

Enthalpies of mixing of di-*n*-butyl ether with isomeric butanols: Enthalpies of hydrogen-bonded complexes[†]

GOPAL PATHAK and SHIRISH PRADHAN*

National Chemical Laboratory, Pune 411 008, India

MS received 16 April 1988; revised 5 August 1988

Abstract. The enthalpies of mixing of four isomeric butanols with di-*n*-butyl ether were determined at 30°C by a Calvet type microcalorimeter. All the four systems showed endothermic behaviour. The enthalpies of complex formation were calculated by the thermochemical cycle. The strength of H-bonding decreases in the order 1-butanol, 1-methyl-1-propanol, 2-methyl-2-propanol, 2-butanol. The results are explained on the basis of a steric effect on interaction.

Keywords. Calorimetry; enthalpy of complex; steric effect; alcohol-ether complexes; binary systems; enthalpy of mixing.

1. Introduction

In continuation of the work on the study of H-bond energies between different proton-acceptor and -donor groups and the effect of the shape of interacting molecules, work on interactions between isomeric butanol and di-*n*-butyl ether is presented.

2. Experimental

AR grade 1-butanol, 1-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol (SD Chemicals) were purified by fractional distillation. Di-*n*-butyl ether, Fluka, AG 99%, GC pure, was used without further purification. All the compounds were dried over activated molecular sieves.

The enthalpies of mixing were determined by a heat flux Calvet type microcalorimeter (C-80 Setaram model) using the batch method. The calorimeter and the experimentation were standardised by determining the enthalpy of a solution of KCl in water. The results were reproducible within 0.7% of the reported standard value.

*For correspondence.

[†]NCL Communication No. 4430.

3. Results and discussion

The enthalpies of mixing of di-*n*-butyl ether with 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol at 30°C have been given in table 1. The data are fitted by means of the least squares method to the Redlich–Kister equation,

$$\Delta H = x_1x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + E(x_1 - x_2)^3]. \quad (1)$$

The parameters of the equation along with the standard deviations for these systems are given in table 2. The enthalpies of mixing as a function of the mole fraction of ether (x_1) have been represented in figure 1.

All the four systems show endothermic behaviour. It has been established that the ether and alcohol pair acts as a proton-acceptor and -donor pair and a hydrogen bond is formed between the hydroxyl H and etheral O (Murthy and Rao 1968). The observed enthalpy of mixing is therefore the net effect of two opposite heat effects, viz. an endothermic effect due to the dissociation of self-associated alcohol polymers by ether molecules and an exothermic effect due to hydrogen-bond

Table 1. The enthalpies of mixing of isomeric butanol (1)-di-*n*-butyl ether (2) systems at 30°C.

x_1 Mole fraction of alcohol	ΔH (J/mol)	x_1 Mole fraction of alcohol	ΔH (J/mol)
<i>1-Butanol-di-n-butyl ether</i>			
0.0642	440	0.5161	934
0.1034	622	0.5749	870
0.1504	761	0.6883	707
0.1954	855	0.7755	554
0.3228	982	0.8464	386
0.3926	985	0.9325	173
<i>2-Methyl-1-propanol-di-n-butyl ether</i>			
0.0525	346	0.4833	1141
0.1040	619	0.6082	1009
0.1936	917	0.6973	845
0.2844	1073	0.8036	590
0.3926	1164	0.9129	284
<i>2-Butanol-di-n-butyl ether</i>			
0.0528	419	0.4905	1262
0.0999	693	0.6061	1177
0.1507	914	0.6787	978
0.3111	1266	0.7478	813
0.4109	1305	0.8588	492
<i>2-Methyl-2-propanol-di-n-butyl ether</i>			
0.0387	313	0.5112	1353
0.0902	650	0.6035	1327
0.1477	926	0.7158	1209
0.1956	1091	0.8548	985
0.3020	1290	0.9308	292
0.3976	1353		

Table 2. The least squares constants of the Redlich-Kister equation and the standard deviations for four isomeric butanol-dibutyl ether systems^a.

System	B (J/mol)	C (J/mol)	D (J/mol)	E (J/mol)	σ (J/mol)
1-Butanol + ether	3711.3	-1387.0	1664.4	-1700.7	9.1
2-Methyl-1-propanol + ether	4494.2	-1455.1	926.7	-647.6	6.5
2-Butanol + ether	5002.9	-1724.9	1282.6	-1051.2	4.4
2-Methyl-2-propanol + ether	5308.8	-1519.7	1370.3	-724.8	5.4

^a All values rounded to first place after decimal.

formation between ether and alcohol molecules. The enthalpy of hydrogen bonding of self-associated alcohol molecules is greater than that between alcohol and ether molecules (Murthy and Rao 1968). The enthalpies of mixing for these systems are therefore positive in spite of the formation of hydrogen-bonded complexes in the solution.

