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APPLICATION OF THE PRIGOGINE–FLORY–PATTERSON AND EXTENDED REAL ASSOCIATED SOLUTION METHOD TO MOLAR EXCESS HEAT OF MIXING OF PYRIDINE BASE–*n*-ALKANE MIXTURES

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ABSTRACT

The binary molar excess heats of mixing of pyridine base–*n*-alkane mixtures were measured at 25 °C. The Prigogine–Flory–Patterson and extended real associated solution methods have been fitted to the experimental results.

INTRODUCTION

In the literature there are many thermodynamic values of *n*-alkanes in different systems [1–3]. In this work the excess molar heats of mixing of pyridine base–(C_6–C_{10})-*n*-alkane binary mixtures have been measured at 25 °C. For such mixtures H^E is positive over the whole composition range. The Prigogine–Flory–Patterson theory and the extended real associated solution (ERAS) method [4–6] have been fitted to the experimental results.

EXPERIMENTAL

Pyridine base (purum, POCh) used in the present paper was the same as in the authors' earlier study [7]. Its purity as determined by GLC was better than 99.99%.

The *n*-alkanes (analytical reagent grade, Reanal)—*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane—were shaken with sulphuric acid, then washed with a sodium carbonate solution and water and dried over P_2O_5. The final purification was by fractional distillation; the middle fraction was used. Its purity, as determined by GLC, was better than 99.95%.

The excess molar heat of mixing was measured using a Unipan type 600 flow microcalorimeter [7]. The precision of the H_m^E determination is estimated to be range of ±2 J mol^{-1}. The method has also been described elsewhere [7].

TABLE 1

Excess heat of mixing, H^E, for binary mixtures of pyridine with (C_6-C_{10})-*n*-alkanes at 298.15 K

Mole fraction of pyridine	H^E (J mol^{-1})
$C_5H_5N + C_6H_{14}$	
0.0418	217.1
0.2016	929.4
0.3476	1357.7
0.3910	1431.4
0.4477	1498.9
0.5212	1541.7
0.6662	1431.4
0.7381	1252.2
0.8553	816.3
0.9649	231.8
$C_5H_5N + C_7H_{16}$	
0.0662	504.9
0.1161	817.8
0.1242	850.7
0.1448	966.7
0.1782	1111.6
0.2327	1328.4
0.3013	1517.1
0.3656	1637.8
0.3817	1659.7
0.3984	1690.5
0.4169	1703.3
0.4594	1722.5
0.4841	1727.6
0.5054	1733.6
0.5301	1727.3
0.5869	1684.2
0.6197	1640.2
0.6556	1567.9
0.7187	1429.6
0.7619	1302.5
0.7757	1251.8
0.8090	1131.0
0.8702	846.9
0.9143	606.8
$C_5H_5N + C_8H_{18}$	
0.0881	641.3
0.1251	854.3
0.1915	1159.5
0.2838	1479.6
0.3317	1589.8
0.3844	1670.3
0.4169	1708.2
0.4355	1722.7
0.4552	1743.2
0.5012	1757.6
0.5473	1750.1
0.5855	1712.9
0.6101	1676.9
0.6169	1671.3
0.6674	1599.8
0.7289	1453.2
0.7518	1365.6
0.8589	931.6
0.8681	886.6
0.9919	638.5
0.9552	351.0
$C_5H_5N + C_9H_{20}$	
0.0661	491.5
0.0959	669.4
0.2067	1236.8
0.2450	1381.8
0.3523	1677.9
0.4224	1801.2
0.4775	1838.0
0.4850	1844.9
0.5036	1847.2
0.5236	1842.8
0.5452	1835.5
0.5834	1800.3
0.6870	1631.4
0.7673	1399.8
0.8014	1249.8
0.8370	1094.5
0.8851	832.2
0.9578	346.3
0.9748	205.5
$C_5H_5N + C_{10}H_{22}$	
0.0850	649.0
0.1323	930.1
0.2213	1364.1
0.2623	1522.7
0.3229	1704.1
0.3730	1812.2
0.4280	1892.8

TABLE 1 (continued)

