

THERMODYNAMIC PROPERTIES OF BINARY MIXTURES OF
2,4-LUTIDINE AND ISO-ALIPHATIC ALCOHOLS

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The molar excess enthalpies of binary mixtures of 2,4-lutidine with isopropanol, iso-butanol and 2-butanol at 293.15 and 303.15 K, and with *tert*-butanol at 303.15 K, were measured over the whole composition range.

The absolute values of all the molar excess functions were found to increase in the order: isobutanol < 2-propanol < 2-butanol < *tert*-butanol.

Experimental

All the iso-alcohols used in the present paper were the same as those used in our previous study [1]. After prolonged standing over pellets of potassium hydroxide, 2,4-lutidine was fractionally distilled with a column of about 30 theoretical plates. All alcohols were purified as suggested by Weissberger [2]. The purities of the final samples were checked by density measurements at 298.15 K, $n_D V_{01}$, and G.C. analysis. The data agreed well with the literature values [2–5] (Table 1).

Table 1
Physical properties of pure substances

Substance	Our work d , g cm ⁻³ $T = 298.15$ K	V_{01} , cm ³ mole ⁻¹	n_D^{25}	Degree of purity, percent**
2,4-lutidine	d 0.92685 n_D 1.4990	115.6	1.4979	99.9
2-propanol	d 0.78095 n_D 1.3747	74.71	1.3768	99.5
2-butanol	d 0.60267 n_D 1.3978	93.34	1.3977	99.8
iso-butanol	d 0.79435 n_D 1.3939	91.98	1.3978	99.5
<i>tert</i> -butanol	d 0.78086 n_D 1.3823	94.92	3	99.9

* Freezing point *tert*-butanol 25.66°

** Determined by gas chromatography

The apparatus and experimental procedure used in this work were the same as in [6].

Results

The experimental results on the molar excess enthalpies of the present mixtures are summarized in Tables 2 and 3. The measured values for 2,4-lutidine with 2-propanol, isobutanol or 2-butanol at 293.15 K and with *tert*-butanol at 303.15 K were correlated through the equation:

$$H^E = x(1 - x) \sum_{i=1}^3 c_n(2x - 1)^{i-1} \quad (1)$$

where H^E is the molar excess enthalpy, and x is the mole fraction of 2,4-lutidine. The adjustable coefficients C_n calculated by the method of least squares are collected in Table 4, together with the standard deviations ($\delta(H^E)$) of the results.

We have found no previous results to compare with our results for H^E .

The excess enthalpies for the systems 2,4-lutidine + 2-propanol, isobutanol or 2-butanol, at 293.15 K are negative over the entire concentration range.

Table 2

Excess enthalpies H^E of mixtures containing mole fraction x of 2,4-lutidine at 293.15 K

x	$-H^E$, J/mol	x	$-H^E$, J/mol	x	$-H^E$, J/mol	x	$-H^E$, J/mol
2,4-Lutidine + 2-Propanol				2,4-Lutidine + isobutanol			
0.0631	92.93	0.3852	393.45	0.0872	290.12	0.6345	675.37
0.1065	162.34	0.4509	370.18	0.1067	320.60	0.6776	591.21
0.1474	188.39	0.4907	349.16	0.2098	512.84	0.7337	500.43
0.1544	181.15	0.5424	312.91	0.2365	564.23	0.7909	399.62
0.1732	212.47	0.6678	230.12	0.3746	705.34	0.8031	395.30
0.2062	242.28	0.6869	208.75	0.4088	730.04	0.8120	333.06
0.3701	397.89	0.6954	211.85	0.5430	735.85	0.8534	290.49
		0.8233	97.95			0.9011	199.09
2,4-Lutidine + 2-butanol							
0.0812	125.01	0.4760	345.69				
0.1538	219.28	0.5941	310.05				
0.1941	267.22	0.6672	275.69				
0.2036	276.41	0.7184	229.69				
0.2495	312.44	0.8239	157.26				
0.3124	340.88	0.9214	106.24				
0.4099	345.13						
0.4282	365.18						
0.4772	365.97						