Murakami and Fujishiro (1966) reported data on the di-*n*-butyl ether and 1-butanol system. Their data ($\Delta H^{\max} \approx 800$ J/mol) are about 20% lower than the present data ($\Delta H^{\max} \approx 985$ J/mol). However, the present data agree well with those reported by Mitteilung (1978).

The enthalpies of hydrogen bond formation between ether and alcohol were calculated by means of the thermo-chemical cycle (Pradhan and Mathur 1979). The ultimate equation of enthalpy of complex formation (ΔH_c) 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 partial molal enthalpies of mixing of alcohol and ether, respectively, in a non-polar solvent, ΔH_3 is the partial molal enthalpy of mixing of alcohol in ether and ΔH_4 is the dipolar stabilization energy. The partial molal enthalpies are obtained by extrapolating the $\Delta H/x_1x_2$ vs. x_1 graph to zero concentration. The ΔH_1 values for the four butanol isomers were obtained from the data of Woycicka and Kalinowska (1977). The enthalpies of mixing of di-*n*-butyl ether in *n*-hexane were determined below a 0.05 mole fraction of ether. The ΔH values at 0.0310, 0.0292, 0.0153 and 0.0097 mole fraction values were 12.4, 11.1, 8.4 and 6.6 J/mol respectively. The partial molal enthalpy of mixing [ΔH_2 of (2)] was found to be 0.9 kJ/mol.

The ΔH_3 values were obtained from the present data. In order to reduce the uncertainty in the extrapolated value of $\Delta H/x_1x_2$ at $x_1 = 0$; the $\Delta H/x_1x_2$ data were generated at an interval of 0.025 mole fraction by means of (1). The data thus obtained were fitted to the polynomial equation

$$\Delta H/x_1x_2 = \sum_{i=0}^3 A_i x_i^i. \quad (3)$$

The value of A_0 represents the value of ΔH_3 .