Mole fraction of pyridine	H^E (J mol^{-1})	Mole fraction of pyridine	H^E (J mol^{-1})
$C_5H_5N+C_{10}H_{22}$ (continued)			
0.4443	1920.0	0.6049	1886.2
0.4788	1938.2	0.6565	1805.0
0.4993	1943.2	0.7051	1698.2
0.5249	1948.5	0.7908	1403.6
0.5452	1938.4	0.8485	1122.5
0.5672	1931.6	0.9232	651.7

RESULTS

The experimental molar excess heat of mixing for the binary systems of pyridine with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane or *n*-decane at 25 °C are presented in Table 1. The Redlich–Kister equation was fitted to the H_m^E data

$$H_m^E\ (\text{J mol}^{-1}) = x_1x_2 \sum_{i=1}^{n} A_i(2x-1)^{i-1} \tag{1}$$

where x_1 is the mole fraction of pyridine base. The smoothing coefficients A_i for pyridine–(C_6–C_{10})-*n*-alkanes determined from the results of Table 1 are presented in Table 2, together with the standard deviations $\delta(H_m^E)$.

For the binary systems of pyridine with (C_6–C_{10})-*n*-alkanes, H_m^E values are positive. The mixtures investigated in this work have already been reported [8]. In both ref. 8 and the present study, the H_m^E values for pyridine–(C_6–C_{10})-*n*-alkanes increase with increasing chain length, but in the present work H_m^E values are higher than in ref. 8.

TABLE 2

Smoothing coefficients A_i and standard deviations $\delta(H_m^E)$ for pyridine–(C_6–C_{10})-*n*-alkanes at 25 °C

Mixture	A_1	A_2	A_3	$\delta(H_m^E)$
Pyridine +				
n-C_6H_{14}	6164.88	673.49	−6.953	6.68
n-C_7H_{16}	6916.63	−236.91	1374.74	2.89
n-C_8H_{18}	7023.72	68.62	1205.75	5.86
n-C_9H_{20}	7372.62	279.22	969.53	5.35
n-$C_{10}H_{22}$	7778.20	438.92	1289.95	5.28

TABLE 3

Parameters for pure components at 298.15 K [a]

Component	d (g cm^{-3})	P (J cm^{-3})	$10^3\alpha$ (K^{-1})	s (A^{-1})	$10^3\mathscr{H}$ (J cm^{-3})	K_M (mol^{-1})	$\Delta H_M^\star$ (kJ mol^{-1})	$\Delta v^\star$ (cm^3 mol^{-1})
Pyridine	0.97812 [6]	656.4 [4]	0.992 [4]	1.0 [4]	0.6996 [4]	0.101 [2]	−17.5 [2]	−8.53 [3]
n-Hexane	0.6550 [5]	423 [5]	1.391 [5]	1.04 [5]				
n-Heptane	0.6793 [5]	432 [5]	1.253 [5]	1.02 [5]				
n-Octane	0.6983 [5]	439 [5]	1.165 [5]	0.99 [5]				
n-Nonane	0.7138 [1]	435 [7]	1.077 [7]	0.90 [8]				
n-Decane	0.7263 [5]	448 [5]	1.05 [5]	0.96 [5]				

[a] Reference given in square brackets after the value.

DISCUSSION

The H_m^E experimental values have been fitted to the Prigogine–Flory–Patterson theory and ERAS method as reported earlier [4–6]. The expression for H^E from Prigogine–Flory–Patterson theory was used in the form

$$H^E = (V_1^\star x_1 + V_2^\star x_2)\left[\phi_1(P_1^\star/\tilde{V}_1) + \phi_2(P_2^\star/\tilde{V}_2) - (P_M^\star/\tilde{V}_M)\right] \tag{2}$$

with

$$\phi_1 = 1 - \phi_2 = V_1^\star x_1/(V_1^\star x_1 + V_2^\star x_2) \tag{3}$$

and

$$P_M^\star = P_1^\star \phi_1 + P_2^\star \phi_2 - \left[\phi_1 \phi_2 \chi_{12}(s_1/s_2)\right]\left[\phi_2 + s_1/s_2 \phi_1\right] \tag{4}$$

where 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, $V_1^\star$ and $V_2^\star$ are the molar hard core volumes of components 1 and 2, $P_1^\star$ and $P_2^\star$ are characteristic pressures of components 1 and 2, $P_M^\star$ and $V_M^\star$ are characteris-

