Thermochimica Acta, 184 (1991) 321–327
Elsevier Science Publishers B.V., Amsterdam

Application of the Prigogine–Flory–Patterson theory and the extended real associated solution method to the excess molar heats of mixing of γ-picoline with *n*-alkane

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(Received 12 November 1990)

Abstract

The excess molar heats of mixing, H^E, for binary mixtures of γ-picoline + *n*-alkane (C_6–C_{10}) were measured at 25 ° C. The Prigogine–Flory–Patterson and extended real associated solution models were fitted to the experimental results.

INTRODUCTION

Previously we have investigated the excess molar heats of mixing in a series of mixtures of pyridine and its isomers, in which the number and position of the $-CH_3$ groups in the pyridine ring were interchanged with C_6–C_{10} *n*-alkanes.

In this paper, we present the excess molar heats of mixing of γ-picoline with (C_6–C_{10}) *n*-alkanes. For such binary mixtures, H^E is positive over the whole composition range. The Prigogine–Flory–Patterson theory and the extended real associated solution (ERAS) method [1–3] have been fitted to the experimental results.

EXPERIMENTAL

Gamma-picoline (analytical reagent grade, Reanal) and *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane (purum, Apolda) were purified in accordance with ref. 4. The purity, as determined by GLC, was better than 99.99% for γ-picoline and 99.95% for the *n*-alkanes.

The excess molar heats of mixing were measured using a Unipan type 600 flow microcalorimeter [5]. The precision of the H^E determination is estimated to be in range ±2 J mol^{-2}. The method has been described elsewhere [6].

0040-6031/91/$03.50

RESULTS

The experimental excess molar heats of mixing for the investigated systems at 25 °C are listed in Table 1. The Redlich–Kister equation was

TABLE 1

Excess molar heats of mixing, H^E, for binary mixtures of γ-picoline with *n*-alkanes (C_6–C_{10}) at 25 °C

Mole fraction of γ-picoline	H^E (J mol^{-1})	Mole fraction of γ-picoline	H^E (J mol^{-1})	Mole fraction of γ-picoline	H^E (J mol^{-1})
$CH_3C_5H_4N + C_6H_{14}$		0.6578	1305.2	0.3796	1424.1
0.0457	186.8	0.7033	1230.1	0.4299	1499.6
0.1039	401.7	0.7463	1130.7	0.4448	1504.4
0.1493	557.1	0.7885	1007.9	0.4947	1541.4
0.2265	766.1	0.8277	878.3	0.5120	1547.1
0.2673	865.1	0.8600	755.1	0.5410	1555.5
0.3189	978.0	0.8677	719.4	0.5593	1543.5
0.3863	1077.7			0.6045	1516.5
0.4185	1119.8	$CH_3C_5H_4N + C_8H_{18}$		0.6045	1516.5
0.4817	1137.5	0.0620	370.9	0.6687	1434.5
0.4910	1163.5	0.1176	545.8	0.7097	1350.3
0.5136	1159.3	0.1802	788.5	0.7586	1210.0
0.5172	1171.2	02.423	1013.3	0.7987	1079.0
0.5400	1160.4	0.2949	1157.0	0.8367	929.8
0.5910	1142.3	0.3056	1184.0	0.8649	806.9
0.5918	1146.2	0.3583	1306.6	0.9015	621.4
0.6303	1116.6	0.3716	1322.5	0.9371	417.5
0.6743	1059.9	0.4224	1396.4		
0.7176	983.7	0.4386	1415.7	$CH_3C_5H_4N + C_{10}H_{22}$	
0.7487	917.4	0.4891	1452.3	0.0611	331.9
0.7936	800.2	0.5081	1465.1	0.1889	903.6
0.8376	670.6	0.5570	1462.1	0.1939	920.9
0.8804	526.6	0.5781	1455.0	0.2438	1096.0
0.9272	339.1	0.6039	1434.1	0.2600	1146.8
		0.6271	1411.5	0.3043	1284.5
$CH_3C_5H_4N + C_7H_{16}$		0.6722	1338.6	0.3650	1430.3
0.0618	280.9	0.7155	1244.4	0.3763	1454.3
0.1272	538.3	0.7574	1233.8	0.4521	1560.4
0.1737	713.2	0.7969	1004.6	0.5005	1608.0
0.2271	898.3	0.8348	875.9	0.5171	1608.2
0.2560	983.3	0.8601	756.3	0.5629	1611.5
0.3124	1114.8	0.9002	576.3	0.5802	1604.2
0.3670	1230.4	0.9361	389.1	0.6251	1561.6
0.3829	1262.3			0.6674	1496.6
0.4367	1338.7	$CH_3C_5H_4N + C_9H_{20}$		0.6872	1457.4
0.5098	1393.6	0.0630	334.4	0.7273	1367.1
0.5323	1390.0	0.1195	597.1	0.7643	1251.0
0.5445	1388.9	0.1815	858.1	0.8233	1041.1
0.5465	1393.9	0.2508	1106.3	0.8751	790.9
0.5611	1392.7	0.3043	1254.3	0.9090	609.8
				0.9418	413.8

