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Note

Application of the Prigogine–Flory–Patterson and extended real associated solution method to molar excess heat of mixing of β-picoline + *n*-alkane mixtures

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Abstract

The binary molar excess heats of mixing of β-picoline + *n*-alkane mixtures were measured at 25°C. A model of associated mixtures proposed by Prigonine, Flory and Patterson and an extended real associated method, applied recently to some pyridine base + *n*-alkane systems, is used to describe the excess molar heat of mixing of binary systems formed by mixing β-picoline with C_6–C_{10} *n*-alkanes. The Prigogine–Flory–Patterson model successfully describes the changes in excess heat of mixing for all the investigated systems over the whole concentration range.

INTRODUCTION

In our previous work we presented experimental values of the excess of enthalpy H^E for pyridine + *n*-alkanes [1,2] and for α-picoline [3] (or γ-picoline [4]) + C_6–C_{10} *n*-alkanes. This work contains the values of H^E for binary mixtures formed by β-picoline + C_6–C_{10} *n*-alkanes.

EXPERIMENTAL

β-Picoline (purum, Fluka AG) *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane (purum, Reachim) were purified in accordance with ref. 1. The final purity, as determined by gas–liquid chromatography, was better than 99.95% for *n*-alkanes and 99.9% for β-picoline. The excess heat of mixing was measured using a UNIPAN type 600 flow microcalorimeter [5]. The method has also been described in ref. 5. The precision of the H_m^E determination is estimated to be about ±2 J mol^{-1}.

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TABLE 1

Excess enthalpy H^E for binary mixtures of β-picoline with C_6–C_{10} n-alkanes at 298.15 K

Mole fraction of β-picoline	H^E (J mol^{-1})	Mole fraction of β-picoline	H^E (J mol^{-1})
$C_6H_7N + C_6H_{14}$		$C_6H_7N + C_7H_{16}$	
0.0491	208.4	0.0518	241.9
0.1039	416.7	0.1050	467.9
0.1478	559.7	0.1493	638.2
0.1478	562.6	0.1961	803.6
0.1966	705.2	0.2489	962.7
0.1966	706.0	0.2667	1006.4
0.2439	830.9	0.3148	1120.3
0.2659	871.3	0.3148	1123.0
0.2659	865.3	0.3615	1210.2
0.3176	968.9	0.4061	1275.2
0.3664	1031.3	0.4518	1315.2
0.3664	1044.8	0.4986	1340.1
0.4180	1083.0	0.5177	1347.2
0.4612	1118.4	0.5441	1346.3
0.4612	1113.9	0.5645	1338.0
0.5131	1124.1	0.5876	1329.5
0.5396	1117.4	0.6093	1315.1
0.5903	1101.4	0.6524	1262.9
0.6393	1057.1	0.6524	1269.2
0.6877	986.8	0.6524	1270.9
0.7175	931.8	0.6940	1199.4
0.7487	865.9	0.6940	1201.4
0.7934	755.9	0.7091	1176.0
0.7934	760.2	0.7474	1091.1
0.8377	640.2	0.7834	985.0
0.8806	491.0	0.8448	774.9
0.9237	338.0	0.8806	637.9
0.9467	250.0	0.9095	507.6
		0.9441	330.5
$C_6H_7N + C_8H_{18}$		$C_6H_7N + C_9H_{20}$	
0.0530	274.0	0.0578	320.3
0.1033	501.9	0.1085	550.9
0.1554	709.6	0.1582	746.6
0.1975	867.2	0.2008	929.8
0.2496	1043.0	0.2135	968.7
0.2662	1077.2	0.2679	1144.7
0.3123	1200.5	0.2679	1142.5
0.3123	1200.3	0.3235	1287.5
0.3330	1247.1	0.3324	1307.8
0.3571	1296.1	0.3789	1393.0
0.4260	1387.6	0.4024	1420.9
0.4549	1426.2	0.4484	1479.3
0.5005	1446.7	0.4625	1487.5
0.5441	1444.1	0.4776	1489.9
0.5860	1421.4	0.5233	1503.5

TABLE 1 (continued)

