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Excess Enthalpies for 4-Methyltoluene + Pyridine, +2-Methylpyridine, +3-Methylpyridine, +4-Methylpyridine, +2,4-Dimethylpyridine, +2,6-Dimethylpyridine, +2,4,6-Trimethylpyridine at 298.15 K

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The excess enthalpies for 4-methyltoluene + pyridine bases were measured at 298.15 K. The pyridine bases which have been used were as follows: pyridine, 2-methlpyridine, 3-methylpyridine, 4-methylpyridine, 2,4-dimethylpyridine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine.

Introduction

This paper is a continuation of the investigations of the effect of the number and position of methyl groups on the benzene ring and on the pyridine ring on the excess molar enthalpies for aromatic hydrocarbon and pyridine base mixtures.

We have reported the results of excess enthalpies for benzene, toluene, *o*-xylene, and *m*-xylene (Wilczura et al., 1996) with pyridine bases. In this paper, we present results of excess enthalpies for *p*-xylene at 298.15 K.

An attempt to describe the excess enthalpy experimental data by the extended real associated solution (ERAS) model (Heintz et al., 1982) 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 Kretchmer−Wiebe model (Kretchmer et al., 1954). The second is given by the equation of state according to the Flory theory (Flory et al., 1964) and describes the nonspecific interaction in solution.

The self-association of pyridine bases is due to strong nonspecific interactions of the n−π type. One confirmation of this concept is the small value of $H^{E}_{\rm chem}$ contribution to the total excess enthalpies for mixtures of picolines with normal alkanes (Wilczura et al., 1995).

The Prigogine−Flory−Patterson (PFP) theory used in our work expresses correctly the concentration dependence of the excess enthalpies and its change with the size of the pyridine base molecule and indicates which kind of intermolecular interaction is predominant in solutions of *p*-xylene with pyridine bases.

Experimental Section

p-Xylene and pyridine bases (POCH, Gliwice, Poland) were purified in accordance with Weissberger (1958). The final purity of *o*-xylene, determined by glc, was better than 99.95 mol %. The pyridine bases were better than 99.9 mol % pure. Water contents in all reagents were checked by glc with a katarometer detector and were less than 0.01 mol %.

The flow microcalorimeter UNIPAN 600 was used. The flow microcalorimetric cell consists of a capillary within which liquids A and B mix, whereupon this mixture flows along a fairly long way, thus permitting complete mixing. The vessels for reagents and their mixtures are isolated from the atmosphere with mercury valves. The dosage system includes an infusion pump. The reagents are placed in vessels A and B, outgassed, and led through a system of capillaries and flow regulators to the pump. After stabilization of the desired measuring temperature, the dosage of reagents is started. The calorimetric signal is recorded till stabilization of the stationary state. Molar flows of reagents were determined from a standard curve presenting the dosage rate of reagents ($\mathrm{cm^3 \cdot s^{-1}}$) as a function of pump setting.

Owing to application of a control loop of the heat equilibrator, the temperature of liquids flowing into the calorimeter vessel exactly equals the temperature of this vessel, with respect to the liquid flow rate, thermal capacity of liquids, and thermal effect of mixing. Moreover, an introduction of a voltmeter to the measuring system improves the precision of determination of the calorimetric signal, as compared with graphic recording of the signal height. The calibration constant *K* was determined by the electric method. The excess heat of mixing was calculated from the equation

$$H^{\rm E}/{\rm J{\cdot}mol^{-1}} = \frac{q}{\sum n} \qquad (1)$$

where $q = VK$ (Watt), V is the voltage corresponding to the calorimetric signal in the stationary state, K is the calibration constant, and $\sum n = n_{\rm A} + n_{\rm B}$ ($\mathrm{mol{\cdot}s^{-1}}$), the molar flow of reagents A and B.

With application of the calibration constants, the excess heat of mixing was determined for the benzene−cyclohexane system at 298.15 K. Our results are consistent with the literature data (Elliott et al., 1976). The technical details of the measurements have been described earlier (Wilczura et al., 1986). The precision of the excess enthalpy determination is estimated to be in the range ±2 $\mathrm{J{\cdot}mol^{-1}}$.

