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Heats of mixing of binary mixture of pyridine bases and *o*-xylene. Experimental results and description according to the theory

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Abstract

Excess heats of mixing of the binary systems pyridine, or 2-picoline, or 3-picoline, or 2,4-lutidine, or 2,6-lutidine, or 2,4,6-collidine and *o*-xylene have been measured at 298.15 K as a function of composition. The Prigogine–Flory–Patterson (PFP) theory is applied to describe the experimental results.

Keywords: Binary system; Excess heat of mixing; Heat of mixing; PFP

1. Introduction

As an extension of our investigation on the effect of the number and position of the methyl groups in pyridine ring, as well as of the number and positions of the methyl groups in a benzene ring, the excess molar enthalpies H_m^E for pyridine, 2-picoline, 3-picoline, 2.4-lutidine, 2,6-lutidine or 2,4,6-collidine + *o*-xylene at 298.15 K have been measured.

We have already reported [7,8] excess molar enthalpies for this kind of mixture, namely pyridine bases with benzene [7], and pyridine bases with toluene [8].

The experimental H_m^E data are compared with values computed using the Prigogine–Flory–Patterson theory, [1–6], which only considers the non-specific interactions in solution.

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2. Experimental

The pyridine bases used in this work are the same as those used previously [7,8]. Their purity as determined by GLC was better than 99.9%.

The *o*-xylene (POCH, Gliwice, Poland) was dried over molecular sieves, and then purified twice by fractional distribution (25 PT). Its purity was better than 99.97%, as checked by GLC. The water contents in all the reagents were checked by GLC with a katharometer detector, and was smaller than 0.01%.

The UNIPAN type 600 flow microcalorimeter, used for the measurements of the excess heat of mixing, has been described in a previous work [9].

3. Results and discussion

The experimentally obtained excess heats of mixing are given in Table 1. The values of the excess heats of mixing were fitted to the Redlich–Kister equation

$$H_m^E(\mathrm{J\,mol^{-1}}) = x_2(1-x_2)\sum_{i=1}^{3} A_i(1-2x_2)^{i-1} \tag{1}$$

where x_2 is the mole fraction of *o*-xylene, and A_i are the smoothing coefficients. These coefficients for the pyridine bases + *o*-xylene systems together with the standard deviations $\delta(H_M^E)$, are listed in Table 1, and presented graphically in Fig. 1.

No excess heats of mixing data for any of our investigated stystems are available in the literature. For all the investigated systems, the values of the excess heat of mixing are positive and higher than for the pyridine bases + benzene, and pyridine bases + toluene systems.

The most remarkable difference is that the excess heat of mixing for 2,4,6-collidine + toluene changes sign from positive to negative as the mole fraction of 2,4,6-collidine increases [8], while the system 2,4,6-collidine + *o*-xylene has a positive excess heat of mixing.

The excess heats of mixing for the binary mixtures of pyridine bases + benzene are always positive, and are smaller than those found for pyridine bases with *o*-xylene. Unfortunately, the 2,4,6-collidine + *o*-xylene system shows a nearly ideal behaviour. This is probably caused by the presence of the methyl groups in the aromatic rings.

The experimental data are compared with the results calculated by the PFP theory. The PFP expressions for H_m^E is

$$H_m^E = (v_1x_1 + v_2x_2)\left[\frac{\varphi_1 p_1^*}{\tilde{v}_1} + \frac{\varphi_2 p_2^*}{\tilde{v}_2} - \frac{p_M^*}{\tilde{v}_M}\right] \tag{2}$$

where the characteristic pressure of mixture p_M^* is

$$p_M^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1\theta_2\chi_{12} \tag{3}$$

Table 1
Experimental excess enthalpies (J mol^{-1}) for pyridine bases with *o*-xylene at 298.15 K: x_1, mole fraction of pyridine base; A_i coefficients of Redlich–Kister polynomial; δ, standard deviations