Mole fraction of β-picoline	H^E (J mol^{-1})	Mole fraction of β-picoline	H^E (J mol^{-1})
$C_6H_7N + C_8H_{18}$		$C_6H_7N + C_9H_{20}$	
0.6053	1400.1	0.5667	1496.9
0.6458	1358.7	0.5848	1482.9
0.6859	1280.3	0.5848	1480.7
0.7222	1200.7	0.6265	1443.0
0.7584	1111.9	0.6660	1381.5
0.7934	995.6	0.6869	1340.6
0.8176	916.4	0.7257	1254.2
0.8513	781.1	0.7619	1155.1
0.8775	666.5	0.7969	1036.1
0.8836	630.1	0.8299	916.2
0.9103	513.9	0.8541	816.0
0.9425	335.7	0.8861	668.7
		0.9166	516.0
		0.9465	335.0
$C_6H_7N + C_{10}H_{22}$		$C_6H_7N + C_{10}H_{32}$	
0.0620	355.4	0.6110	1531.9
0.1160	616.2	0.6476	1489.6
0.1640	832.7	0.6660	1455.5
0.2078	992.8	0.6850	1425.2
0.2135	1011.6	0.7216	1342.1
0.2664	1189.2	0.7562	1241.3
0.3244	1341.6	0.7890	1134.4
0.3337	1367.3	0.8205	1022.7
0.3789	1450.9	0.8419	933.1
0.4004	1480.9	0.8652	824.0
0.4571	1542.5	0.8949	665.8
0.5141	1576.2	0.9141	569.8
0.5717	1563.5	0.9188	545.3
0.5717	1565.9	0.9417	405.2

RESULTS AND DISCUSSION

The experimental excess enthalpies of mixing for β-picoline with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane at 25°C are listed in Table 1 and shown graphically in Figs. 1–5.

The Redlich–Kister equation was fitted to the H_m^E data

$$H_m^E(\text{J mol}^{-1}) = x_1 x_2 \sum_{i=1}^{n} A_i (2x - 1)^{i-1} \quad (1)$$

where x_1 is the mole fraction of β-picoline. The smoothing coefficients A_i for β-picoline + C_6–C_{10} *n*-alkanes are presented in Table 2, together with the standard deviations $s(H_m^E)$.

The H_m^E values for the investigated system are positive. In refs. 1–4 and in the present work, the H_m^E values increase with increasing chain length.

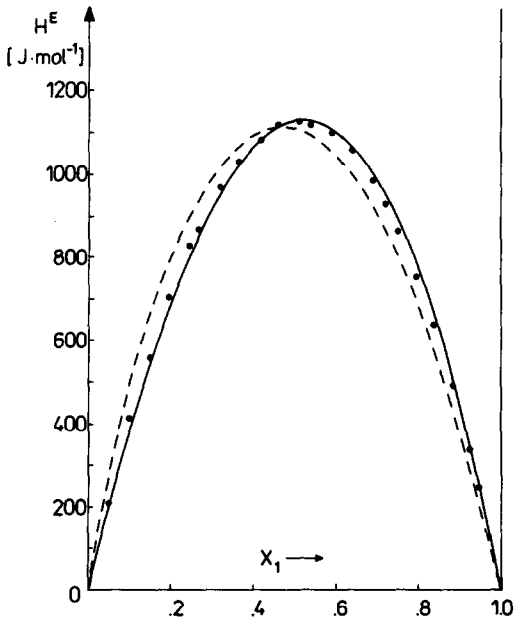

Fig. 1. Excess molar enthalpy H_m^E for binary mixture of β-picoline with n-hexane at 298.15 K (x_1, mole fraction of β-picoline): •, experimental data; ——, calculated from Prigogine–Flory–Patterson theory; — — —, calculated from ERAS method.

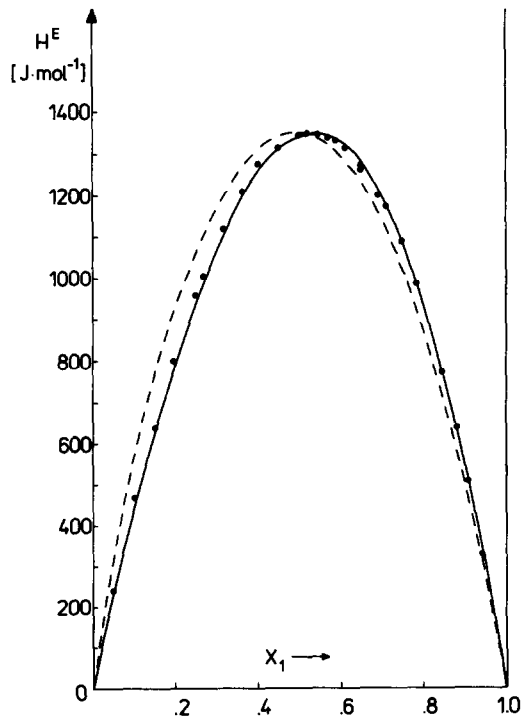

Fig. 2. Excess molar enthalpy H_m^E for binary mixture of β-picoline with n-heptane at 298.15 K. Symbols as for Fig. 1.

