and standardised by determining the heats of solution of KCl in water.

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The excess volumes were determined by a density method; densities were measured using an Anton Paar D.M.A. 60/602, using a differential cell arrangement. The temperature of the oscillator tubes was kept constant to within ± 0.005 K by a Hetofrig thermostat. The densities were accurate to $\pm 1.0 \times 10^{-5}$ g cm⁻³.

Both properties were determined at 303.15 K.

RESULTS AND DISCUSSION

Excess enthalpy data for the four isomeric systems is reported in Table 1. All the sets of data were fitted to the expression

$$V^E \text{ or } H^E = x_1 x_2 \sum_{i=0}^3 A_i (x_1 - x_2)^i \quad (1)$$

by the method of least squares, with all points equally weighted. V^E is the volume change on mixing, H^E is the excess enthalpy of mixing, and x_1 and x_2 are the mole fractions of butanol and acetone respectively. The values of coefficients A_i of eqn. 1 and standard deviations (s) for excess enthalpies are reported in Table 2.

The values for H^E as a function of mole fraction of alcohol (x_1) are presented in Fig. 1. All the systems show endothermic behaviour due to the dissociation of self-associated alcohol species by acetone molecules. The keto-O is a weak electron donor and can form a hydrogen bond with the hydroxyl H, as has been confirmed by spectroscopy [6,7]. The observed enthalpy of mixing is therefore the net effect of endothermic and exothermic

TABLE 1

Excess enthalpies of mixing of isomeric butanols with acetone at 303.15 K

<i>n</i> -Butanol		<i>i</i> -Butanol		<i>s</i> -Butanol		<i>t</i> -Butanol	
x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)
0.0984	654	0.0947	589	0.0449	311	0.0950	512
0.1085	655	0.1313	760	0.1196	680	0.1995	986
0.2117	1155	0.2009	1049	0.1860	970	0.2793	1228
0.3010	1419	0.2867	1365	0.2961	1310	0.3770	1440
0.3790	1545	0.3780	1545	0.3967	1480	0.4829	1532
0.5116	1641	0.4915	1691	0.4927	1560	0.5971	1437
0.6328	1591	0.5952	1652	0.6002	1540	0.6496	1388
0.7154	1449	0.6813	1519	0.6997	1419	0.7240	1192
0.8024	1155	0.7464	1310	0.7609	1252	0.7854	970
0.8841	765	0.8282	1006	0.8228	1075	0.8299	804
0.9433	414	0.8946	684	0.9029	708	0.8945	535

TABLE 2

The least-squares coefficients of eqn. 1 for the excess enthalpies of mixing of isomeric butanol–acetone systems at 303.15 K

Isomer	A_0^a	A_1	A_2	A_3	s
<i>n</i> -Butanol	6659.76	429.00	1079.43	-228.44	17.0
<i>i</i> -Butanol	6720.08	539.37	407.99	-436.28	12.6
<i>s</i> -Butanol	6177.80	664.71	1874.94	88.02	16.0
<i>t</i> -Butanol	6121.16	-277.66	-491.22	76.10	11.6

^a All values given in J mol^{-1} .

interactions. As the hydrogen bonding between ketone and alcohol is weaker than the self-association of alcohol, the effective enthalpy of mixing is positive.

The hydrogen bond energies of the acetone–butanol complexes were determined by means of thermochemical cycles [8]. The overall equation used to obtain the enthalpies of complex formation is

$$\Delta H_c = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 \quad (2)$$

Where ΔH_1 and ΔH_2 are the partial molar enthalpies of alcohol and acetone in a non-polar solvent, ΔH_3 is the partial molar enthalpy of alcohol in

