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Enthalpy of mixing for binaries: *m*-xylene + pyridine bases. Experimental data at 298.15 K and theoretical description

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Abstract

Enthalpies of mixing for the binaries *m*-xylene + pyridine and its methyl derivatives have been measured at 298.15 K. The pyridine bases used for the measurements were pyridine, 2-, 3-, and 4-methylpyridine, 2,4-, and 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine.

The Prigogine–Flory–Patterson (PFP) model has been applied to describe the experimental results.

Keywords: Enthalpy of mixing; Prigogine–Flory–Patterson (PFP) model; Pyridine bases; *m*-Xylene

1. Introduction

This paper presents our new results in the investigation of the effect of the number and position of methyl groups in benzene and the pyridine ring on the excess molar enthalpies H_m^E for pyridine bases and hydrocarbons.

Now we present experimental H_m^E data for *m*-xylene + pyridine, or + 2-, + 3-, + 4-methylpyridine, + 2,4-, + 2,6-dimethylpyridine, + 2,4,6-trimethylpyridine at 298.15 K.

The experimental data are compared with values calculated using the Prigogine–Flory–Patterson model.

So far we have reported enthalpy of mixing results for benzene [1], toluene [2] and *o*-xylene [3] with pyridine bases.

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2. Experimental

The pyridine bases used in this work were the same as those used previously [3]. Their purity (checked by GLC) was better than 99.9%.

The m-xylene (POCH, Gliwice, Poland) was dried over molecular sieves and then purified twice by fractional distillation (25PT). Its purity determined by GLC was better than 99.96%.

Water contents in all reagents were checked by GLC using a catharometer detector and were smaller than 0.01%.

The enthalpies of mixing were measured using the UNIPAN 600 flow microcalorimeter (Poland). The method of measurement and the working parameters of the apparatus have been described in a previous paper [4].

3. Results and discussion

The experimental values of the enthalpy of mixing for m-xylene with pyridine bases at 298.15 K are listed in Table 1. The Redlich–Kister polynomial was fitted to the H^E_m data

$$H^E_m/(\mathrm{J\,mol^{-1}}) = x_1 x_2 \Sigma C_i (2x - i)^{i-1} \tag{1}$$

Table 1

Experimental values of H^E_m for pyridine bases with m-xylene at 298.15 K: x_1, mole fraction of pyridine base; C_i, coefficients of Redlich–Kister polynomial; δ, standard deviation

x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$
		Pyridine + m-xylene			
0.1169	250.4	0.4710	476.9	0.7134	354.0
0.1743	333.6	0.5167	466.7	0.8363	235.0
0.2315	393.3	0.5627	445.5	0.7766	303.6
0.2884	444.3	0.6119	422.8	0.9001	157.3
0.3611	466.4	0.6622	394.0		
	$C_1 = 1875.5$	$C_2 = -462.5$	$C_3 = 353.6$	$\delta = 3.1$	
		2-Methylpyridine + m-xylene			
0.1180	129.1	0.3187	229.9	0.6169	203.8
0.1674	162.6	0.3575	226.8	0.6634	188.5
0.2158	193.6	0.3976	231.8	0.7284	164.4
0.2158	200.4	0.4569	235.5	0.7851	136.9
0.2610	207.1	0.5000	231.8	0.8355	108.4
0.3187	219.5	0.5591	221.7	0.8878	77.9
	$C_1 = 917.3$	$C_2 = -281.8$	$C_3 = 169.3$	$\delta = 3.9$	
		3-Methylpyridine + m-xylene			
0.1684	156.2	0.3225	219.6	0.7309	164.0
0.1684	163.1	0.3796	227.0	0.7935	130.5
0.2177	183.0	0.4600	227.6	0.8423	102.3
0.2782	212.2	0.5189	220.9	0.8890	75.1

