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EXCESS HEAT OF MIXING OF PYRIDINE BASES WITH TOLUENE
Experimental results and theoretical description

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Abstract

The excess heats of mixing of pyridine bases with toluene at 298.15 K were measured, and the Prigogine–Flory–Patterson theory was applied to describe the experimental results.

Keywords: excess heat of mixing, Prigogine–Flory–Patterson theory, pyridine bases, toluene

Introduction

We have earlier reported experimental values of the excess heats of mixing of the binary systems of pyridine, α-, β- and γ-pycoline, and 2,4- and 2,6-lutidine with normal alkanes (C_6–C_{10}) at 298.15 K [1–8], and with benzene [9]. The experimental data were described by using the Prigogine–Flory–Patterson (PFP) theory [10–15], and the Extended Real Associated Solution (ERAS) method [16]. Benzene, toluene and *m*-xylene were used in these calculations as homomorphic substances for pyridine, picolines and lutidines, respectively.

Unambiguous data on the excess enthalpies of mixing of these homomorphic substances with pyridine bases are not to be found in the available literature. Systematic investigations of the heats of mixing of the binary systems formed by benzene, toluene and xylenes with pyridine bases will allow a discussion of the problems of the specific interactions in pyridines and also the influence of the methyl groups on the aromatic ring on the molecular interactions and the structures of the pyridine bases.

In this paper, as a continuation of our investigations on the thermodynamic properties of pyridine base+hydrocarbon mixtures, we present experimental H^E data for the binary systems of pyridine, α-picoline, 2,6-lutidine and 2,4,6-collidine with toluene. Experimental values of H^E are compared with $H^E_{\text{calc.}}$ data computed by using the PFP theory, which considers only the contribution of physical interactions to the excess properties of mixtures.

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Experimental

The pyridine bases were purified as described previously [1–8]. Their purity as determined by glc was better than 99.9%. Toluene was dried over molecular sieves, then purified by repeated fractional distillation (25 PT). Its purity was better than 99.97% (as checked by glc). The water contents in all reagents were checked by glc with a katharometer detector, and were less than 0.01%.

The heats of mixing were measured with a UNIPAN 600 flow microcalorimeter, described previously [1].

Results and discussion

The experimental molar excess heats of mixing for the binary mixtures of pyridine bases with toluene at 298.15 K are listed in Table 1. The Redlich–Kister equation was fitted to the H^E data by the polynomial

$$H^E[\mathrm{J\cdot mol^{-1}}] = x_2(1 - x_2)\sum_{i=1}^{3} C_i(1 - 2x_2)^{i-1} \tag{1}$$

where x_2 is the mole fraction of toluene, and C_i are the smoothing coefficients. These coefficients for the pyridine base +toluene systems, together with the standard deviations $\delta(H^E)$, are presented in Table 1.

For the binary systems of pyridine, α-picoline and 2,6-lutidine with toluene, the H^E values are positive, while for the system of 2,4,6-collidine with toluene, H^E is positive for $x_1 < 0.1$ and negative for $x_1 > 0.1$; the H^E curve is *S*-shaped.

H^E data for pyridine and α-picoline with toluene were published by Woycicki *et al.* [17], Merlin *et al.* [19] and Findlay [18]. Our experimental results and literature data are presented in Fig. 1. Because of the very small standard deviations of the fitting of $H^E = f(x)$ by the Redlich–Kister equation, our results are indicated by full lines. The H^E values for pyridine+toluene are comparable within experimental error with the data of Woycicki *et al.* and significantly smaller than those of Findlay. The results presented for α-picoline+toluene are a little higher (≈5 J·mol^{-1}) than those of Woycicki *et al.* and Merlin. No excess enthalpy data for the systems of 2,6-lutidine, and 2,4,6-collidine with toluene are available in the literature.

Our experimental results were evaluated by the PFP theory [10–15].