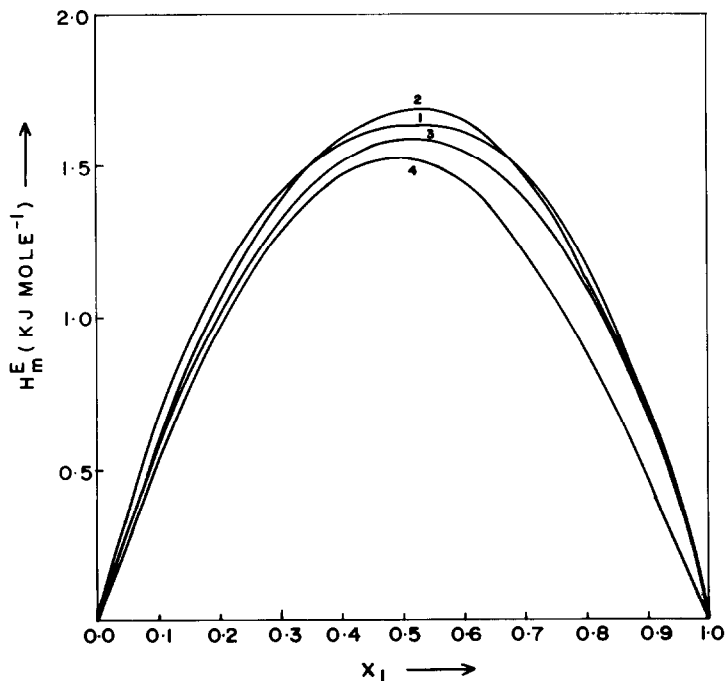


Fig. 1. Molar excess enthalpies for isomeric butanols + acetone at 303.15 K as a function of mole fraction of alcohol. 1: *n*-butanol; 2: *i*-butanol; 3: *s*-butanol; 4: *t*-butanol.

TABLE 3

The enthalpies of acetone–isomeric butanol complexes determined by a thermochemical cycle (eqn. 2)

System	ΔH_1^a	ΔH_2	ΔH_3	ΔH_4	ΔH_c
<i>n</i> -Butanol + <i>n</i> -heptane	26.2				
<i>i</i> -Butanol + <i>n</i> -heptane	24.5				
<i>s</i> -Butanol + <i>n</i> -heptane	24.4				
<i>t</i> -Butanol + <i>n</i> -heptane	25.1				
Acetone + <i>n</i> -hexane		9.0			
<i>n</i> -Butanol + acetone			7.5	9.3	-18.4
<i>i</i> -Butanol + acetone			7.0	9.3	-18.2
<i>s</i> -Butanol + acetone			7.4	9.3	-17.7
<i>t</i> -Butanol + acetone			5.8	9.3	-19.0

^a All values given in kJ mol⁻¹.

acetone and ΔH_4 is a dipolar stabilisation energy of the acetone–butanol complex.

The values of ΔH_1 were obtained from the literature [9]. The ΔH_2 value reported by Murakami and Fujishiro [10] was used in this calculation. The values of ΔH_3 were obtained by extrapolating the $\Delta H/x_1x_2$ vs. x_1 curves to zero mole fraction of alcohol.

The dipolar stabilisation energy of the *n*-butanol–acetone complex has been reported in the literature [10]. The dipolar stabilisation energy depends on the dipole moment of the complex and the temperature dependence of the dielectric constant of the medium [11]. As the dipole moments and the temperature dependence of dielectric constants are nearly the same for all butanol isomers, the dipolar stabilisation energy was considered to be the same for the four alcohols. The values of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4 and ΔH_c are reported in Table 3.

The enthalpies of complex formation show some isomeric effect, having the order

t-butanol > *n*-butanol > *i*-butanol > *s*-butanol

The hydrogen atom of *t*-butanol is a little more acidic due to the electromeric effect of three methyl groups on an α -carbon atom [12], which enhances the hydrogen bonding. In the case of secondary butanol one methyl group at the α -carbon atom does not contribute an electromeric effect but imposes a steric hindrance to hydrogen bond formation. Our previous study on the energetics of complex formation of isomeric butylamines with methanol showed the same trend, i.e. of the four, the tertiary isomer forms the strongest complex and the secondary isomer forms the weakest.

The excess volume data for these systems are reported in Table 4 and the least squares parameters for eqn. 1 are reported in Table 5.

TABLE 4

Volume change on mixing of isomeric butanol (1) and acetone (2) systems at 303.15 K

