

Enthalpies of mixing of acetonitrile with isomeric butanols: Enthalpies of hydrogen-bonded complexes[†]

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MS received 29 March 1990; revised 17 November 1990

Abstract. The enthalpies of mixing of four isomeric butanols with acetonitrile were determined at 30°C by a Calvet type microcalorimeter. All the four systems showed endothermic behaviour. The enthalpies of hydrogen bonded complex formation were determined by means of a thermochemical cycle. 1-butanol formed a stronger bonding (–13 kJ/mole) than the other three isomers (–11.20 kJ/mole). The strength of the H-bond of alcohol with C≡N is much less than that with C–N.

Keywords. Calorimetry; enthalpy of mixing; enthalpy of complex; alcohol acetonitrile complexes.

1. Introduction

In a systematic study on the energies of H-bond complex formation between different proton donor and acceptor groups, we have determined the enthalpies of complex formations between primary amine, diamine, triamine and alcohol, alcohol and ether, amine and chloroform (Pradhan and Mathur 1979; Pradhan 1981; Pradhan and Pathak 1986; Pathak and Pradhan 1987, 1988). In the present communication work on the enthalpies of complex formation between isomeric butanols and acetonitrile has been reported.

2. Experimental

Four isomeric butanols (SD Chemicals, AR grade), acetonitrile (>99% Extra Pure, SD Chemicals) were purified by fractional distillation. All the compounds were dried by freshly activated molecular sieves. The enthalpies of mixing were determined by heat flux micro-calorimeter (C-80 Setaram) at 30°C.

3. Result and discussion

The enthalpies of mixing of acetonitrile 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

[†]NCL communication no. 4883

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Table 1. The excess enthalpies of mixing of isomeric butanol (1) and acetonitrile (2) systems at 30°C. X_1 = mole fraction of alcohol.

X_1	$\Delta H(\text{J/mole})$	X_1	$\Delta H(\text{J/mole})$
<i>1-Butanol + acetonitrile</i>		<i>2-Butanol + acetonitrile</i>	
0.0535	498	0.0706	629
0.1199	1010	0.1398	1169
0.1666	1277	0.1476	1207
0.2605	1693	0.2494	1792
0.3409	1926	0.3546	2050
0.4109	1956	0.4733	2200
0.5011	1835	0.4849	2196
0.6098	1571	0.5116	2184
0.6948	1321	0.6034	2041
0.7926	900	0.6947	1802
<i>2-Methyl-1-propanol + acetonitrile</i>		<i>2-Methyl-2-propanol + acetonitrile</i>	
0.0716	691	0.0518	511
0.0998	889	0.1144	924
0.1367	1140	0.1864	1414
0.1748	1320	0.2466	1688
0.2877	1711	0.3362	1940
0.3191	1743	0.4901	2116
0.3871	1825	0.6151	2024
0.4614	1796	0.7055	1819
0.5315	1694	0.8147	1368
0.6686	1306	0.8969	903
0.7058	1167		
0.8057	722		

Table 2. The least square parameters for excess enthalpies of mixing for isomeric butanol + acetonitrile systems at 30°C.

System	B (J/mole)	C (J/mole)	D (J/mole)	E (J/mole)	Standard deviation
1-Butanol + acetonitrile	7432.7	-3228.6	-359.7	325.7	19.3
2-Methyl-1-propanol + acetonitrile	7008.2	-2877.3	-500.8	-1959.2	7.4
2-Butanol + acetonitrile	8794.0	-1018.7	1222.5	1441.3	29.5
2-Methyl-1-propanol + acetonitrile	8433.1	11.4	2011.8	-55.6	21.6

