THE HEAT OF MIXING FOR BINARY MIXTURES OF PYRIDINE WITH HYDROCARBONS*

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The author has recently been engaged in a programme of measuring the thermodynamic properties of solutions containing an alcohol and an amine (Copp and Findlay 1960 ; Findlay 1961). In the course of this work, measurements were made of the heats of mixing for binary mixtures of pyridine with toluene and with p-xylene. These results supplement Stott's unpublished data for the vapour pressure of these solutions.

Experimental

Toluene was purified by shaking Analar toluene with conc. H_2SO_4 (Beal and Souther 1927), washing with water, drying over Na, and fractionally distilling.

p-Xylene was treated (Mathews 1926) with H_2SO_4, NaOH, and Hg, dried over P_2O_5, and fractionally distilled. The product was subsequently fractionally frozen twice, and the best fraction redistilled.

Pyridine was dried over NaOH pellets and fractionally distilled.

Results

The physical properties of the purified products (Table 1) appear to be in reasonable agreement with the literature values quoted and with the data of Timmermans (1950).

The calorimeter used, which was based on the design of Cheesman and Ladner (1955), was the same as that used previously (Findlay 1961).

TABLE 1

PHYSICAL PROPERTIES OF LIQUIDS

Properties	Toluene	p-Xylene	Pyridine
B.p. range in °C (uncorr.)	$110 \cdot 67 \pm 0 \cdot 02$	$138 \cdot 46 \pm 0 \cdot 03$	$115 \cdot 40 \pm 0 \cdot 05$
d_4^{25}	$0 \cdot 8620_6$	$0 \cdot 8567_5$	$0 \cdot 9780_4$
d_4^{25} (lit.)	$0 \cdot 86231$ (Rossini *et al.* 1956)	$0 \cdot 85669$ (Rossini *et al.* 1956)	$0 \cdot 97806$ (Timmermans 1920 ; Biddiscombe *et al.* 1954)

The heat of mixing data for toluene+pyridine and p-xylene+pyridine at $25 \cdot 0_0$ °C, $45 \cdot 0_0$ °C (and $65 \cdot 0_0$ °C for the latter system), are given in Tables 2 and 3. The results were fitted to the equation

$$H^E = x_1 x_2 [P + Q(x_1 - x_2)], \qquad (1)$$

where x_2 is the mole fraction of pyridine, and the values of the parameters, P and Q, appear in Table 4. The estimated uncertainties in P, Q, and H^E were calculated using the formulae given by Deming (1948).

TABLE 2

HEAT OF MIXING TOLUENE (1)+PYRIDINE (2)

$25 \cdot 0_0$ °C				$45 \cdot 0_0$ °C			
x_2	H^E (cal/g-mol)	x_2	H^E (cal/g-mol)	x_2	H^E (cal/g-mol)	x_2	H^E (cal/g-mol)
0·095	19·2	0·586	43·2	0·081	17·5	0·475	54·6
0·229	40·4	0·665	34·9	0·094	23·5	0·578	49·7
0·235	38·6	0·779	23·9	0·143	29·7	0·589	53·3
0·334	46·4	0·820	25·3	0·158	31·4	0·664	39·8
0·471	44·8	0·852	12·7	0·226	45·6	0·676	42·1
0·473	45·6	0·857	13·4	0·316	48·9	0·780	26·4
0·570	42·6	0·944	6·5	0·449	54·6	0·858	21·9
						0·946	8·2

TABLE 3

HEAT OF MIXING p-XYLENE (1)+PYRIDINE (2)

25·0₀ °C		45·0₀ °C		65·0₀ °C	
x_2	H^E (cal/g-mol)	x_2	H^E (cal/g-mol)	x_2	H^E (cal/-gmol)
0·119	44·2	0·102	38·9	0·248	92·3
0·284	75·3	0·172	64·9	0·330	100·7
0·373	86·2	0·263	87·0	0·510	120·8
0·517	92·1	0·365	102·8	0·697	94·9
0·591	90·8	0·507	109·5	0·799	70·9
0·624	88·5	0·517	107·3	0·892	43·5
0·710	75·9	0·622	95·2		
0·712	74·1	0·704	87·4		
0·821	51·8	0·792	64·2		
0·874	33·7	0·880	42·8		
0·952	16·5	0·954	17·4		

TABLE 4

VALUES OF P AND Q IN EQUATION (1) FOR MIXTURES OF PYRIDINE WITH A HYDROCARBON

Hydrocarbon	Temp. (°C)	P (cal/g-mol)	Q (cal/g-mol)	σ_H (cal/g-mol)
Toluene	25·0₀	178±6	73±12	2·3
	45·0₀	211±6	59±12	2·3
p-Xylene	25·0₀	370±7	25±14	2·5
	45·0₀	431±6	38±12	2·0
	65·0₀	471±9	39±18	3·3

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