TABLE 2

Smoothing coefficients A_i, and standard deviations, s, for mixtures of γ-picoline with n-alkanes (C_6–C_{10}) at 25 °C

Mixture	A_1	A_2	A_3	s
γ-Picoline +				
n-C_6H_{14}	−0.817	−1.060	0.402	0.005
n-C_7H_{16}	0.208	−1.142	0.246	0.007
n-C_8H_{18}	0.956	−1.000	0.119	0.008
n-C_9H_{20}	1.551	−0.979	−0.022	0.005
n-$C_{10}H_{22}$	1.962	−0.668	−0.079	0.006

fitted to the data using

$$H^E\ (\mathrm{J\ mol^{-1}}) = x_1 x_2 \sum_{i=1}^{3} A_i (2x-1)^{i-1} \tag{1}$$

where x_1 is the mole fraction of γ-picoline.

The smoothing coefficients, A_i, for γ-picoline + (C_6–C_{10})n-alkane mixtures are presented in Table 2, together with the standard deviations, s.

Figures 1–5 show the experimental excess molar heats of mixing, H^E, as a function of the composition of the γ-picoline + n-alkane mixtures. For all binary systems of γ-picoline with (C_6–C_{10}) n-alkanes, the H^E values are positive, and increase with increasing chain length. No excess molar heats of mixing were available in the literature.

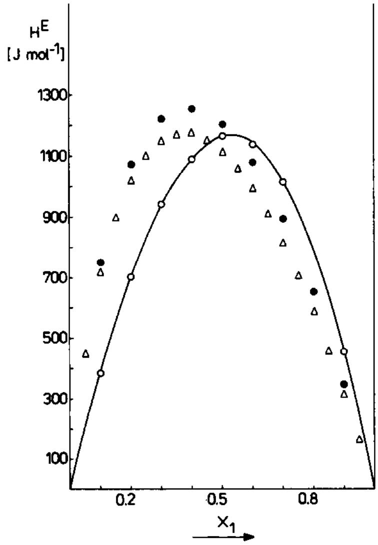

Fig. 1. Molar excess heats of mixing versus mole fractions of γ-picoline for γ-picoline–n-hexane at 25 °C: ○, experimental data; △, ERAS method data; ●, Prigogine–Flory–Patterson theory data.

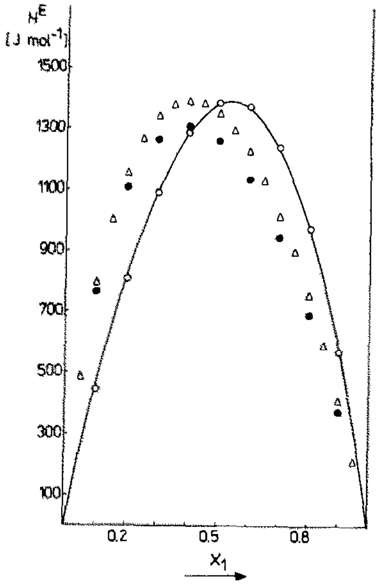

Fig. 2. Molar excess heats of mixing versus mole fractions of γ-picoline for γ-picoline–*n*-heptane at 25 °C: ○, experimental data; △, ERAS method data; ●, Prigogine–Flory–Patterson theory data.

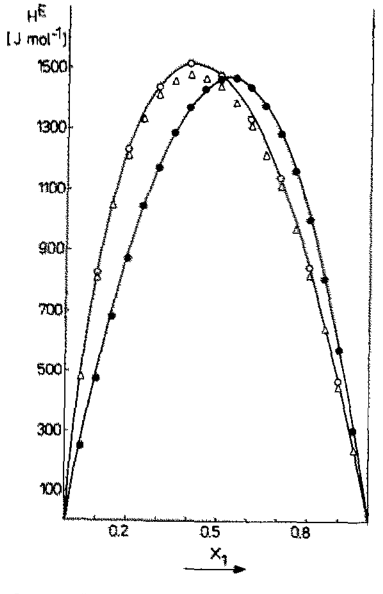

Fig. 3. Molar excess heats of mixing versus mole fractions of γ-picoline for γ-picoline–*n*-octane at 25 °C: ○, experimental data; △, ERAS method data; ●, Prigogine–Flory–Patterson theory data.