x_1	H^E	x_1	H^E	x_1	H^E
Pyridine + *o*-xylene					
0.1390	245.1	0.4235	375.5	0.5907	308.1
0.1941	307.9	0.4235	374.3	0.6582	264.5
0.2100	333.6	0.4923	363.2	0.7099	217.1
0.2144	333.6	0.4955	355.0	0.7738	160.4
0.3015	375.3	0.5093	359.0		
0.3566	378.2	0.5588	324.0		
$A_1 = 1422.2370$	$A_2 = -886.8868$	$A_3 = 50.9864$	$\delta = 5.9$		
2-Picoline + *o*-xylene					
0.1160	149.9	0.3530	238.8	0.6005	189.7
0.1439	171.9	0.4122	240.7	0.6595	160.9
0.2128	216.9	0.4521	232.3	0.7081	143.4
0.2718	233.1	0.4989	224.7	0.7687	105.0
0.3530	240.0	0.5412	209.1	0.7687	104.5
$A_1 = 884.5905$	$A_2 = -586.2829$	$A_3 = 156.4727$	$\delta = 3.9$		
3-Picoline + *o*-xylene					
0.1380	115.4	0.4553	177.2	0.6820	143.1
0.1380	117.1	0.4553	182.9	0.7199	129.9
0.1859	141.9	0.5142	171.8	0.7276	127.2
0.2345	162.9	0.5142	174.4	0.7355	127.0
0.2345	166.5	0.5142	181.7	0.7355	126.1
0.2966	174.3	0.5717	165.4	0.7710	107.2
0.3566	179.4	0.6201	159.6	0.7780	108.5
0.3566	178.5	0.6201	158.9	0.7909	103.6
0.4154	182.1	0.6201	158.6		
0.4553	173.4	0.6802	144.5		
$A_1 = 707.1368$	$A_2 = -234.3877$	$A_3 = 210.0917$	$\delta = 3.5$		
2,4-Lutidine + *o*-xylene					
0.1418	66.9	0.3149	87.6	0.5384	89.4
0.1858	79.5	0.3711	90.3	0.5936	83.6
0.1858	74.8	0.4270	91.4	0.6494	77.4
0.2004	73.9	0.4418	90.1	0.7063	64.4
0.2596	82.3	0.4818	88.4	0.7653	58.9
$A_1 = 352.0146$	$A_2 = -119.4971$	$A_3 = 159.9565$	$\delta = 3.2$		
2,6-Lutidine + *o*-xylene					
0.1341	64.1	0.4578	94.4	0.5727	84.9
0.2043	79.9	0.4578	85.7	0.6048	81.9
0.2466	84.1	0.4837	93.3	0.6599	73.8
0.2990	88.3	0.4932	95.2	0.7148	64.5
0.3523	90.1	0.5274	88.7	0.7225	59.2
0.4048	90.9	0.5515	89.3		
$A_1 = 360.1700$	$A_2 = -139.6839$	$A_3 = 101.4902$	$\delta = 3.4$		
2,4,6-Collidine + *o*-xylene					
0.1439	22.3	0.4256	21.2	0.6562	17.4
0.1828	25.9	0.4627	21.8	0.7172	14.1
0.2367	26.8	0.5108	21.9	0.7679	15.1
0.2893	26.1	0.5509	20.6	0.8242	11.2
0.3426	25.3	0.6024	17.6		
$A_1 = 83.5683$	$A_2 = -64.4996$	$A_3 = 103.4335$	$\delta = 1.1$		

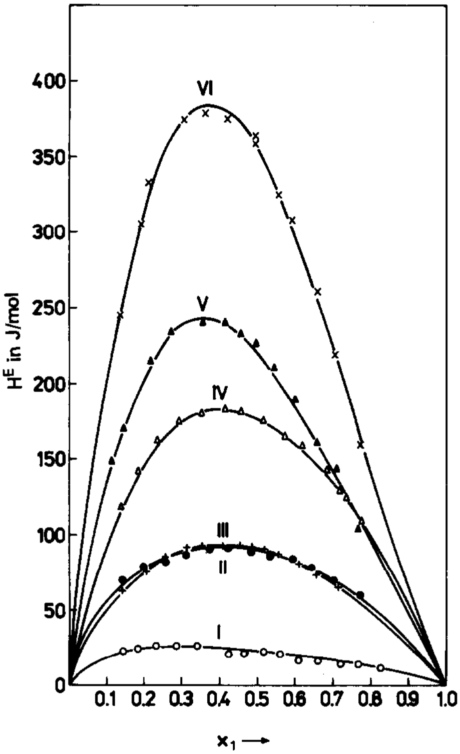

Fig. 1. Excess heats of mixing for pyridine bases(1) + *o*-xylene at 298.15 K: —, smoothed experimental results, × pyridine + *o*-xylene; ▲, 2-picoline + *o*-xylene; △, 3-picoline + *o*-xylene; +, 2,6-lutidine + *o*-xylene; ●, 2,4-lutidine + *o*-xylene; ○, 2,4,6-collidine + *o*-xylene.

where χ_{12} is the interaction energy parameter, and θ_2 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 φ_1 is the hard volume fraction given by

$$\varphi_1 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \tag{5}$$

where v_i^* are hard core volumes, p_i^* characteristic pressures, $\hat{v}_i$ reduced volumes of components, and $\hat{v}_M$ reduced volumes of mixture.

The reduced and characteristic quantities were estimated from the pure component properties given in Table 2, using Flory's equation of state [2]. The expression for H_m^E contained only one adjustable parameter χ_{12}, see Table 3.