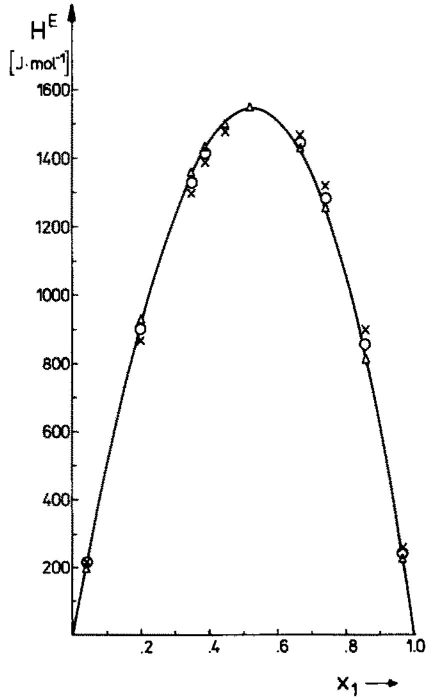

Fig. 1. Molar excess heat of mixing versus molar fraction of pyridine for pyridine–*n*-hexane at 25 °C. △, Experimental data; ○, ERAS method data; ×, Prigogine–Flory–Patterson method data.

TABLE 4

Values of parameters χ_{12} of Prigogine–Flory–Patterson (P–F–P) and ERAS equations, and the standard error of the fit

Mixture	χ_{12}		$\delta(H_M^E)$ (J mol^{-1})	
	P–F–P	ERAS	P–F–P	ERAS
Pyridine +				
n-hexane	74.03	61.22	47.8	21.4
n-heptane	79.71	64.89	144.4	123.6
n-octane	78.24	60.07	148.4	135.5
n-nonane	78.43	58.42	153.2	145.7
n-decane	81.5	60.9	177.11	151.8

tic pressure and volumes for the mixture. The reduced volume $\tilde{V}_M$ of the mixture can be calculated from the reduced equation of state

$$\tilde{p}\tilde{V}/\tilde{T} = -\tilde{V}^{1/3}/(\tilde{V}^{-1/3} - 1) - 1/\tilde{V}\tilde{T} \quad (5)$$

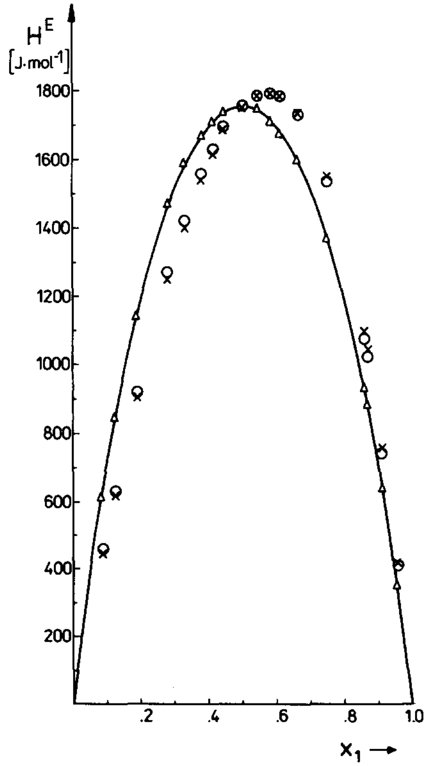

Fig. 2. Molar excess heat of mixing versus molar fraction of pyridine for pyridine–*n*-octane at 25 °C. △, Experimental data; ○, ERAS method data; ×, Prigogine–Flory–Patterson method data.