Table 1 (*Continued*)

x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$
0.2782	211.5	0.6244	203.7		
0.3225	217.2	0.6858	181.8		
	$C_1 = 904.3$	$C_2 = -249.4$	$C_3 = 132.3$	$\delta = 3.2$	
		4-Methylpyridine + *m*-xylene			
0.1190	128.8	0.3218	224.9	0.6191	202.2
0.2177	192.7	0.3801	229.0	0.6759	185.3
0.1684	168.0	0.4426	228.8	0.7306	162.3
0.2782	211.7	0.4426	232.4	0.7871	137.6
0.2782	214.0	0.5024	226.9	0.8421	107.8
0.3218	219.4	0.5622	216.6	0.8889	82.6
	$C_1 = 903.2$	$C_2 = -263.3$	$C_3 = 220.9$	$\delta = 2.0$	
		2,4-Dimethylpyridine + *m*-xylene			
0.1200	75.1	0.3552	118.9	0.6622	99.4
0.1615	92.8	0.4088	121.3	0.7169	90.5
0.1615	89.8	0.4606	121.3	0.7682	79.6
0.2053	103.7	0.5000	118.3	0.8384	62.5
0.2633	112.3	0.5538	114.0		
0.3015	114.8	0.6077	108.9		
	$C_1 = 470.1$	$C_2 = -144.7$	$C_3 = 209.5$	$\delta = 1.7$	
		2,6-Dimethylpyridine + *m*-xylene			
0.1362	99.0	0.3934	151.5	0.6091	136.2
0.1791	117.0	0.3934	150.7	0.6638	126.1
0.2306	129.8	0.4479	150.9	0.7182	112.1
0.2842	141.0	0.4479	151.0	0.7693	97.1
0.3385	147.6	0.5018	149.4	0.8172	84.1
0.3385	145.3	0.5554	144.1		
	$C_1 = 591.2$	$C_2 = -164.1$	$C_3 = 198.4$	$\delta = 1.9$	
		2,4,6-Trimethylpyridine + *m*-xylene			
0.1753	78.8	0.3794	87.9	0.7813	51.8
0.2269	82.0	0.4303	92.1	0.8894	27.7
0.2765	86.5	0.5156	89.6		
0.3273	88.5	0.6156	74.7		
	$C_1 = 345.3$	$C_2 = -156.6$	$C_3 = 135.8$	$\delta = 3.7$	

where x_1, x_2 are the mole fraction of pyridine base and *m*-xylene, respectively. The smoothing coefficients C_i together with the standard deviations $\delta(H^E_m)$ are given in Table 1. The smoothed experimental curves for all the investigated binaries are presented graphically in Fig. 1.

The values of the enthalpy of mixing for all investigated systems are positive and a little higher than for the systems of benzene, toluene or *o*-xylene + pyridine bases [1–3]. The values of H^E_{max} for the *m*-xylene + pyridine base systems increase in the order: 2,4,6-collidine(92.0) < 2,4-(121.8) < 2,6-lutidine(151.7) < 3-(230.4) ~ 4-(231.5)

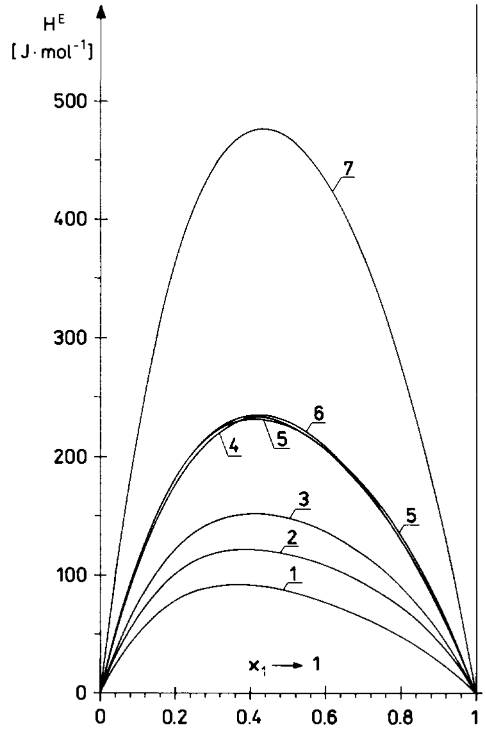

Fig. 1. Smoothed experimental curves H^E_m for *m*-xylene + pyridine base systems at 298.15 K: 1, *m*-xylene + 2,4,6-trimethylpyridine; 2, *m*-xylene + 2,4-dimethylpyridine; 3, *m*-xylene + 2,6-dimethylpyridine; 4, *m*-xylene + 3-methylpyridine; 5, *m*-xylene + 4-methylpyridine; 6, *m*-xylene + 2-methylpyridine; 7, *m*-xylene + pyridine.