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

Component	d in g cm^{-3}	p^* in J mol^{-1}	α in k K^{-1}	s in Å^{-1}
Ppyridine	0.9782 [a]	656.4 [a]	0.9920 [a]	1.21 [d]
2-Picoline	0.93948 [a]	617.7 [a]	1.0020 [a]	1.09 [d]
3-Picoline	0.9527 [a]	629.6 [a]	0.9720 [a]	1.09 [d]
2,4-Lutidine	0.9266 [e]	596.0 [d]	0.9544 [d]	0.97 [d]
2,6-Lutidine	0.9178 [a]	582.0 [a]	1.002 [a]	0.97 [d]
2,4,6-Collidine	0.91029 [c]	606.6 [i]	1.0094 [f]	0.85 [g]
o-xylene	0.8760 [b]	445.6 [1]	0.9590 [h]	0.76 [g]

Key: d, density; p^*, characteristic pressure; α, expansion coefficient; s, molecular surface-to-volume ratio. [a] Ref. [10]. [b] Ref. [11]. [c] Ref. [12]. [d] Ref. [13]. [e] Ref. [14]. [f] Estimated from the data for other pyridine bases [10] on a group contribution basis. [g] Authors own unpublished data. [h] Private communication (A. Zywocinski). [i] Obtained from the Flory formalism.

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

System	χ_{12} in J mol^{-1}	$\delta(H^E)$ in J mol^{-1}
Pyridine + *o*-xylene	22.5	57.5
2-Picoline + *o*-xylene	12.1	38.0
3-Picoline + *o*-xylene	9.5	14.6
2,4-Lutidine + *o*-xylene	4.3	9.0
2,6-Lutidine + *o*-xylene	4.2	8.0
2,4,6-Collidine + *o*-xylene	1.0	5.4

The experimental values of the excess heats of mixing and those computed by PFP theory are presented graphically in Fig. 2. We obtained a good qualitative agreement between the experimental and calculated values of the excess heats of mixing, although an observed slight asymmetry in the experimental H^E curves is not predicted by the PFP model, as only one adjustable parameter is fitted to the equimolar H^E value. This asymmetry is probably due to self-association of pyridine bases, a very complicated problem in itself.

An attempt to describe the H^E experimental data by the extended real associated solution (ERAS) model [15] did not give reasonable results. In the ERAS model, excess enthalpy is described as the sum of two contributions. The first arises from self-association of pyridine bases, and is evaluated according to the Kretschmer–Wiebe model [16].

The second is given by the equation of state according to the Flory theory [2–6], and describes the non-specific interactions in solution.

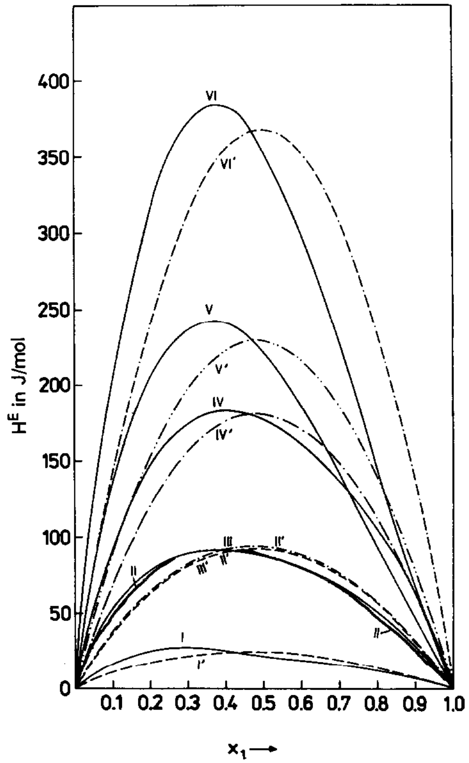

Fig. 2. Excess heats of mixing for pyridine bases(1) + *o*-xylene at 298.15 K: —, experimental data; — — —, values from PFP theory for: I, 2,4,6-collidine + *o*-xylene; II, 2,4-lutidine + *o*-xylene; III, 2,6-lutidine + *o*-xylene; IV, 3-picoline + *o*-xylene; V, 2-picoline + *o*-xylene, VI, pyridine + *o*-xylene.

In our opinion, the self-association of pyridine bases is due to strong non-specific interactions of n–Π and Π–Π type. One confirmation of this concept is the small value of the $H^{\mathrm{E}}_{\mathrm{chem}}$ contribution to the total H^{E} values for mixtures of picolines with normal alkanes [17]. This agrees with the theory suggested by Woycicki and Sodowska [18] for the molecular interactions in solutions formed by pyridines.

The problem of the molecular interactions in the pure pyridine bases will be discussed in detail in a separate paper.

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