The PFP expression for the excess enthalpy H^E is given by:

$$H^E = (v^*_1x_1 + v^*_2x_2)\left[\frac{\varphi_1 p^*_1}{\tilde{v}_1} + \frac{\varphi_2 p^*_2}{\tilde{v}_2} - \frac{p^*_M}{\tilde{v}_M}\right] \tag{2}$$

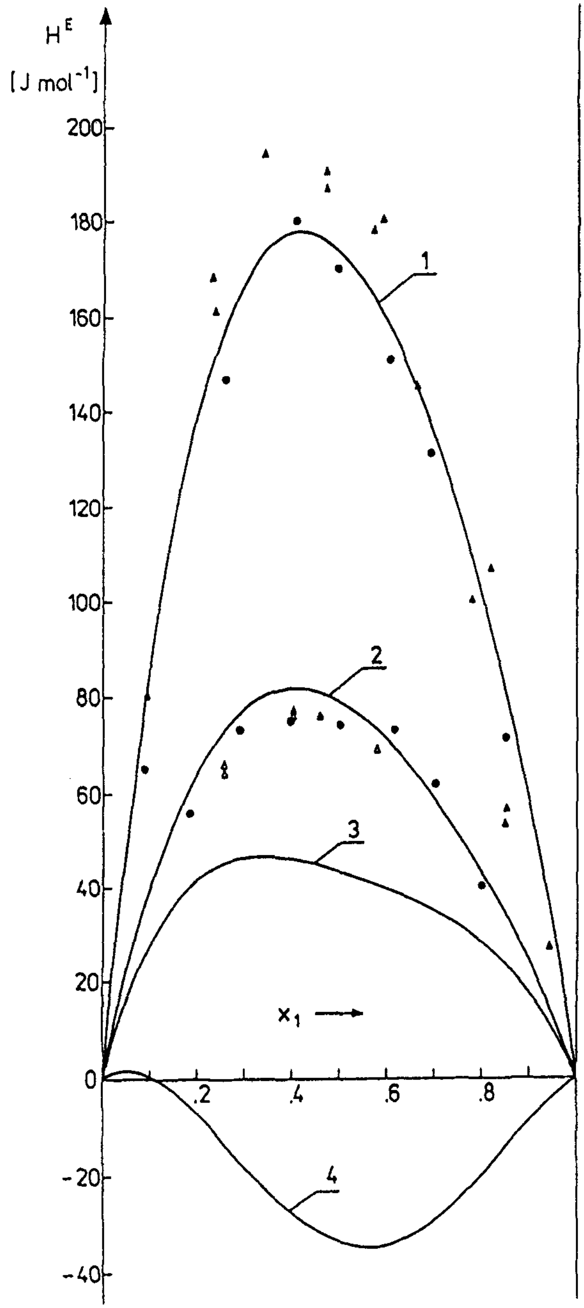

Fig. 1 Excess heat of mixing at 298.15 K in the systems pyridine base$_1$ + toluene; —— experimental curves: (1) pyridine, (2) α-picoline, (3) 2,6-lutidine, (4) 2,4,6-collidine; • – Woycicki *et al.*, Δ – Merlin *et al.*, ▲ – Findlay

Table 1 Excess enthalpies for pyridine, α-picoline, 2,6-lutidine and 2,4,6-collidine with toluene at 298.15 K, x_1 – mole fraction of pyridine base. C_i – coefficients of Redlich-Kister equation, δ – standard deviations

x_1	H^E/ J·mol^{-1}	x_1	H^E/ J·mol^{-1}	x_1	H^E/ J·mol^{-1}
		pyridine+toluene			
0.1142	98.0	0.5018	171.0	0.6642	144.0
0.1787	131.9	0.5018	175.5	0.7036	134.3
0.2463	153.8	0.5043	171.4	0.7668	110.6
0.3034	167.5	0.5043	176.0	0.8529	77.3
0.3501	173.0	0.5678	167.6	0.8842	65.9
0.3795	176.4	0.6048	156.9		
	C_1 = 694.70	C_2 =−201.40	C_3 = 155.11	δ = 2.1	
		α-picoline+toluene			
0.0640	27.6	0.4456	80.1	0.5901	71.7
0.1460	53.1	0.4456	82.6	0.6945	58.9
0.2547	72.0	0.5006	77.8	0.7635	48.9
0.3008	77.4	0.5006	81.2	0.8673	31.0
0.3736	81.8	0.5534	74.4	0.9157	21.5
	C_1 = 315.42	C_2 =−111.15	C_3 = 60.24	δ = 1.1	
		2,6-lutidine+toluene			
0.0801	24.6	0.4434	45.1	0.7007	35.5
0.1530	35.8	0.4434	44.2	0.7656	30.9
0.1530	37.9	0.5088	44.9	0.7656	29.9
0.2486	44.3	0.5088	44.2	0.8699	19.2
0.3570	45.2	0.5088	43.1	0.9020	18.4
0.3776	46.6	0.5919	41.9		
	C_1 = 175.06	C_2 =−69.24	C_3 = 118.08	δ = 1.3	
		2,4,6-collidine+toluene			
0.0274	3.4	0.4470	−32.3	0.7259	−28.0
0.0274	3.6	0.4928	−32.1	0.7335	−24.5
0.0547	−0.8	0.5064	−32.7	0.7585	−23.8
0.1630	−4.4	0.5101	−33.9	0.8305	−16.7
0.1791	−5.2	0.5419	−33.3	0.8305	−15.8
0.2408	−12.2	0.6200	−35.8	0.8715	−10.5
0.3562	−21.7	0.6933	−30.7		
0.4320	−29.3	0.6933	−31.6		
	C_1 =−133.78	C_2 =−66.79	C_3 = 137.23	δ = 1.5	

