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EXCESS HEAT OF MIXING OF BINARY MIXTURES OF PYRIDINE WITH *n*-ALKANES AT 313.15 K

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The molar excess enthalpies of binary mixtures of pyridine with C_6–C_9 *n*-alkanes have been measured at 313.15 K in the entire composition range. The measured H^E values were compared with those calculated by means of the Prigogine–Flory–Patterson theory and by the ERAS method.

Experimental

Pyridine (analytical reagent grade, POCH), *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane all purum POCH, were dried in accordance with recommendations of [1]. The purities of the substances were checked by g.l.c. The densities and refractive indexes of the samples at 298.15 K agree reasonably well with values in the literature [2–4]. The purity of the substances determined by g.l.c. was better than 99.95%. Heats of mixing have been measured using a flow microcalorimeter UNIPAN type 600 [3]. The precision of the H^E determination is estimated to be within ± 2 J mol^{-1}.

Results and discussion

The experimental results for H^E for the binary mixtures pyridine + *n*-hexane, or *n*-heptane, *n*-octane, or *n*-nonane at 313.15 K are presented. Each set of results for H^E was fitted to the Redlich–Kister polynomial:

$$H^E/\text{J mol}^{-1} = x_1 x_2 \sum_{i=1}^{4} A_i (x_1 - x_2)^i \qquad (1)$$

The experimental values of H^E, coefficients A_i and standard errors are given in Table 1.

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Table 1 Excess enthalpies for pyridine + C_6 to C_9 *n*-alkane at 313.15 K, x_1 – mole fraction of pyridine, s – standard error

x_1	H^E, J.mol^{-1}	x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}
		Pyridine + *n*-Hexane			
0.0825	488.4	0.3473	1439.9	0.6662	1443.2
0.1223	707.2	0.4292	1578.8	0.7162	1323.5
0.2042	1060.6	0.4569	1585.7	0.8496	801.5
0.2589	1245.4	0.5547	1592.0	0.9228	460.1
	$A_1 = 6435.16$ $A_2 = 139.31$ $A_3 = 63.14$ $A_4 = -473.56$ $s = 12.05$				
		Pyridine + *n*-Heptane			
0.0482	377.4	0.4053	1717.5	0.7015	1521.5
0.1033	706.4	0.4941	1766.9	0.8070	1200.0
0.2026	1195.9	0.5590	1755.1	0.9446	463.4
0.2453	1353.9	0.5591	1761.0	0.9691	243.5
0.3384	1610.0	0.6468	1657.9		
	$A_1 = 7082.45$ $A_2 = 69.28$ $A_3 = 1323.15$ $A_4 = 377.43$ $s = 12.3$				
		Pyridine + *n*-Octane			
0.0498	400.9	0.4131	1908.1	0.8067	1245.2
0.0949	711.9	0.4993	1948.2	0.8140	1216.8
0.1065	782.6	0.5273	1953.1	0.8566	980.7
0.1398	987.5	0.5910	1898.0	0.9141	632.1
0.2171	1377.4	0.6453	1819.8	0.9409	459.8
0.3043	1687.9	0.7040	1657.5	0.9461	426.9
	$A_1 = 7846.80$ $A_2 = -12.44$ $A_3 = 570.46$ $A_4 = -164.40$ $s = 7.9$				
		Pyridine + *n*-Nonane			
0.0414	402.8	0.4886	2175.8	0.6501	1988.2
0.0894	810.8	0.5162	2181.8	0.7109	1817.8
0.1321	1111.2	0.5169	2176.8	0.7481	1665.1
0.2374	1699.3	0.5281	2165.2	0.8560	1115.9
0.2806	1850.0	0.5562	2142.0	0.9466	479.6
0.4028	2146.8	0.5886	2103.7		
	$A_1 = 8736.52$ $A_2 = -474.54$ $A_3 = 1326.16$ $A_4 = 131.07$ $s = 7.6$				

For all the systems considered H^E is of large positive values and H^E increases with increasing chain-length of the *n*-alkanes (Fig. 1).