The ERAS model proposed by Heintz and Lichtenthaler [6] combines the Kretchmer-Wiebe association model [9] with the equation of state developed by Flory [10] for non-polar chain-like molecules. This model expresses H^{E} in the form

$$H^{\mathrm{E}} = K\Delta h^{\star} x_1(\varphi_1 - \varphi_2) - x_1 P_M^{\star}/\tilde{V}_M K\Delta V^{\star}(\varphi_1 - \varphi_1^0) + (V_1^{\star} x_1 + V_2^{\star} x_2)(\phi_1 P_1^{\star}/\tilde{V}_1 + \phi_2 P_2^{\star}/\tilde{V}_2 - P_M^{\star}/\tilde{V}_M) \qquad (6)$$

ϕ_1 and $P_{\mathrm{M}}^{\star}$ are the same values as in eqns. (3) and (4). The expression for H^{E} (eqn. (6)) separates the two contributions. The first term is the chemical contribution, and the second term is the physical contribution. The properties of the pure components are given in Table 3. The parameters were computed from experimental $H_{\mathrm{m}}^{\mathrm{E}}$ values at 25 °C. Using eqns. (2) and (6), together with pure component data, the $H_{\mathrm{m}}^{\mathrm{E}}$ values have been calculated (Table 4).

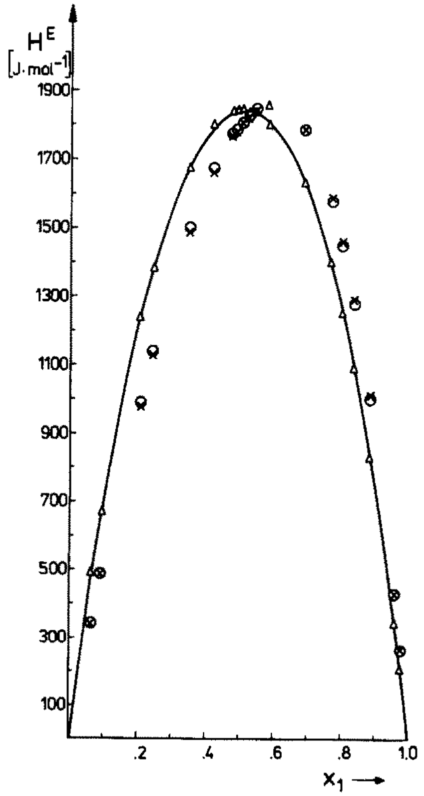

Fig. 3. Molar excess heat of mixing versus molar fraction of pyridine for pyridine–*n*-nonane at 25 °C. △, Experimental data; o, ERAS method data; ×, Prigogine–Flory–Patterson method data.

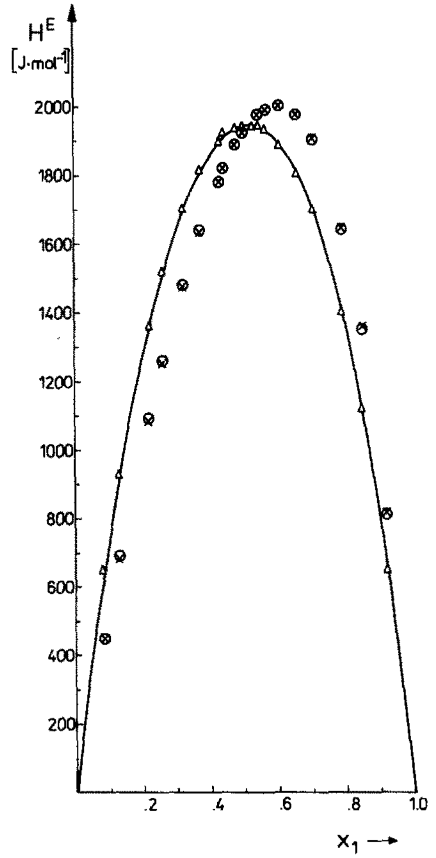

Fig. 4. Molar excess heat of mixing versus molar fraction of pyridine for pyridine–*n*-decane at 25 °C. △, Experimental data; ○, ERAS method data; ×, Prigogine–Flory–Patterson method data.

The H_m^E values computed using the Prigogine–Flory–Patterson theory and the ERAS method are compared with the experimental data in Figs. 1–4. The methods used reproduced the main features of the experimental data, although quantitative agreement was not achieved.

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