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Excess molar enthalpies of mixing of benzene with pyridine bases

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Abstract

The excess molar enthalpies of benzene + pyridine or +*o*-methylpyridine, +*m*-methylpyridine, +*p*-methylpyridine, +2,4-dimethylpyridine, or +2,6-dimethylpyridine at 298.15 K were measured. The results for the benzene + pyridine base mixtures did not correlate with the pK_a or the dipole moments of the pyridine bases. We observe different activities of the methyl group depending on its position in the molecule, and different excess enthalpies resulting from compensations of all the effects.

INTRODUCTION

This paper records some of our measurements of excess molar enthalpies H_m^E of benzene, or one of its methyl homologues, with pyridine, or one of its methyl homologues.

Different investigators have reported H_m^E values for benzene + pyridine [1–7] but some of the results are not in agreement with each other, or with our own recent measurements. In this work, we report H_m^E values for mixtures of high-purity benzene and pyridine bases using a calorimeter in which humidification of the samples is practically impossible.

EXPERIMENTAL

The calorimeter used was similar to that described in ref. 8. The benzene (thiophene-free purum, POCH) used in the present paper was purified in accordance with ref. 9. The final purity as determined by gas chromatography was better than 99.9%. The pyridine bases (purum, POCH)

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were purified in accordance with ref. 9. The final purity, as determined by GC was better than 99.9%.

RESULTS AND DISCUSSION

The experimental values of the molar excess enthalpies of mixing $H^{\mathrm{e}}_{\mathrm{m}}$ are given in Table 1. The results were fitted to an expression of the form

$$H^{\mathrm{E}}_{\mathrm{m}}/(\mathrm{J\ mol^{-1}}) = x_2(1-x_2)\sum_{i=1}^{3} C_i(i-2x_2)^{i-1} \tag{1}$$

TABLE 1

Experimental excess heats of mixing $H^{\mathrm{E}}_{\mathrm{m}}$ at 298.15 K

Mole fraction of pyridine base x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ in J $\mathrm{mol^{-1}}$	Mole fraction of pyridine base x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ in J $\mathrm{mol^{-1}}$	Mole fraction of pyridine base x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ in J $\mathrm{mol^{-1}}$
$x_2C_6H_6 + x_1C_6H_5N$					
0.0675	5.2	0.3179	10.0	0.6280	6.8
0.1264	7.9	0.3369	9.9	0.7576	5.7
0.1899	9.6	0.4023	9.2	0.8214	5.0
0.2035	9.8	0.4958	8.1	0.9435	2.3
0.3168	10.1	0.5404	7.9		
$x_2C_6H_6 + x_1o\text{-}CH_3C_5H_4N$					
0.1110	14.2	0.5004	39.0	0.8371	24.5
0.1949	22.8	0.6052	38.7	0.9155	14.5
0.3030	31.2	0.6052	38.7	0.9157	15.0
0.4031	36.4	0.6967	35.6		
0.5004	39.0	0.7955	28.7		
$x_2C_6H_6 + x_1m\text{-}CH_3C_5H_4N$					
0.1107	4.1	0.3954	8.4	0.7800	13.9
0.1993	5.8	0.5126	10.6	0.8840	10.7
0.2970	7.0	0.6923	13.9	0.9408	6.6
$x_2C_6H_6 + x_1p\text{-}CH_3C_5H_4N$					
0.0581	5.6	0.3960	16.6	0.7678	20.3
0.1107	9.2	0.4831	18.0	0.8841	14.9
0.2248	13.5	0.5747	19.6	0.9408	9.1
0.2985	15.1	0.6929	20.9		
$x_2C_6H_6 + x_1\text{2,4-}CH_3C_5H_3N$					
0.0495	19.1	0.3877	79.6	0.8121	51.4
0.1013	35.6	0.4980	81.4	0.8792	36.8
0.1957	57.9	0.6138	76.6	0.9412	19.7
0.3013	73.1	0.6902	69.7		
$x_2C_6H_6 + x_1\text{2,6-}CH_3C_5H_3N$					
0.0476	18.5	0.4124	75.1	0.8103	52.8
0.0986	34.5	0.5178	76.0	0.8836	37.6
0.1925	55.2	0.6106	73.2	0.9406	21.6
0.2978	68.5	0.7280	64.2		