x_1	$d_{1,2}$ (Density of mixture)	V^E (ml mol^{-1})	x_1	$d_{1,2}$ (Density of mixture)	V^E (ml mol^{-1})	x_1	$d_{1,2}$ (Density of mixture)	V^E (ml mol^{-1})	x_1	$d_{1,2}$ (Density of mixture)	V^E (ml mol^{-1})
<i>n</i>-Butanol + acetone											
0.0000	0.77868	—	0.0000	0.77868	—	0.0000	0.77868	—	0.0000	0.77868	—
0.0484	0.78000	0.0079	0.0273	0.77911	0.0086	0.0319	0.77909	0.0349	0.0576	0.77735	0.1082
0.1003	0.78141	0.0137	0.0639	0.77960	0.0276	0.0684	0.77946	0.0836	0.1003	0.77651	0.1769
0.1419	0.78250	0.0199	0.1061	0.78019	0.0460	0.1094	0.77991	0.1341	0.1813	0.77493	0.3116
0.1957	0.78390	0.0258	0.1962	0.78141	0.0852	0.1494	0.78040	0.1775	0.2408	0.77401	0.3904
0.2307	0.78479	0.0299	0.2607	0.78228	0.1102	0.2095	0.78104	0.2505	0.2695	0.77359	0.4271
0.2963	0.78642	0.0376	0.2904	0.78268	0.1209	0.3213	0.78262	0.3410	0.3182	0.77306	0.4716
0.3524	0.78780	0.0417	0.3906	0.78409	0.1463	0.3960	0.78388	0.3753	0.3358	0.77287	0.4878
0.3944	0.78881	0.0449	0.4809	0.78550	0.1485	0.4588	0.78506	0.3877	0.4272	0.77215	0.5464
0.4277	0.78960	0.0472	0.5548	0.78670	0.1408	0.5588	0.78708	0.3852	0.4834	0.77193	0.5596
0.4592	0.79035	0.0480	0.6074	0.78753	0.1354	0.6277	0.78858	0.3661	0.5137	0.77186	0.5615
0.4997	0.79131	0.0479	0.6904	0.78896	0.1092	0.7161	0.79065	0.3186	0.5653	0.77187	0.5506
0.5422	0.79230	0.0478	0.7657	0.79023	0.0838	0.7722	0.79207	0.2722	0.5967	0.77194	0.5367
0.5866	0.79334	0.0450	0.7874	0.79060	0.0752	0.8438	0.79391	0.2048	0.6448	0.77216	0.5022
0.6545	0.79487	0.0434	0.8761	0.79207	0.0410	0.9405	0.79657	0.0845	0.7033	0.77245	0.4569
0.7016	0.79594	0.0385	0.9370	0.78304	0.0186	1.0000	0.79825	—	0.7774	0.77301	0.3755
0.8182	0.79855	0.0213	1.0000	0.79398	—	—	—	—	0.8057	0.77330	0.3348
0.8652	0.79954	0.0176	—	—	—	—	—	—	0.8525	0.77377	0.2678
0.9041	0.80036	0.0129	—	—	—	—	—	—	0.9170	0.77463	0.1478
0.9554	0.80144	0.0046	—	—	—	—	—	—	0.9387	0.77482	0.1189
—	—	—	—	—	—	—	—	—	1.0000	0.77565	—
<i>s</i>-Butanol + acetone											
0.0000	0.77868	—	0.0000	0.77868	—	0.0000	0.77868	—	0.0000	0.77868	—
0.0484	0.78000	0.0079	0.0273	0.77911	0.0086	0.0319	0.77909	0.0349	0.0576	0.77735	0.1082
0.1003	0.78141	0.0137	0.0639	0.77960	0.0276	0.0684	0.77946	0.0836	0.1003	0.77651	0.1769
0.1419	0.78250	0.0199	0.1061	0.78019	0.0460	0.1094	0.77991	0.1341	0.1813	0.77493	0.3116
0.1957	0.78390	0.0258	0.1962	0.78141	0.0852	0.1494	0.78040	0.1775	0.2408	0.77401	0.3904
0.2307	0.78479	0.0299	0.2607	0.78228	0.1102	0.2095	0.78104	0.2505	0.2695	0.77359	0.4271
0.2963	0.78642	0.0376	0.2904	0.78268	0.1209	0.3213	0.78262	0.3410	0.3182	0.77306	0.4716
0.3524	0.78780	0.0417	0.3906	0.78409	0.1463	0.3960	0.78388	0.3753	0.3358	0.77287	0.4878
0.3944	0.78881	0.0449	0.4809	0.78550	0.1485	0.4588	0.78506	0.3877	0.4272	0.77215	0.5464
0.4277	0.78960	0.0472	0.5548	0.78670	0.1408	0.5588	0.78708	0.3852	0.4834	0.77193	0.5596
0.4592	0.79035	0.0480	0.6074	0.78753	0.1354	0.6277	0.78858	0.3661	0.5137	0.77186	0.5615
0.4997	0.79131	0.0479	0.6904	0.78896	0.1092	0.7161	0.79065	0.3186	0.5653	0.77187	0.5506
0.5422	0.79230	0.0478	0.7657	0.79023	0.0838	0.7722	0.79207	0.2722	0.5967	0.77194	0.5367
0.5866	0.79334	0.0450	0.7874	0.79060	0.0752	0.8438	0.79391	0.2048	0.6448	0.77216	0.5022
0.6545	0.79487	0.0434	0.8761	0.79207	0.0410	0.9405	0.79657	0.0845	0.7033	0.77245	0.4569
0.7016	0.79594	0.0385	0.9370	0.78304	0.0186	1.0000	0.79825	—	0.7774	0.77301	0.3755
0.8182	0.79855	0.0213	1.0000	0.79398	—	—	—	—	0.8057	0.77330	0.3348
0.8652	0.79954	0.0176	—	—	—	—	—	—	0.8525	0.77377	0.2678
0.9041	0.80036	0.0129	—	—	—	—	—	—	0.9170	0.77463	0.1478
0.9554	0.80144	0.0046	—	—	—	—	—	—	0.9387	0.77482	0.1189
—	—	—	—	—	—	—	—	—	1.0000	0.77565	—

TABLE 5

Least-squares parameters for volume change on mixing of isomeric butanol-acetone systems at 303.15 K

Isomer	A_0^a	A_1	A_2	A_3	s
<i>n</i> -Butanol	0.19122	0.01529	-0.06598	-0.05002	0.0010
<i>i</i> -Butanol	0.59845	-0.12799	-0.29940	0.09767	0.0015
<i>s</i> -Butanol	1.59070	-0.04660	-0.25220	0.26903	0.0037
<i>t</i> -Butanol	2.23816	0.03398	-0.32549	-0.1276	0.0030

^a All values given in ml mol^{-1} .