< 2-picoline (234.9) < pyridine (476.5 J mol^{-1}). The PFP model [5–10], considering only the contribution of the physical interactions to the excess properties of the mixture, was used to describe experimental H^E data for all the above binaries. The PFP expression for H^E is

$$H^E = (v_1^* x_1 + v_2^* x_2)\left[\frac{\varphi_1 p_1^*}{\tilde{v}_1} + \frac{\varphi_2 p_2^*}{\tilde{v}_2} - \frac{p_M^*}{\tilde{v}_M}\right] \tag{2}$$

with the characteristic pressure of the mixture being

$$p_M^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \Theta_2 \chi_{12} \tag{3}$$

where χ_{12} is the interaction energy parameter, and Θ_2 the surface fraction

$$\Theta_2 = \frac{\varphi_2 s_2}{\varphi_1 s_1 + \varphi_2 s_2} \tag{4}$$

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

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

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

The characteristic and reduced quantities were obtained from Flory formalism as well as estimated on a group contribution basis. The parameters of the pure components at 298.15 K used in these calculations are given in Table 2.

In the PFP model, these H_m^E expression contains only one adjustable parameter χ_{12}. This parameter represents the energy of molecular interaction in solution. The values of the χ_{12} parameter and standard deviations $\delta(H_m^E)$ for the investigated systems are listed in Table 3.

Table 2
Parameters of pure components at 298.15 K

Component	$d/(\mathrm{g\,cm^{-3}})$	$\alpha/(\mathrm{k\,K^{-1}})$	$p^*/(\mathrm{J\,cm^{-3}})$	$s/(\mathrm{Å^{-1}})$
C_5H_5N	0.9782 [a]	0.9920 [a]	656.4 [a]	1.21 [d]
o-$(CH_3)C_5H_4N$	0.93948 [a]	1.0020 [a]	617.7 [a]	1.09 [d]
m-$(CH_3)C_5H_4N$	0.9527 [a]	0.9720 [a]	629.6 [a]	1.09 [d]
p-$(CH_3)C_5H_4N$	0.9506	0.9680	642.5	1.09 [d]
2,4-$(CH_3)_2C_5H_3N$	0.9266 [e]	0.9544 [d]	596.0 [d]	0.97 [d]
2,6-$(CH_3)_2C_5H_3N$	0.9178 [a]	1.0020 [a]	582.0 [a]	0.97 [d]
2,4,6-$(CH_3)_3C_5H_2N$	0.91029 [c]	1.0094 [f]	606.6 [i]	0.85 [g]
m-$(CH_3)_2C_6H_4$	0.8599 [b]	0.9880 [h]	555.6 [i]	0.76 [g]

Key: d, density; p^*, characteristic pressure; α, expansion coefficient; s, molecular surface-to-volume ratio. [a] Ref. [11]. [b] Ref. [12]. [c] Ref. [13]. [d] Ref. [14]. [e] Ref. [15]. [f] Estimated from the data for other pyridine bases [11] on a group contribution basis. [g] Authors own unpublished data. [h] Private communication (A. Zywocinski). [i] Obtained from the Flory formalism.