TABLE 2

Parameters for eqn. (1) and standard deviation $\delta(H^{E}_{m})$

Mixture: benzene+	C_1	C_2	C_3	$\delta(H^{E}_{m})$
C_6H_5N	32	−23	40	0.98
o-$CH_3C_5H_4N$	156	26	14	2.47
m-$CH_3C_5H_4N$	42	41	53	1.43
p-$CH_3C_5H_4N$	73	34	77	1.23
2,4-$CH_3C_5H_3N$	326	26	71	1.79
2,6-$CH_3C_5H_3N$	305	−10	118	2.69

where benzene is component 2. The smoothing coefficients C_i for benzene + pyridine bases determined from experimental results are presented in Table 2, together with the standard deviations $\delta(H^{E}_{m})$. In our work, all values of H^{E}_{m} for the binary mixtures of benzene with pyridine bases are positive.

The binary systems pyridine base + benzene, especially pyridine + benzene, have been investigated by some authors [1–8], but the results are different, even as to the sign of the H^{E} function.

In the works of Amaya [1], Wóycicki and Sadowska [2], Murakami et al. [3] and Travers [4], the curve of the $H^{c}_{m} = f(x)$ plot is S-shaped or negative. Wóycicki [8] then repeated his measurements six years later, and got positive values; the investigations carried by Garrett et al. [6] confirmed these results. Both Wóycicki [8] and Garrett et al. [6] claim that the S-shaped curve of $H^{E} = f(x)$ could have been caused by an impurity in the materials used and to the presence of water, or in the case of Wóycicki [8], by using a non-humidity-proof calorimeter. Pyridine bases are particularly hygroscopic substances.

For the o-methylpyridine + benzene system, our experimental results are similar to those published by Murakami et al. [3] and Garrett et al. [6].

The H^{E}_{m} values for m-methylpyridine + benzene published in the work of Murakami et al. [3] and Garrett et al. [6] give an S-shaped curve: this S-shape was not confirmed by our measurements.

The H^{E}_{m} values for p-methylpyridine + benzene published by Murakami et al. [3] and Diez et al. [7] give an S-shaped curve, which we were unable to confirm in our measurements.

No excess enthalpies are available in the literature for the 2,4-dimethylpyridine + benzene and for the 2,6-dimethylpyridine + benzene systems.

In our work, we used high purity, dry materials and employed a calorimeter with a separate dosage system [8].

We have compared the experimental H^{E}_{m} data for the investigated systems with the results calculated by applying the Prigogine–Flory–Patterson theory [10–12]. The expression for H_m^E from the Prigogine–Flory–Patterson theory was used in the form

$$H_m^E = (v_1^* x_1 + v_2^* x_2)(\phi_1 P_1^* / \tilde{v}_1 + \phi_2 P_2^* / \tilde{v}_2 - P_M^* / v_M^*) \tag{2}$$

where

$$P_M^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 \chi_{12} \tag{3}$$

$$\theta_2 = x_2 v_2^* s_2 (x_1 v_1^* s_1 + x_2 v_2^* s_2)^{-1} \tag{4}$$

$$\phi_1 = 1 - \phi_2 \times v_1^* x_1 (v_1^* x_1 + v_1^* x_2)^{-1} \tag{5}$$

In this equation, s is the molecular surface volume ratio for the components, ϕ_1 and ϕ_2 are the hard-core volume fractions of components 1 and 2, P_1^* and P_2^* are characteristic pressures of components 1 and 2, and P_M^* is the characteristic pressure and v_M^* the characteristic volume for the mixture. The reduced volume $\tilde{v}_M$ of the mixture can be calculated from the reduced equation of state

$$\tilde{p}\tilde{v}/\tilde{T} = v^{1/3}/(v^{-1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{6}$$

The interaction parameter χ_{12} was computed from experimental values of excess enthalpies for $x_1 = x_2 = 0.5$, for equimolar concentrations.