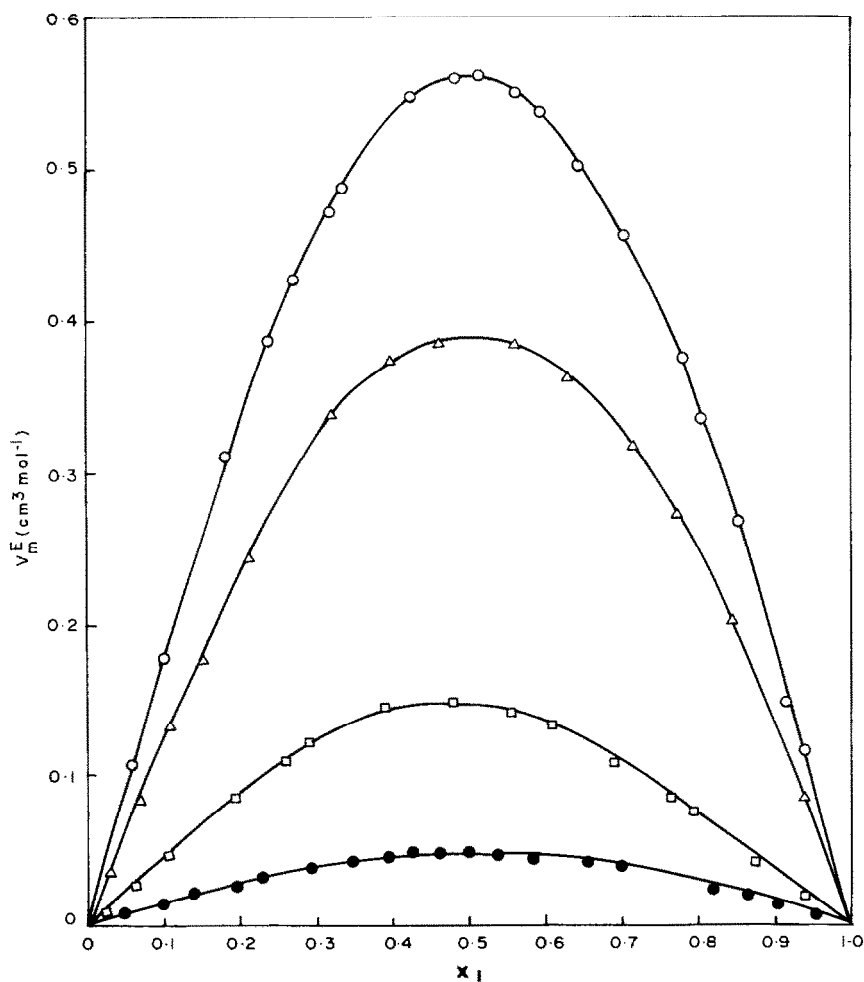


Fig. 2. Molar excess volumes for isomeric butanols + acetone at 303.15 K as a function of mole fraction of alcohol. ● *n*-butanol; □ *i*-butanol; △ *s*-butanol; ○ *t*-butanol.

TABLE 6

Excess volumes of isomeric butanols with *n*-heptane and acetone at 303.15 K

Alcohol	V^E (ml mol ⁻¹)	
	<i>n</i> -Heptane [13]	Acetone
<i>n</i> -Butanol	0.24	0.05
<i>i</i> -Butanol	0.37	0.15
<i>s</i> -Butanol	0.57	0.38
<i>t</i> -Butanol	1.02	0.56

The V^E vs. x_1 curves are represented in Fig. 2. The excess volumes are also positive, on account of the breaking of the alcohol structure by acetone. The structure of alcohol has a pronounced effect on the excess molar volumes, which show the trend

t-butanol > *s*-butanol > *i*-butanol > *n*-butanol

The volume change on mixing the two liquids is due to the change in the molecular configuration, and hence the shape of the interacting molecules plays an important part, as shown by the present results. The maximum excess volumes of the present systems and those of isomeric butanols with *n*-heptane [13] are given in Table 6. It is clear that the isomeric trend is the same in both sets of data, but the positive excess volumes are smaller in the case of acetone systems, due to the formation of acetone–alcohol complexes.

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