Table 3
Values of χ_{12} parameters in calculations of H_m^E by PFP model and standard deviations $\delta(H_m^E)$

Binary mixture	$\chi_{12}/(\mathrm{J\,mol^{-1}})$	$\delta(H_m^E)/(\mathrm{J\,mol^{-1}})$
m-$(CH_3)_2C_6H_4$		
+		
C_5H_5N	28.9	29.5
o-$(CH_3)C_5H_4N$	12.3	14.2
m-$(CH_3)C_5H_4N$	12.4	14.7
p-$(CH_3)C_5H_4N$	12.4	14.2
2,4-$(CH_3)_2C_5H_3N$	5.7	8.8
2,6-$(CH_3)_2C_5H_3N$	7.0	8.2
2,4,6-$(CH_3)_3C_5H_2N$	3.7	6.4

The results of calculations of H_m^E by the PFP model and comparison with experimental values are presented graphically in Figs. 2 and 3 for the chosen systems. We received a good qualitative agreement between the experimental and computed values of the enthalpy of mixing. However we observed that the slight asymmetry of the experimental H_m^E curves is not predicted by the PFP model used. This is because the adjustable parameter is fitted to the equimolar H_m^E value. In our opinion this asymmetry is due to self-association of the pyridine bases, a very complicated problem in itself.

As shown above, the H_{max}^E values for *m*-xylene + pyridine base systems change (increase) significantly when the number of methyl groups in the pyridine base molecule decreases. The position of the $-CH_3$ groups in the pyridine base molecule also has an influence on the free electron pair of the nitrogen atom because they represent a steric hindrance to the nitrogen atom.

The problem of intermolecular interactions in solutions of pyridine bases and hydrocarbons was discussed in detail earlier [16]. The recent experimental results confirm that the presence of methyl groups in the pyridine molecule results in the contribution of n–Π interactions decreasing in the order given above, whereas the energy of the Π–Π interactions predominates.

An attempt to describe the H_m^E experimental data by the Extended Real Associated Solution (ERAS) model [17], also taking into account the specific interaction contribution to the excess properties of the mixture, did not give reasonable results. It confirmed

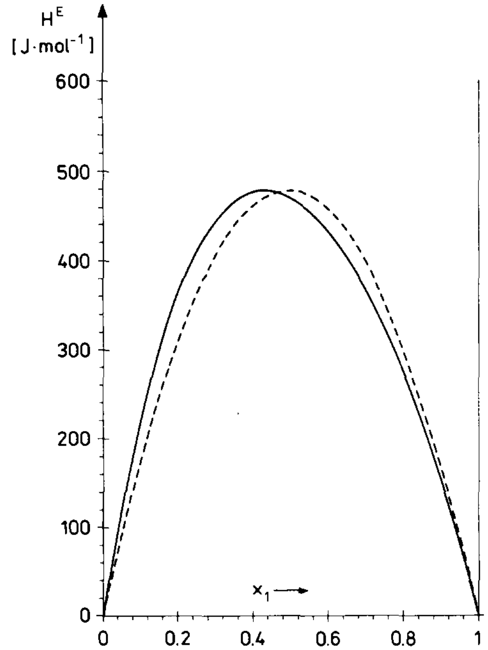

Fig. 2. Enthalpy of mixing for the *m*-xylene + pyridine system at 298.15 K: —, smoothed experimental results: – – –, values from PFP model.

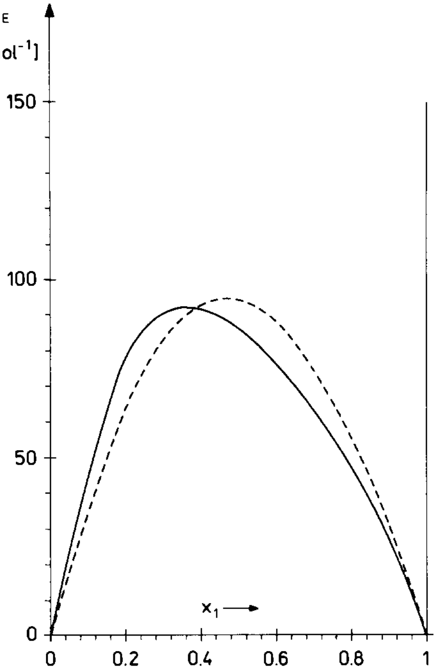

Fig. 3. Enthalpy of mixing for the *m*-xylene + 2,4,6-trimethylpyridine system at 298.15 K: —, smoothed experimental results; - - -, values from PFP model.

our suggestion that the self-association of pyridine bases is due to n–Π and Π–Π interactions.

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