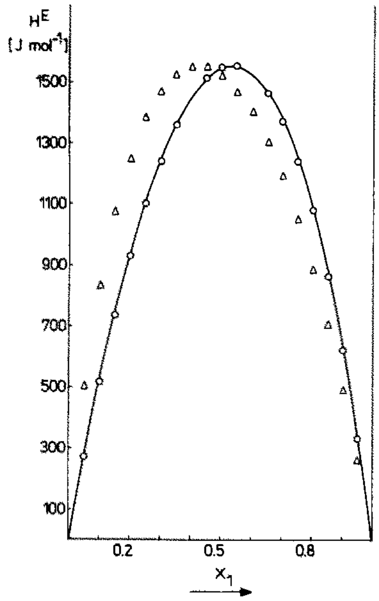

Fig. 4. Molar excess heats of mixing versus mole fractions of γ-picoline for γ-picoline–*n*-nonane at 25 °C: ○, experimental data; △, ERAS method data.

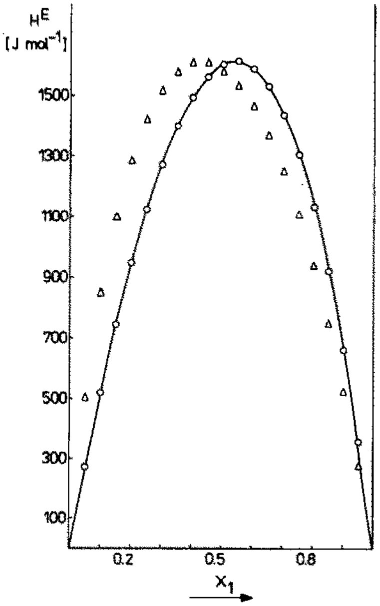

Fig. 5. Molar excess heats of mixing versus mole fractions of γ-picoline for γ-picoline–*n*-decane at 25 °C: ○, experimental data; △, ERAS method data.

TABLE 3

Parameters for pure components at 25 °C

Component	P^* (J cm^{-3})	s ($Å^{-1}$)	$\alpha \times 10^4$ (K^{-1})	K	$\alpha^* \cdot 10^4$ (K^{-1})	κ (Pa^{-1})	Δh^* (J mol^{-1})	Δv^* (cm^3 mol^{-1})
γ-Picoline	642.5 [7]	1.09 [7]	9.68 [8]	8.41	2.22	6.92 [9]	−18.58	−5.79
n-Hexane	423 [10]	1.04 [10]	13.91 [11]					
n-Heptane	432 [12]	1.02 [13]	12.53 [13]					
n-Octane	439 [10]	0.99 [10]	11.65 [11]					
n-Nonane	443 [11]	0.97 [11]	10.65 [9]					
n-Decane	448 [10]	0.96 [10]	10.50 [11]					

α^* is the contribution to α arising from association effects [13]. $\alpha^* = \Delta v^*/v^* \cdot \Delta h^*/RT^2 \{[(4K+1)^{1/2} - 2K(4K+1)^{-1/2} - 1]/2K\}$.

TABLE 4

Values of the parameter χ_{12} for the mixtures

Mixture	χ_{12} (J cm^{-3})
γ-Picoline +	
n-hexane	9.3
n-heptane	13.6
n-octane	11.9
n-nonane	11.7
n-decane	10.6

DISCUSSION

The fitting procedure described previously for mixtures of pyridine with *n*-alkanes [6] was used here. The model parameters, χ_{12}, Δh^*, Δv^*, P, K, s, α and κ, are listed in Tables 3 and 4.

The calculated excess molar heats of mixing curves for γ-picoline + *n*-alkane systems are plotted in Figs. 1–5, together with the curves representing the smoothed experimental results.

The model used expresses the concentration dependence of the excess heats of mixing and its change with increasing number of carbon atoms in the alkane chain. These values are compared with the experimental results. The model and theory predict correctly the magnitude of the excess enthalpy of mixing and its change with the size of the alkane molecule.

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