Results and Discussion

The excess enthalpies of 4-methyltoluene + pyridine, +2-methylpyridine, +3-methylpyridine, +4-methylpyridine, +2,4-dimethylpyridine, +2,6-dimethylpyridine, and +2,4,6-trimethylpyridine at 298.15 K are given in Table 1. The results were fitted to the Redlich−Kister equation:

$$H^{\rm E} = x_2(1 - x_2)\sum_{i=1}^{3} A_i(1 - 2x_2)^{i-1} \qquad (2)$$

where x_2 is the mole fraction of 4-methyltoluene. The coefficients A_i for the mixtures, together with the standard

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Table 1. Excess H^E at 298.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Pyridine (1) + *p*-Xylene (2)			
0.1111	203.9	0.4982	406.7
0.1657	269.2	0.4982	407.7
0.2201	325.9	0.5469	394.8
0.2742	371.4	0.6126	367.4
0.3187	384.9	0.6630	340.9
0.3615	399.9	0.7143	304.5
0.4063	407.8	0.7855	245.6
0.4515	411.2	0.8889	144.9
2-Methylpyridine (1) + *p*-Xylene (2)			
0.1121	114.3	0.4839	208.5
0.1591	145.8	0.5458	198.5
0.2166	175.2	0.6176	182.6
0.2763	192.1	0.6538	173.2
0.3373	201.7	0.7125	153.5
0.3986	205.7	0.7725	128.9
0.3986	206.5	0.8315	102.6
0.4410	214.1	0.8878	71.7
3-Methylpyridine (1) + *p*-Xylene (2)			
0.1194	134.9	0.5041	214.2
0.1690	167.7	0.5491	207.4
0.2185	193.1	0.5963	200.6
0.2185	190.6	0.6208	195.5
0.2789	206.1	0.6771	178.5
0.3412	217.4	0.7318	160.3
0.3826	218.6	0.7817	140.9
0.4377	216.7	0.8854	81.9
4-Methylpyridine (1) + *p*-Xylene (2)			
0.0951	104.1	0.5340	220.1
0.1488	141.3	0.5876	210.2
0.2068	176.7	0.6311	200.3
0.2644	195.8	0.6859	181.1
0.2644	196.3	0.7393	159.8
4-Methylpyridine (1) + *p*-Xylene (2)			
0.3225	215.8	0.7881	134.6
0.3601	221.1	0.8382	110.8
2,4-Dimethylpyridine (1) + *p*-Xylene (2)			
0.1141	103.6	0.4617	159.7
0.2175	143.0	0.4617	161.2
0.2175	147.0	0.5140	157.1
0.3202	160.2	0.5659	146.4
0.3202	160.9	0.6797	123.0
0.4097	160.8	0.7855	93.7
0.4097	164.1	0.8890	55.7
2,6-Dimethylpyridine (1) + *p*-Xylene (2)			
0.1204	59.2	0.4749	122.4
0.1631	79.5	0.5271	118.5
0.2081	94.2	0.5447	120.7
0.2649	110.4	0.5997	112.7
0.2649	110.2	0.6555	106.3
0.3212	117.5	0.6555	104.1
0.3593	120.1	0.7118	87.0
0.4171	121.3	0.7703	74.6
0.4171	124.1	0.8183	61.2
2,4,6-Trimethylpyridine (1) + *p*-Xylene (2)			
0.1046	−9.6	0.5105	−22.1
0.1046	−8.4	0.6163	−21.4
0.2005	−12.9	0.7245	−18.7
0.3022	−15.6	0.7245	−19.2
0.4331	−19.0	0.8355	−16.9
0.4331	−21.5	0.8949	−11.9
0.5105	−20.9		

deviations $\delta(H^E)$, are listed in Table 2. The smoothed experimental curves for systems are presented graphically in Figure 1.

