

## ENTHALPY OF MIXING FOR THE BINARY MIXTURES 2,4,6-COLLIDINE + ISOALIPHATIC ALCOHOLS

*T. Kasprzycka-Guttman and K. Chreptowicz*

DEPARTMENT OF CHEMICAL TECHNOLOGY, UNIVERSITY OF WARSAW,  
02-093 WARSAW, PASTEURA 1, POLAND

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The relationships between the enthalpies of mixing for the binary mixtures 2,4,6-collidine + iso-propanol, iso-butanol, sec-butanol and tert-butanol were studied.

### Experimental

The purity of the 2,4,6-collidine was estimated to be 99.99 mole percent. All the iso-alcohols used in the present paper were the same as those used in our previous study [1]. The apparatus and method used for the measurement of  $h^M$  have already been described [2].

### Results and discussion

Measurements of the enthalpy of mixing  $h^M$  were made vs. the mole fraction of 2,4,6-collidine. The enthalpies of mixing for three binary systems at 293.15 and 303.15 K and for 2,4,6-collidine + tert-butanol at 313.15 and 323.15 K are given in Table 1.

The measured values were correlated through the equation:

$$h^M (\text{Jmol}^{-1}) = x(1-x) \sum_{n=1}^4 C_n (2x-1)^{n-1} \quad (1)$$

where  $h^M$  is the enthalpy of mixing and  $x$  is the mole fraction of 2,4,6-collidine.

The adjustable coefficients  $C_n$  calculated by the method of least squares are listed in Table 2, together with the standard deviations  $\delta(h^M)$  of the results for  $h^M$ .

The enthalpies of mixing for the binary mixtures 2,4,6-collidine + iso-propanol,

**Table 1** Heat of mixing of 2,4,6-collidine + iso-aliphatic alcohols ( $x$ -mole fraction of 2,4,6-collidine)

$T, K$	$x$	$h^M,$ $Jmol^{-1}$	$T, K$	$x$	$h^M,$ $Jmol^{-1}$
2,4,6-collidine + iso-propyl alcohol			2,4,6-collidine + iso-propyl alcohol		
293.15	0.0901	-211.05	303.15	0.0601	-110.10
	0.1475	-332.91		0.1366	-302.79
	0.2104	-440.10		0.2001	-365.11
	0.2402	-480.08		0.2901	-480.73
	0.3124	-574.08		0.3414	-517.04
	0.4560	-628.32		0.3448	-520.85
	0.5684	-626.41		0.3635	-534.96
	0.5737	-625.39		0.4996	-609.05
	0.6503	-562.09		0.5632	-592.11
	0.7009	-506.01		0.6082	-574.58
	0.8202	-350.21		0.6501	-536.12
	0.8902	-243.85		0.7061	-504.90
				0.8574	-243.07
2,4,6-collidine + iso-butyl alcohol			2,4,6-collidine + iso-butyl alcohol		
293.15	0.0489	-185.50	303.15	0.0631	-220.12
	0.1407	-483.15		0.1467	-486.57
	0.1492	-487.59		0.2200	-720.52
	0.2546	-738.63		0.3501	-1010.13
	0.3512	-960.50		0.4223	-1099.20
	0.4721	-1030.23		0.5183	-1159.37
	0.6591	-933.50		0.6184	+1087.39
	0.6874	-917.56		0.6820	-950.71
	0.7102	-849.39		0.7850	-741.62
	0.7559	-750.00		0.7913	-675.58
	0.8053	-561.96		0.8323	-515.11
	0.8719	-320.37		0.8718	-406.30
2,4,6-collidine + sec-butanol			2,4,6-collidine + sec-butanol		
293.15	0.0564	-120.22	303.15	0.0655	-141.27
	0.2073	-416.38		0.1590	-294.68
	0.2263	-480.30		0.1850	-287.51
	0.2704	-557.98		0.2304	-370.11
	0.3003	-600.52		0.3062	-440.69
	0.4018	-715.20		0.3857	-541.72
	0.4605	-710.23		0.4831	-616.67
	0.5462	-686.10		0.4867	-588.44
	0.7006	-505.21		0.5009	-594.09
	0.7394	-373.07		0.5673	-529.38
	0.7792	-305.55		0.6099	-495.12
	0.8352	-232.80		0.7177	-392.48
				0.8012	-350.86
				0.8768	-204.91

Table 1 Continued

<i>T</i> , K	<i>x</i>	$h^M$ , Jmol <sup>-1</sup>	<i>T</i> , K	<i>x</i>	$h^M$ , Jmol <sup>-1</sup>
2,4,6-collidine + tert-butyl alcohol			2,4,6-collidine + tert-butyl alcohol		
313.15	0.0481	- 65.93	323.15	0.0702	- 78.49
	0.0865	- 38.21		0.1439	- 106.61
	0.1492	96.95		0.2166	- 133.55
	0.1641	122.44		0.3326	- 67.01
	0.2210	174.11		0.3355	- 77.01
	0.3299	346.39		0.3888	- 48.78
	0.4382	398.45		0.3920	- 25.18
	0.5358	408.09		0.5261	114.31
	0.7045	371.05		0.6119	243.38
	0.7211	368.05		0.7025	275.49
0.7951	291.10	0.7844	222.06		
0.8674	166.97	0.9082	140.78		