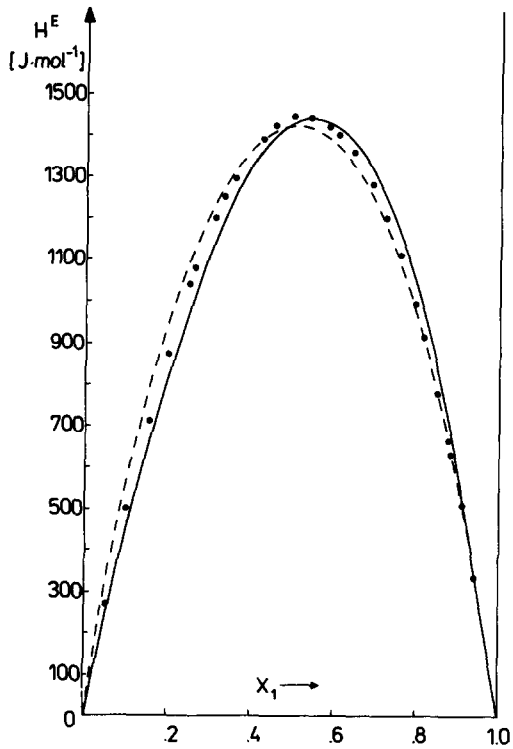

Fig. 3. Excess molar enthalpy H_m^E for binary mixture of β-picoline with n-octane at 298.15 K. Symbols as for Fig. 1.

The experimental H_m^E values have been fitted to the Prigogine–Flory–Patterson theory and by the extended real associated solution (ERAS) method as reported earlier [6–8]. The relationships and notation are the same as in our earlier work [1–4].

TABLE 2

Smoothing coefficients A_i and standard deviations s for β-picoline + C_6–C_{10} n-alkanes at 298.15 K

Mixture	A_1	A_2	A_3	s
β-picoline +				
n-C_6H_{14}	4499.8910	159.9776	164.5968	4.6
n-C_7H_{16}	5374.5970	630.2520	287.8952	4.2
n-C_8H_{18}	5772.7110	505.2360	49.6408	4.4
n-C_9H_{20}	6013.2280	529.2258	273.8045	4.1
n-$C_{10}H_{22}$	6281.6640	677.2212	513.0299	4.3

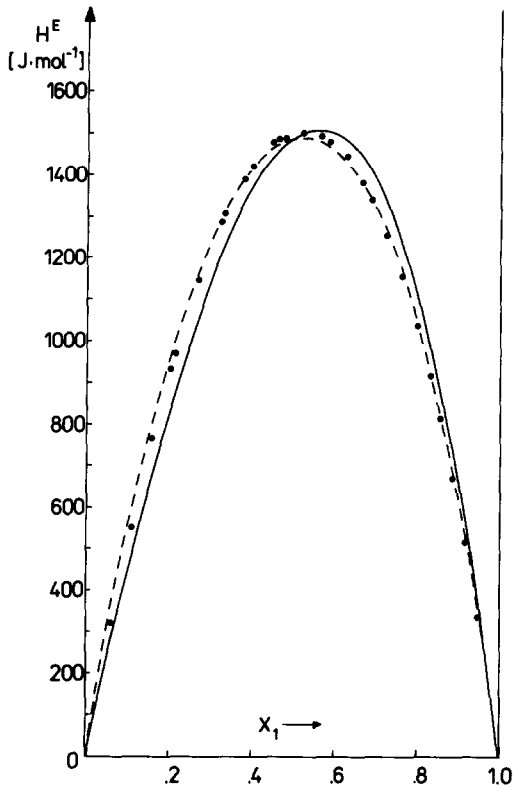

Fig. 4. Excess molar enthalpy H_m^E for binary mixture of β-picoline with n-nonane at 298.15 K. Symbols as for Fig. 1.