with the characteristic pressure of the mixture

$$p^*_M = \varphi_1 p^*_1 + \varphi_2 p^*_2 - \varphi_1 \theta_2 \chi_{12} \tag{3}$$

where χ_{12} is the interaction energy parameter, and θ_2 is the surface fraction:

$$\theta_2 = \frac{\varphi_2 s_2}{\varphi_1 s_1 + \varphi_2 s_2} \tag{4}$$

where s is the molecular surface-to-volume ratio, and the hard core volume fraction is

$$\varphi_1 = \frac{x_1 v^*_1}{x_1 v^*_1 + x_2 v^*_2} \tag{5}$$

The remaining symbols: v^*_i are the hard core volume, p^*_i are the characteristic pressures and $\tilde{v}_i$ are the reduced volumes, all related to the components, and $\tilde{v}_M$ is the reduced volume of mixture.

Table 2 Parameters of pure components at 298.15 K used in calculations H^E for binaries: pyridine base+toluene by the PFP theory

Component	d/ g·cm^{-3}	p^*/ J·mol^{-1}	α/ kK^{-1}	s/ Å^{-1}
pyridine	0.97820^a	656.4^a	0.9920^a	1.21^d
α-picoline	0.93948^a	617.7^a	1.0020^a	1.09^d
2,6-lutidine	0.91780^a	582.0^a	1.0020^a	0.97^d
2,4,6-collidine	0.91029^c	606.6^f	1.0094^h	0.85^g
toluene	0.86230^b	376.6^f	1.0670^e	0.88^g

[a] Ref. [20]; b: Ref. [21]; [c] Ref. [22]; d: Ref. [23]; [e] Ref. [24]; f: Obtained from the Flory formalism
[g] Authors' own published data; [h] Estimated from the data for other pyridine bases (Griot *et al.*, 1982) on a group contribution bases

In the PFP calculations, the reduced and characteristic quantities were estimated from the pure component properties given in Table 2 by using Flory's reduced' equation of state [11]. The expression for H^E contained only one adjustable parameter, χ_{12}. This parameter represents the energy of molecular interaction in solution. The values of the parameter χ_{12}, together with the standard errors of the fits, are listed in Table 3.

The experimental data on the enthalpies of mixing are compared with the computed values in Fig. 2. The calculated excess enthalpies correspond satisfactorily to the experimental data as concerns both the magnitude and the concentration dependence of H^E. However, some systematic shifts in the calculated curves in comparison to the experimental ones are observed.