The parameter s was computed using the group contribution method [13]. Using eqn. (2) and data for pure components from Table 3, and the χ_{12} values in Table 4, values computed using the Prigogine–Flory–Patterson theory were compared with the experimental data in Fig. 1.

The P–F–P theory used in our work expresses correctly the concentration dependence of the excess heats of mixing and its change with the size of the pyridine base molecule, and indicates which kind of intermolecular interaction is predominant in solutions of benzene with pyridine bases.

TABLE 3

Parameter for pure components at 298.15 K

Component	d in g cm^{-3}	P^* in J cm^{-3}	$\alpha \times 10^4$ in K^{-1}	s
C_6H_6	0.8738 [14]	628.0 [14]	12.23 [14]	1.00 [15]
C_5H_5N	0.9782 [16]	656.4 [16]	9.92 [16]	1.21 [15]
o-$CH_3C_5H_4N$	0.93948 [14]	617.7 [14]	10.02 [14]	1.09 [15]
m-$CH_3C_5H_4N$	0.95268 [17]	629.6 [14]	9.72 [14]	1.09 [14]
p-$CH_3C_5H_4N$	0.95065 [17]	642.5 [14]	9.68 [14]	1.09 [14]
2,4-$CH_3C_5H_3N$	0.92564 [17]	696.0 [14]	9.54 [15]	0.97 [15]
2,6-$CH_3C_5H_3N$	0.9178 [14]	582.0 [14]	10.02 [14]	0.97 [15]

Key: d, density; P^*, characteristic pressure; α, expansion coefficient; s, molecular surface volume ratio.

TABLE 4

Values of the interaction parameter χ_{12} for the mixtures

Mixture C_6H_6+	χ_{12}	Mixture C_6H_6+	χ_{12}
C_6H_5N	1.254	p-$CH_3C_5H_4N$	1.841
o-$CH_3C_5H_4N$	2.657	2,4-$CH_3C_5H_3N$	4.635
m-$CH_3C_5H_4N$	1.384	2,6-$CH_3C_5H_3N$	4.241

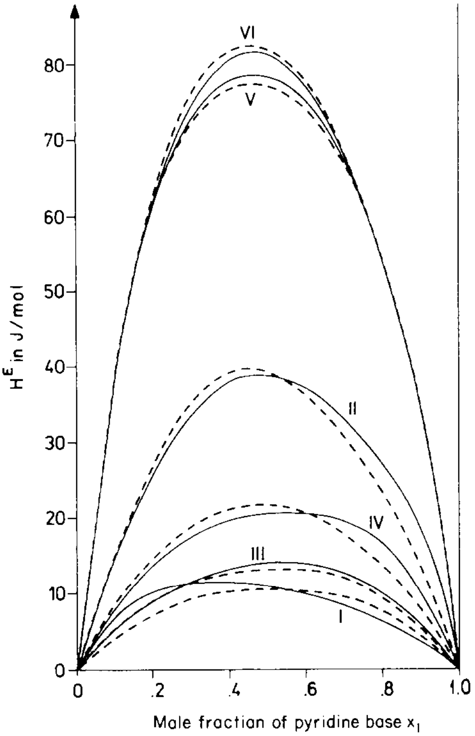

Fig. 1. Excess molar heats of mixing of benzene + pyridine base mixtures at 298.15 K: —, experimental values; ---, values from P–F–P theory: I, $C_6H_6 + C_6H_5N$; II, C_6H_6 + o-$CH_3C_5H_4N$; III, C_6H_6 + m-$CH_3C_5H_4N$; IV, C_6H_6 + p-$CH_3C_5H_4N$; V, C_6H_6 + 2,4-$CH_3C_5H_3N$; VI, C_6H_6 + 2,6-$CH_3C_5H_3N$.

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