The thermodynamic association constant K_t was calculated by the relationship proposed by Buchowski [9]

$$K_t = \frac{P_h}{P_a} - 1 \tag{2}$$

TABLE 3

Parameters for pure components and parameters used in calculations of H^E for β-picoline + C_6–C_{10} n-alkane at 298.15 K by the Prigogine–Flory–Patterson theory and the ERAS model

Component	d (g cm^{-3})	p^* (J cm^{-3})	$\alpha \times 10^3$ (K^{-1})	s (A^{-1})	$\kappa \times 10^3$ (J cm^{-3})	K	h^* (J mol^{-1})	V^* (cm^3 mol^{-1})
β-Picoline	0.95268	629.6	0.972	1.09	0.7100	3.78	−8748	−6.01
n-Hexane	0.6550	423.0	1.391	1.04	1.7039	–	–	–
n-Heptane	0.6793	432.0	1.253	1.02	1.4606	–	–	–
n-Octane	0.6983	439.0	1.165	0.99	1.3024	–	–	–
n-Nonane	0.7139	443.0	1.090	0.97	1.1754	–	–	–
n-Decane	0.7263	448.0	1.050	0.96	1.1096	–	–	–

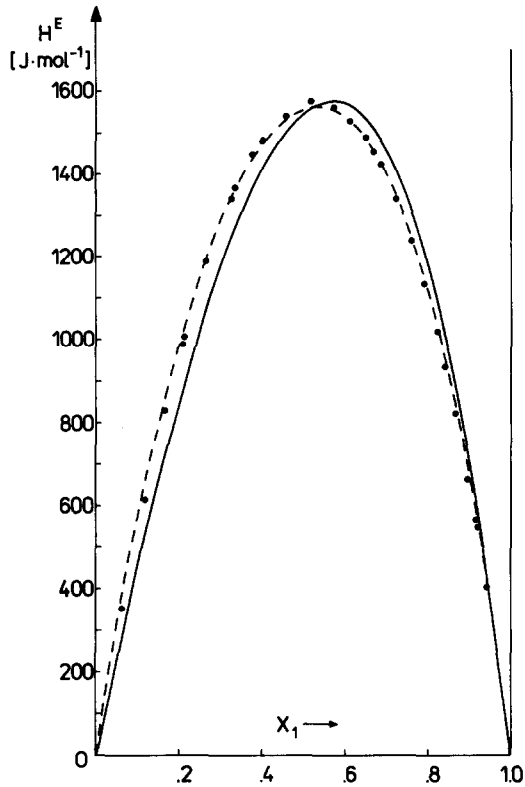

Fig. 5. Excess molar enthalpy H_m^E for binary mixtures of β-picoline with n-decane at 298.15 K. Symbols as for Fig. 1.

where P_h is the vapour pressure for a homomorph toluene [10], and P_a is the vapour pressure for β-picoline [11,12]. The enthalpy of self-association was calculated from the van't Hoff equation in the form

$$-h_{ass} = R\left[\ln\left(\frac{K_{t298.15}}{K_{t353.15}}\right)\right]\left(\frac{1}{298.15} - \frac{1}{353.15}\right)^{-1} \quad (3)$$

where $R = 8.315$ J mol^{-1} K^{-1}.

TABLE 4

Numerical values of parameters χ_{12} of Prigogine–Flory–Patterson (P–F–P) and ERAS equations and the standard error of fit (δ) at 298.15 K

Mixture	χ_{12} (J cm^{-3})		δ (J mol^{-1})	
	P–F–P	ERAS	P–F–P	ERAS
β-Picoline (1) + n-hexane	51.4	29.1	19.6	62.3
β-Picoline (1) + n-heptane	57.5	34.2	11.5	63.8
β-Picoline (1) + n-octane	58.8	32.8	43.3	37.3
β-Picoline (1) + n-nonane	59.2	31.7	61.1	21.4
β-Picoline (1) + n-decane	59.5	31.4	74.8	14.5

The parameters of the pure components are given in Table 3. Table 4 lists the exchange interaction parameter χ_{12} for the investigated systems.

The values of H_m^E computed by the Prigogine–Flory–Patterson theory and the ERAS model are compared with the experimental data in Figs. 1–5. The models used correctly predict the magnitude of the excess enthalpy and its change with the size of the alkane molecule, as was reported previously for pyridine and for α- and γ-picoline [1–4].

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