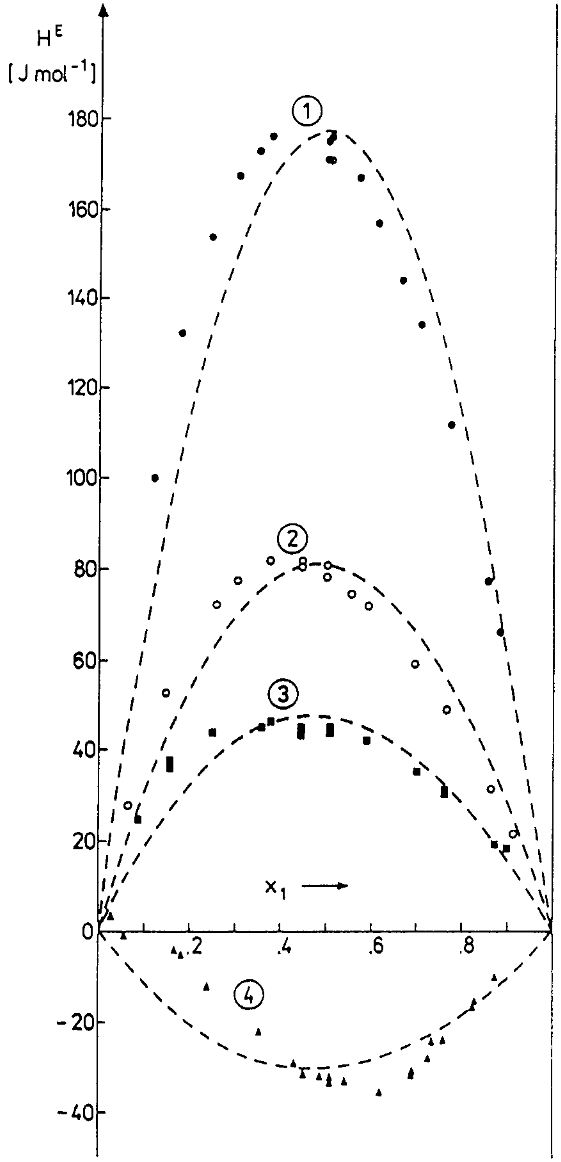

Fig. 2 Excess heat of mixing at 298.15 K in the systems: (1) pyridine$_1$ + toluene, (2) α-picoline$_1$ + toluene, (3) 2,6-lutidine$_1$ + toluene, (4) 2,4,6-collidine$_1$ + toluene; • – pyridine, o – α-picoline, ■ – 2,6-lutidine, ▲ – 2,4,6-collidine; – – – values calculated from PFP theory

The good agreement of the measured and calculated H^E values in all investigated systems confirms the hypothesis that the association of pyridine bases is rather weak; the PFP theory takes into account only the nonspecific interactions in solution.

The main interactions in pyridine bases are n–Π and Π–Π association making only a small contribution. The presence of methyl groups significantly decreases the endothermic effect of H^E in the sequence

pyridine > α-picoline > 2,6-lutidine > 2,4,6-collidine.

This is connected with the influence of the position of the CH_3 groups on the free electron pair on the nitrogen atom, and on the steric hindrance at the nitrogen atom. The presence of the three CH_3 groups in the collidine molecule leads to the contribution of the n–Π interactions being negligible, and the energy of the Π–Π interactions between the different molecules predominating. The effect of the heat of mixing in the 2,4,6-collidine+toluene mixture is therefore exothermic. These conclusions are confirmed by the sign and values of the parameter χ_{12} (Table 3), which is a measure of the molecular interaction energy in solution. The values of χ_{12} decrease in the sequence

pyridine > α-picoline > 2,6-lutidine > 2,4,6-collidine

and only for the 2,4,6-collidine+toluene mixture is its sign negative.

Table 3 Parameters χ_{12} in calculations H^E by PFP theory with corresponding standard errors $\delta(H^E)$

System	χ_{12} / J·mol^{-1}	$\delta(H^E)$ / J·mol^{-1}
pyridine+toluene	10.84	13.3
α-picoline+toluene	4.26	5.8
2,6-lutidine+toluene	2.17	5.0
2,4,6-collidine+toluene	–1.19	6.4

A closer approach to the solution of the above-described problems of the molecular interactions in pyridine bases will probably be achieved when studies of the excess enthalpies of mixing in the binary systems formed by pyridine bases with xylenes and mesitylene are completed.

* * *

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Zusammenfassung — Die molaren Überschussenthalpien binärer Mischungen von Pirydin, α–Picolin, 2,6-Lutidin, 2,4,6-Kollidin mit Toluol wurden bei 298.15 K im ganzen Zusammensetzungsbereich gemessen. Die gemessenen H^E Werte wurden mit denen verglichen, die mit Hilfe von Prigogine–Flory–Patterson Theorie berechnet worden waren.