Table 2 Coefficients of Redlich-Kister equation [1] and standard deviations  $\sigma(n^m)$ 

Mixtures; 2,4,6-collidine +	<i>T</i> , K	<i>C</i> <sub>1</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>3</sub>	<i>C</i> <sub>4</sub>	$\delta(h^M)$ , Jmol <sup>-1</sup>
iso-propanol	293.15	-2540.52	178.73	52.90	48.59	8.67
	303.15	-2401.60	-199.97	401.31	834.99	15.14
iso-butanol	293.15	-4294.71	-532.81	1438.98	2049.20	23.71
	303.15	-4618.58	-251.16	1516.51	849.32	16.72
sec-butanol	293.15	-2852.75	748.86	1820.68	- 65.83	20.11
	303.15	-2279.29	155.08	575.40	- 291.12	12.64
tert-butanol	313.15	1743.68	144.98	-1199.06	1462.39	33.80
	323.15	406.89	2396.63	- 194.65	-1266.47	17.91

iso-butanol and sec-butanol are negative, but 2,4,6-collidine + tert-butanol gives *S*-shaped curves at 313.15 and 323.15 K.

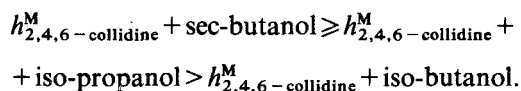
The values of  $h^M$  for systems containing iso-propanol, iso-butanol or sec-butanol and 2,4,6-collidine are higher than those for other pyridine bases (pyridine,  $\alpha$ ,  $\beta$  and  $\gamma$ -picoline, 2,4- and 2,6-lutidine) [1, 3, 4-7]. The association constant  $K_{as}$  is a measure of the association ability of an alcohol; for *n*-alcohols it decreases with the length of the alkyl chain. In earlier papers it has been reported that the participation of bond breaking in the destruction of the structure of the pure *n*-alcohol decreases slightly with lengthening of the carbon chain of the alcohol. The higher the alcohol, the less

mobile are its molecules and the more difficult is their orientation with the OH groups towards the N of the pyridine bases. Studies by Wóycicka and Kalinowska [7] on  $h^M$  for mixtures of butanols with *n*-heptane in infinite dilution show that the tendency of alcohols to associate increases upon changing from more diluted to less diluted solutions, in the following sequence:



Analogous findings have been reported by Brown [8] from studies of the heats of mixing of butanols with *n*-hexane in infinite dilution. It is stressed that the constant  $K_{as}$  of an alcohol is related to the shape of the carbon chain and order of the alcohol. In iso-aliphatic alcohols, steric hindrance in the form of  $\text{CH}_3$  groups at carbons 1 and 2 limits the possibilities of coassociate formation.

The strength and length of the formed bond of the  $\begin{array}{c} \diagup \\ \text{N} \dots \text{H}-\text{O}-\text{C} \\ \diagdown \end{array}$  type depend on the order of the alcohol and the type of the pyridine base [9]:



Geisler [10] reports the association constants of the butanols, obtained from spectral data:

$$\begin{array}{cccc} K_{n\text{-but.}} & > & K_{\text{iso-but.}} & > & K_{\text{sec-but.}} & > & K_{\text{tert-but.}} \\ 4.2 & & 3.7 & & 3.2 & & 2.2 \end{array}$$

The values of the association constants of the butanols suggest that the coassociation energy is highest for tert-butanol. Should the  $\text{CH}_3$  group at carbon 2 of iso-butanol not represent a significant steric hindrance for coassociate formation, then it could be assumed that the overall effects of intermolecular interactions (measured as  $h^M$ ) are most exothermic for the systems formed by all bases with iso-butanol, as compared with the remaining iso-alcohols studied.

For the system 2,4,6-collidine + tert-butanol, the course of  $h^M = f(x)$  points to the predominance of coassociation over dissociation at low base contents. This seems to be due to the "loose" structure of pure tert-butanol, in the nearly spherical molecule of which the OH group is screened (shielded). It seems possible that single molecules of the pyridine base penetrate into the "loose" structure of tert-butanol, within which the free OH groups of non-associated tert-butanol molecules may coassociate. On a temperature elevation by  $10^\circ$ , for all the investigated systems of 2,4,6-collidine with iso-alcohols,  $\frac{dh}{dT} < 0$ . This testifies to an increase in the exothermic effects, resulting from "loosening" of the structures of tert-butanol and

2,4,6-collidine prior to mixing. Therefore, the contribution of the dissociation energy ( $E^+$ ) of the different components decreases with temperature rise, and the overall effect  $h^M$  is more negative. It is impossible on the basis of enthalpy alone to evaluate qualitatively the different kinds of interactions, e.g. strong hydrogen-bonds, dispersive effects, specific interactions of  $n-\pi$  and  $\pi-\pi$  type, orientation and induction effects.

The present considerations illustrate the relationships between  $h^M = f(x)$  and the compositions of the investigated systems, as functions of the chemical natures of the components and the structural properties of their molecules.

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