Table 3

Excess enthalpies H^E of mixtures containing mole fraction x of 2,4-lutidine at 303.15 K

x	$-H^E$, J/mol	x	$-H^E$, J/mol	x	$-H^E$, J/mol	x	$-H^E$, J/mol
2,4-Lutidine + 2-propanol				2,4-Lutidine + isobutanol			
0.0495	73.51	0.6431	311.19	0.2135	354.95	0.6637	650.48
0.1550	194.81	0.7641	276.14	0.2901	501.43	0.7226	525.14
0.1633	191.08	0.7794	225.70	0.3543	610.45	0.7317	527.19
0.2652	273.36	0.7840	209.33	0.4123	685.43	0.7457	465.99
0.3809	320.99	0.8065	182.62	0.4803	780.76	0.7945	447.14
0.4617	339.19	0.8322	142.14	0.5269	817.11	0.8333	355.31
0.4640	332.84	0.9162	76.24	0.5919	781.95	0.8597	260.13
0.6106	329.20			0.6327	684.54		
2,4-Lutidine + 2-butanol				2,4-Lutidine + <i>tert</i> -butanol			
0.1113	180.25	0.4724	427.49	0.0617	75.25	0.4316	288.42
0.2112	289.61	0.5718	410.32	0.1015	157.82	0.4528	274.93
0.2677	355.21	0.6616	384.99	0.1878	263.27	0.6926	199.26
0.2877	372.80	0.7116	304.65	0.3044	287.62	0.5958	185.15
0.3134	392.00	0.7896	243.67	0.3317	313.08	0.7405	27.00
0.3564	408.67	0.7927	228.79	0.3739	325.42	0.8105	+ 5.07
0.4340	425.23	0.8333	196.24	0.4225	313.86	0.8845	+ 45.43
		0.9182	112.59			0.9541	+ 30.12

The sign and composition-dependence of the excess function are expected to be determined by various factors such as the specific interaction between like components (self-association) and those between unlike components (complex formation due to hydrogen-bonding).

Table 4

Coefficients of Eq. (1) for binary mixtures

Mixtures: 2,4-Lutidine +	T , K	A_1	A_2	A_3	$\delta(H^E)$
2-propanol	293.15	-1426.97	-778.21	-883.84	18.15
Isobutanol		-2962.81	621.77	408.32	20.44
2-butanol		-1379.04	456.00	-112.19	11.56
2-propanol	303.15	-1377.60	123.19	128.04	18.51
Isobutanol		-3081.38	-437.76	2430.36	31.69
2-butanol		-1719.69	295.31	223.18	10.72
<i>tert</i> -butanol		-1038.09	1349.25	707.44	13.98

2,4-Lutidine + *tert*-butanol mixtures at 303.15 K display positive deviations for small *tert*-butanol concentrations and negative deviations for high *tert*-butanol concentrations.

These effects are small. The absolute values of H^E for isobutanol are appreciably larger than those for 2-propanol, 2-butanol and *tert*-butanol. This may be ascribed to the self-association of isobutanol being of minor degree and, accordingly, the endothermic contribution due to the destruction of self-association may be smaller. Hydrogen-bond formation is difficult in *tert*-butanol because of special limits, and is very simple in isobutanol. The H^E values vary in the sequence isobutanol < 2-butanol < 2-propanol for 293.15 K and isobutanol < 2-butanol < 2-propanol < *tert*-butanol for 303.15 K.

References

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ZUSAMMENFASSUNG — Die molaren Überschubenthalpien binärer Mischungen von 2,4-Lutidin mit Isopropanol, Isobutanol und 2-Butanol wurden bei 293.15 und 303.15 K, sowie mit *tert*-Butanol bei 303.15 K im ganzen Zusammensetzungsbereich gemessen. Es zeigte sich, daß die absoluten Werte sämtlicher molarer Überschubfunktionen in der Reihenfolge Isobutanol < 2-Propanol < 2-Butanol < *tert*-Butanol zunehmen.

Резюме — Измерены молярные избыточные энтальпии во всей области смешений бинарных смесей 2,4-лутидина с изопропанолом, изобутанолом и 2-бутанолом при 293.15 К 303.15 К, а также с трет-бутанолом при 303.15 К. Найдено, что абсолютные значения всех молярных избыточных энтальпий увеличиваются в ряду изобутанол < 2-пропанол < 2-бутанол < трет-бутанол.