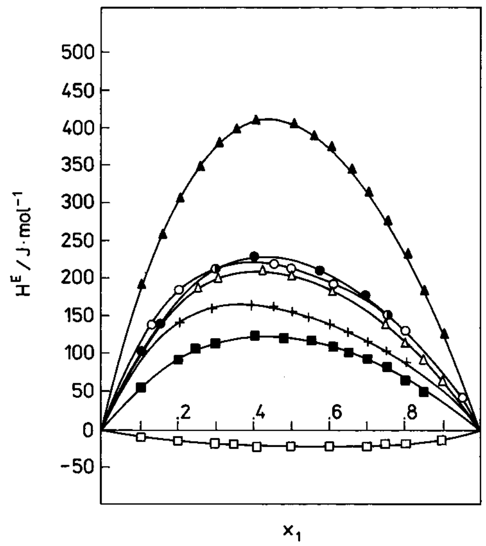

Figure 1. Smoothed experimental curves H^E for *p*-xylene (2) + pyridine bases (1) at 298.15 K: (▲) *p*-xylene + pyridine; (△) p-xylene + 2-methylpyridine; (○) *p*-xylene + 3-methylpyridine; (●) *p*-xylene + 4-methylpyridine; (+) *p*-xylene + 2,4- dimethylpyridine; (■) *p*-xylene + 2,6-dimethylpyridine; (□) *p*-xylene + 2,4,6-trimethylpyridine.

Table 2. Parameters of Redlich−Kister Equation 2 Obtained by Least Squares Together with Standard Deviation $\delta(H^E)$

system	A_1	A_2	A_3	$\delta(H^E)$/ J·mol^{-1}
pyridine + *p*-xylene	1622.1	−379.9	205.7	2.6
2-methylpyridine + *p*-xylene	817.5	−349.0	192.5	2.7
3-methylpyridine + *p*-xylene	857.6	−257.2	352.0	3.0
4-methylpyridine + *p*-xylene	888.9	−204.2	163.4	2.5
2,4-dimethylpyridine + *p*-xylene	621.7	−258.2	264.6	2.5
2,6-dimethylpyridine + *p*-xylene	490.8	−126.1	10.1	2.3
2,4,6-dimethylpyridine + *p*-xylene	−83.1	−21.4	−37.6	1.1

The values of excess enthalpies for all investigated systems are positive except for 4-methyltoluene + 2,4,6-trimethylpyridine. The maximum values of excess enthalpies diminish in the order pyridine (410) > 4-methylpyridine (225) > 3-methylpyridine (220) > 2-methylpyridine (210) > 2,4-dimethylpyridine (165) > 2,6-dimethylpyridine (125) > 2,4,6-trimethylpyridine (−21). The curves are asymmetrical, and their maximum values are shifted toward a lower concentrations of pyridine bases ($x_1 = 0.35-0.45$). For 4-methyltoluene + 2,4,6-trimethylpyridine the minimum value of excess enthalpies is shifted to $x_1 \cong 0.6$.

A certain asymmetry of the experimental curves is due to self-association of pyridine bases. The presence of one methyl group on the pyridine changes significantly the value of H^E for pyridine + *p*-xylene. For example, the differences between H^E_{max} for pyridine + *p*-xylene and one methyl derivative pyridine + *p*-xylene is ≈180 J·mol^{-1} whereas the differences for 2-, 3-, and 4-methylpyridine + *p*-xylene mixtures between their H^E_{max} values are 10 J·mol^{-1}. Introduction of a second methyl group onto pyridine diminishes the H^E value to 50 J·mol $^{-1}$ for 2,4-dimethylpyridine + *p*-xylene and about 85 J·mol $^{-1}$ for 2,6-dimethylpyridine + *p*-xylene when compared to the one methyl derivatives of pyridine. The H^E values for 2,4,6-trimethylpyridine + *p*-xylene are smallest and negative. Our information about the exothermic effect of mixing for 2,4,6-trimethylpyridine + toluene is given in the literature (Wilczura et al., 1995). Values of H^E_{min} for 2,4,6-trimethylpyridine with toluene and *p*-xylene are comparable.

The problem of the molecular interactions in the pure pyridine bases will be discussed in detail in a separate paper (Wilczura et al., 1995). A closer approach to the solution of the above described problems of the molecular interactions in pyridine bases will be achieved when studies of the excess enthalpies of mixing in the binary systems formed by pyridine bases with mesitylene are completed.

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