The values of H^E for the investigated systems, were compared with the H^E values calculated from Prigogine–Flory–Patterson theory (P–F–P) [12, 13], and by the Extended Real Associated Solution (ERAS) model [14]. The parameters X_{12} in the P–F–P and ERAS method were determined from experimental H^E values.

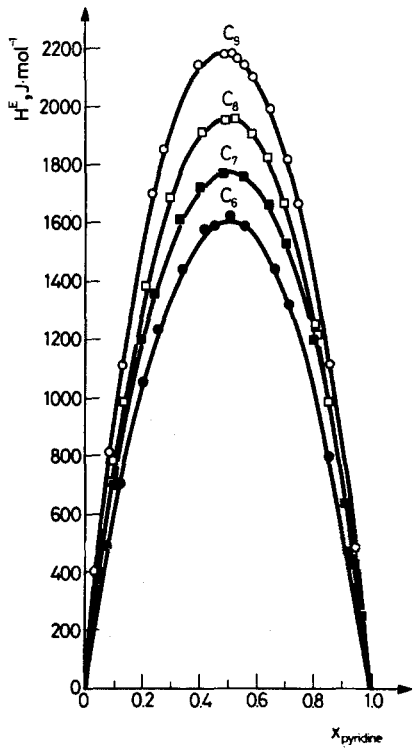

Fig. 1 H^E for pyridine + (C_6–C_9) alkanes at 313.15 K; dots: experiments, line: R–K polynomial

Table 2 Parameters for pure components

Component	d, g cm^{-3}	P^* J cm^{-3}	$10^3\,\alpha$, K^{-1}	s_1, A^{-1}	$10^3\,\varkappa$, J cm^{-3}	K_M, mol^{-1}	ΔH^*_M, kJ mol^{-1}	ΔV^*, cm^3 mol^{-1}
Pyridine	0.9782[5]	654.5[5]	0.992[5]	1.00[5]	0.6996[5]	0.101[10]	−17.5[10]	−8.53[11]
n-Hexane	0.6550[6]	423 [7]	1.391[6]	1.04[7]				
n-Heptane	0.6793[6]	432 [6]	1.253[6]	1.02[8]				
n-Octane	0.6983[6]	439 [7]	1.165[6]	0.99[7]				
n-Nonane	0.7176[9]	443 [9]	1.065[9]	0.97[9]				

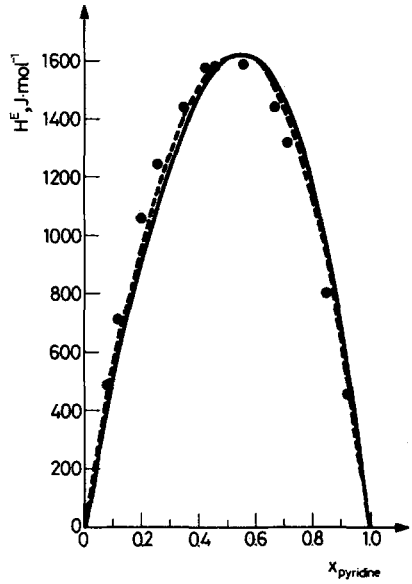

Fig. 2 H^E for pyridine + *n*-hexane at 313.15 K; dots: experiment, line: P–F–P theory, dotted line ERAS model

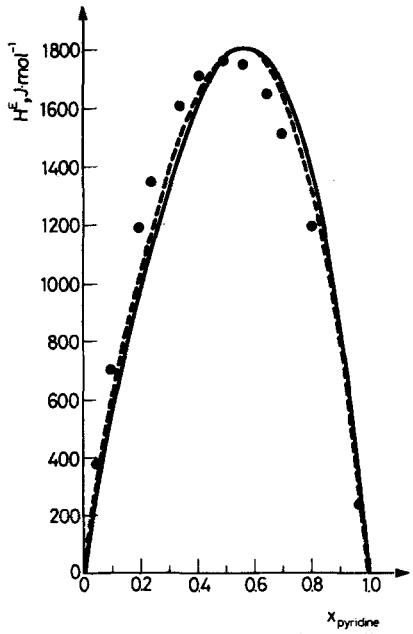

Fig. 3 H^E for pyridine + *n*-heptane at 313.15 K; dots: experiment, line: P–F–P theory, dotted line: ERAS model