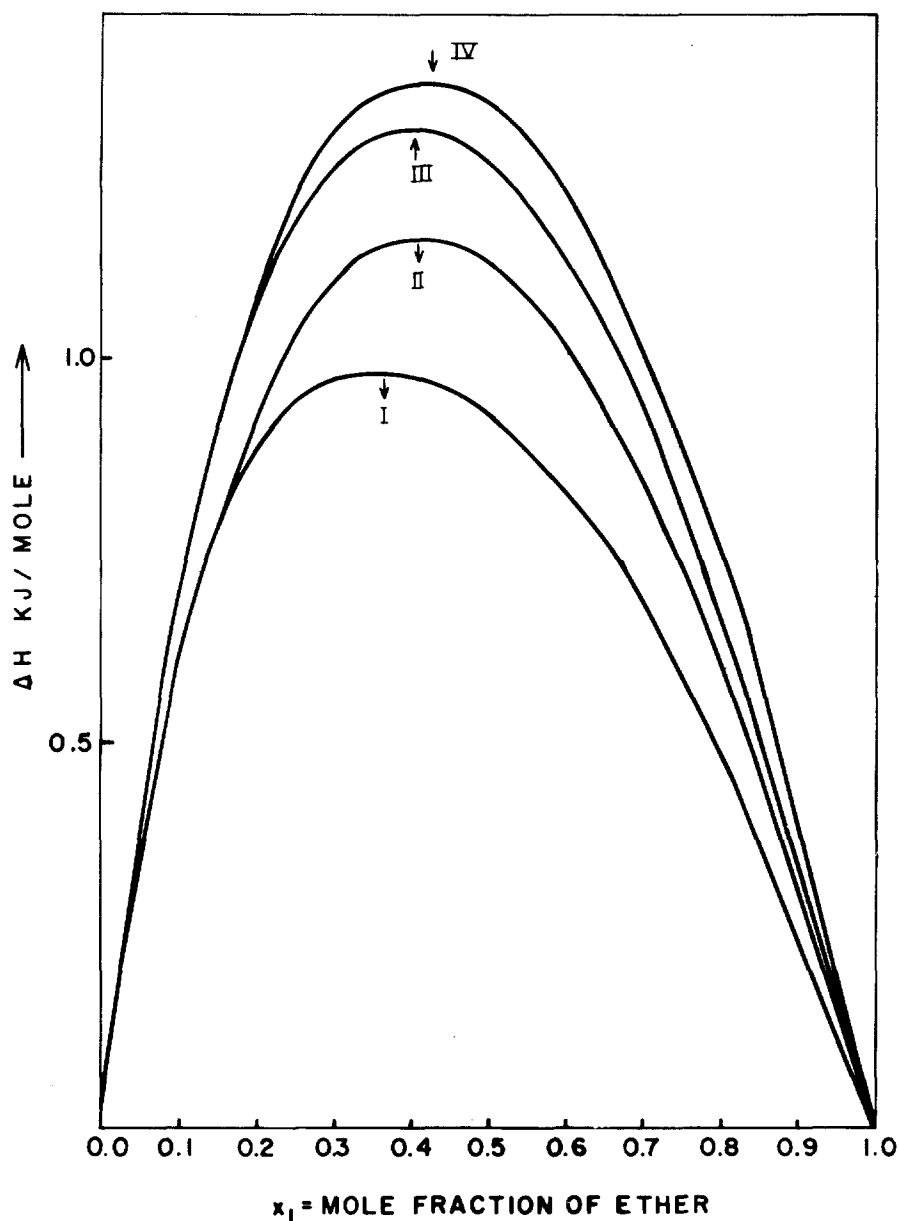


Figure 1. ΔH vs. x_1 plots for isomeric butanol (1) and di-*n*-butyl ether (2) systems. (I-1-butanol; II-2-methyl-1-propanol; III-2-butanol; IV-2-methyl-2-propanol.)

The ΔH_4 values were calculated by means of standard procedures (Pradhan and Mathur 1979).

All the values of ΔH_1 , ΔH_2 , ΔH_3 , and ΔH_4 and the enthalpies of complex formation (ΔH_c) are reported in table 3.

The strength of di-*n*-butyl ether-butyl alcohol complexes show a small variation with branching in the butyl chain in the order - 1-butanol > 1-methyl-1-propanol > 2-methyl-2-propanol > 2-butanol.

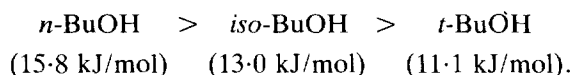
Table 3. The enthalpies of dibutyl ether - isomeric butanol complexes calculated by (2).

System	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	ΔH_3 (kJ/mol)	ΔH_4 (kJ/mol)	ΔH_r (kJ/mol)
1-Butanol + <i>n</i> -heptane	26.2 ± 0.2	—	—	—	—
2-Methyl-1-propanol + <i>n</i> -heptane	24.5 ± 0.2	—	—	—	—
2-Butanol + <i>n</i> -heptane	24.4 ± 0.2	—	—	—	—
2-Methyl-2-propanol + <i>n</i> -heptane	25.1 ± 0.2	—	—	—	—
Dibutyl ether + <i>n</i> -hexane	—	0.9 ± 0.1	—	—	—
1-Butanol + ether	—	—	8.5 ± 0.2	0.4	-18.2 ± 0.5
2-Methyl-1-propanol + ether	—	—	7.5 ± 0.2	0.4	-17.5 ± 0.5
2-Butanol + ether	—	—	9.1 ± 0.2	0.4	-15.7 ± 0.5
2-Methyl-2-propanol + ether	—	—	8.9 ± 0.2	0.4	-16.7 ± 0.5

In our earlier work it was found that in the case of 2-aminobutane and 2-butanol the H-bonded complex formations were the weakest (Pathak and Pradhan 1984). The present trend is consistent with previous observations.

In the case of the tertiary butyl molecule the strength of H-bonding depends on the geometry of the second interacting molecule. Due to the electromeric effect of three methyl groups at the α -carbon atom, the H-bonding tends to become stronger. Thus the enthalpies of H-bonded complexes of *t*-butylamine-*n*-butanol and *t*-butanol-*n*-butylamine are higher than the enthalpy of *n*-butanol-*n*-butylamine complex. However, if the second interacting molecule is branched the steric effect weakens the interaction. Thus the strength of the *t*-butylamine-*t*-butanol complex is less than that of *n*-butylamine-*n*-butanol. In the presently studied systems the strength of the ether-*t*-butanol complex is less than that of the ether-*n*-butanol complex. This indicates that there is a significant steric repulsion between di-*n*-butyl ether and *t*-butanol.

Motoyama and Jarboe (1967) determined the enthalpies of H-bonding between normal, iso and tertiary butanols with diethyl ether by spectroscopic methods and reported the following trend



The trends for the isomeric butanol, ether interactions observed by two techniques are mutually consistent.

References

- Mitteilung K 1978 *Phys. Chem. (Leipzig)* **259** 992
 Motoyama I and Jarboe C H 1967 *J. Phys. Chem.* **71** 2723
 Murakami S and Fujishiro R 1966 *Bull. Chem. Soc. Jpn.* **39** 720
 Murthy A S N and Rao C N R 1968 *Appl. Spectrosc. Rev.* **2** 69
 Pathak G and Pradhan S D 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 831
 Pradhan S D and Mathur H B 1979 *Proc. Indian Acad. Sci. (Chem. Sci.)* **A88** 337
 Woycicka M K and Kalinowska B 1977 *Bull. Acad. Pol. Sci.* **25** 639