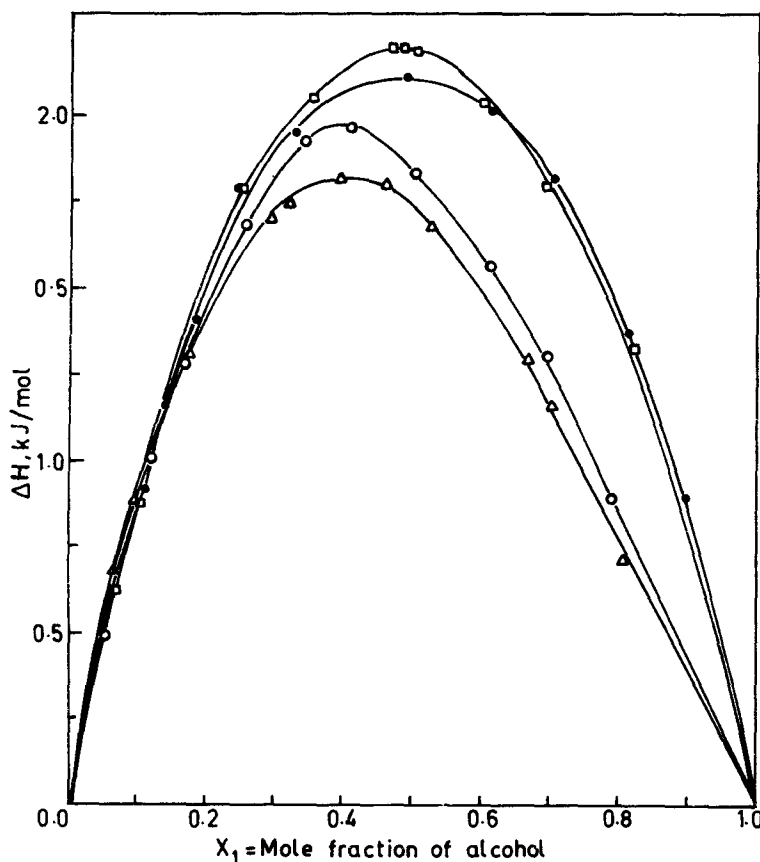


Figure 1. ΔH vs. X_1 plots for isomeric butanol (1)-acetonitrile (2) systems. \circ - 1-Butanol, Δ - 2-methyl-1-propanol, \square - 2-butanol, \bullet - 2-methyl-2-propanol.

means of least squares method to the equation,

$$\Delta H_{\text{mix}} = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + E(x_1 - x_2)^3]. \quad (1)$$

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 mole fraction of alcohol (x_1) have been represented in figure 1.

All the four systems show endothermic behaviour which is attributed to the breaking of the associated alcohol species by acetonitrile. However, the nitrile group having two lone electrons is an electron donor group and can form an H-bond with the hydroxyl hydrogen. The spectroscopic data has established the formation of such bonding (Lopes and Thompson 1968). Hence, in addition to dissociation of alcohol polymers, alcohol-acetonitrile complex formation also takes place in the solution. The enthalpies of such complexes were determined by means of a thermochemical cycle (Murakami and Fujishiro 1966). The ultimate equation to get the enthalpy of complex formation (ΔH_c) is:

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

Table 3. The enthalpies of isomeric butanol-acetonitrile complexes calculated by thermo-chemical cycle.

System	ΔH_1 (kJ/mole)	ΔH_2 (kJ/mole)	ΔH_3 (kJ/mole)	ΔH_4 (kJ/mole)	ΔH_c (kJ/mole)
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	—	—	—	—
Acetonitrile + <i>n</i> -hexane	—	12.6 ± 2	—	—	—
1-Butanol + acetonitrile	—	—	10.1 ± 0.2	15.7	-13.0
1-Methyl-1-propanol + acetonitrile	—	—	10.4 ± 0.2	15.7	-11.0
2-Butanol + acetonitrile	—	—	9.9 ± 0.2	15.7	-11.4
2-Methyl-2-propanol + acetonitrile	—	—	10.3 ± 0.2	15.7	-11.2

where ΔH_1 , ΔH_2 are the partial molal enthalpies of mixing of alcohol and acetonitrile in a non-polar solvent, ΔH_3 is the partial molal enthalpy of alcohol in acetonitrile and ΔH_4 is the dipolar stabilisation energy (Pradhan and Mathur 1979). The values of ΔH_1 and ΔH_2 were obtained from the literature (Murakami and Fujishiro 1966; Woycicka and Kalinowska 1977) data and the ΔH_3 value was obtained in the present work by extrapolating the $\Delta H/X_1 X_2$ vs. X_1 curve to zero mole fraction of alcohol. Murakami and Fujishiro (1966) have reported the dipolar stabilisation energy for the 1-butanol acetonitrile complex. The temperature dependence of dielectric constants of all the four butanol isomers are nearly the same. The dipolar stabilisation energies of all the isomers are therefore taken to be the same as reported by Murakami and Fujishiro (1966). The values of ΔH_1 , ΔH_2 , ΔH_3 and ΔH_c are presented in table 3. The enthalpies of complex formation for 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol are nearly the same viz. -11.2 ± 0.2 kJ/mole. The 1-butanol complex has the strongest hydrogen bond formation of all having an enthalpy of -13.0 kJ/mole.

From our earlier studies on the hydrogen bond energies between four isomeric butanols and tributyl amine (Pradhan and Pathak 1986) it is clear that the interaction between hydroxyl H and N of triamine is much stronger than that between hydroxyl H and nitrile N. Surjit Singh *et al* (1962) studied the relative hydrogen-bonding strengths of tributyl amine and acetonitrile by NMR and observed the same trend. The hydrogen bond energy of tributylamine-methanol (Gramstad 1962) and that of acetonitrile and methanol (Mitra 1962) determined by IR spectroscopy are reported to be -3.8 and -2.2 kcal/mole. Although the actual values are not comparable, it is clear that the triamine-alcohol H-bonding is nearly twice as strong as the nitrile-alcohol H-bonding, which is consistent with the present observation. All these consistent observations are attributed to the different characters of the electronic configuration of nitrogen in the triamine and nitrile groups. The nitrogen of triamine has less *s* character and more *p* character than the nitrogen of nitrile group (Rowlinson 1969). Hence the triamine nitrogen becomes a better electron donor than the nitrile N and hence it forms a stronger hydrogen bonding.

As far as the isomeric effect on $-\text{O}-\text{H}\cdots\text{N}-\text{C}$ and $-\text{O}-\text{H}\cdots\text{N}\equiv\text{C}-$ interactions is concerned, in both the functional groups, the branching of the alkyl chain of alcohol weakens the interactions and the position of branching has no effect on the strength of such interactions.

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