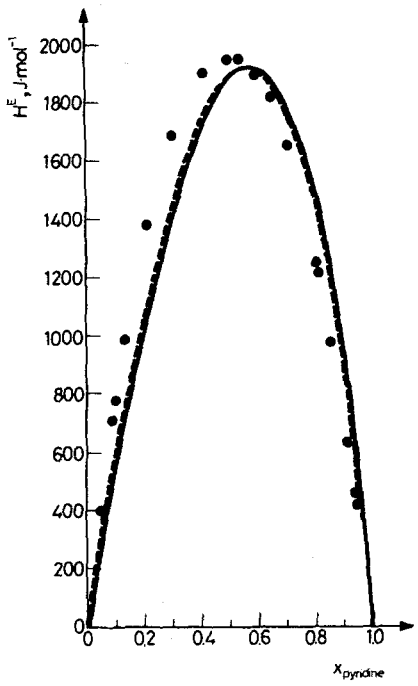

Fig. 4 H^E for pyridin+octane at 313.15 K; dots: experiment; line: P–F–P theory, dotted line: ERAS model

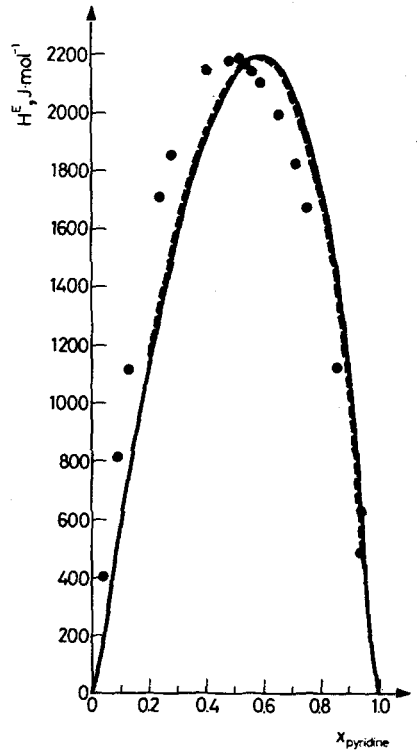

Fig. 5 H^E for pyridine+n-octane at 313.15 K; dots: experiment; line: P–F–P theory, dotted line: ERAS model

Table 3 Values of parameters X_{12} of Prigogine–Flory–Patterson theory and ERAS model and standard error δ

Mixture	X_{12}		δ, J mol^{-1}	
	P–F–P	ERAS	P–F–P	ERAS
Pyridine+n-hexane	78.1	65.5	102.7	74.5
Pyridine+n-heptane	82.6	67.9	123.6	103.8
Pyridine+n-octane	84.7	67.0	178.2	163.2
Pyridine+n-nonane	93.0	72.2	224.1	217.2

Parameters for pure components are shown in Table 2, and parameters of X_{12} in Table 3.

Figures 2, 3, 4 and 5 show the experimental values of the excess heat of mixing and those calculated from the P–F–P theory and from the ERAS model for the

systems investigated. The H^E_{max} is shifted to the pyridine-rich region only for pyridine + *n*-hexane, the H^E_{max} value from the P–F–P and ERAS theory is similar to the experimental H^E_{max}.

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Zusammenfassung — Die molaren Überschußenthalpien binärer Mischungen von Pyridin mit C_6–C_9 *n*-Alkanen wurden bei 313,15 K im ganzen Zusammensetzungsbereich gemessen. Die gemessenen H^E Werte wurden mit denen verglichen, die mit Hilfe von Prigogine–Flory–Patterson Theorie und nach der ERAS-Methode berechnet wurden.

Резюме — Измерены при темпертуре 313,5 К молярные избыточные энтальпии двойных смесей пиридина с *n*-алканами (C_6–C_9) во всей области их состава. Измеренные величины H^E были сопоставлены с вычисленными на основе теории Пригогина–Флори–Петтерсона и по методу расширенного действительно связанного решения (ERAS).