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EXCESS HEAT OF MIXING OF α–PICOLINE WITH *n*–ALKANES
Comparison with the Prigogine-Flory-Patterson theory and the extended real associated solution method

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The excess heats of mixing for binary mixtures α-picoline +*n*–alkanes (C_6 to C_{10}) at 298.15 K were measured and a comparison was made with the Prigogine–Flory–Patterson theory and the extended real associated solution method.

Keywords: α-picoline with *n*-alkanes, extended real associated solution method, Prigogine-Flory-Patterson theory

Introduction

As an extension of our investigations of the effects of the chain length of an *n*–alkane, and the number and positions of methyl groups in a pyridine base ring [1, 2], excess molar heats of mixing H^E for α–picoline +*n*-alkane, (C_6 to C_{10}) have been measured at 298.15 K. For the α–picoline +*n*–nonane system, no H^E values were available in the literature. The systems α–picoline +*n*–hexane, *n*–heptane, *n*–octane and *n*–decane were investigated [3].

Experimental

The α–picoline used in the present work was the same as that used in our previous study [4]. Its purity as determined by glc was better than 99.99%.

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The *n*–hexane, *n*–heptane, *n*–octane, *n*–nonane and *n*–decane were the same as those used in [5]. Water content was checked with Fischer's reagent and was on te limit of detectability. The purity as determined by glc was better than 99.95%.

The heats of mixing were measured with a UNIPAN type 600 flow microcalorimeter [6]. The precision of the H^E determination is estimated to be ± 2 J·mol^{-1}.

Results and discussion

The experimental H^E results for the binary systems at 298.15 K are presented in Table 1. The Redlich–Kister equation was fitted to the data by using

$$H^E(\text{J·mol}^{-1}) = = x_1 x_2 \cdot \sum_{i=1}^{3} A_i \cdot (2x-1)^{i-1} \qquad (1)$$

The constants A_i and the standard errors are given in Table 1; x_1 and x_2 are the mole fractions of the components of the binary mixtures. No measurements for H^E for α–picoline +*n*–nonane at 298.15 K have been reported in the literature.

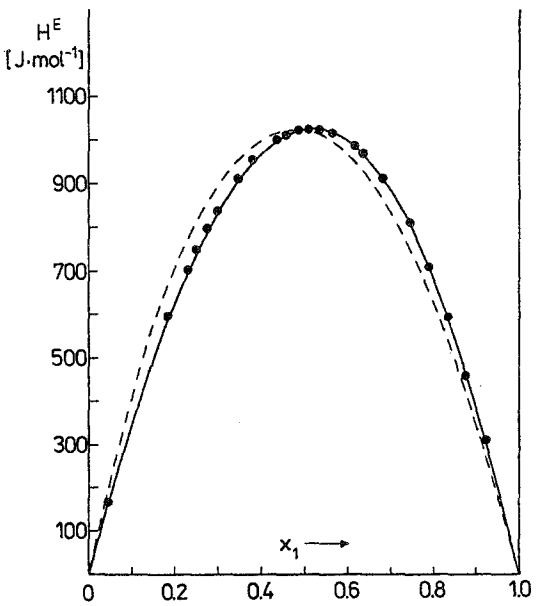

Fig. 1 Excess molar enthalpy H^E for binary mixture of α–picoline with *n*–hexane at 298.15 K, x_1 mole fraction of α–picoline: • experimental data, (——) calculated from P–F–P theory, (— — —) calculated from ERAS method

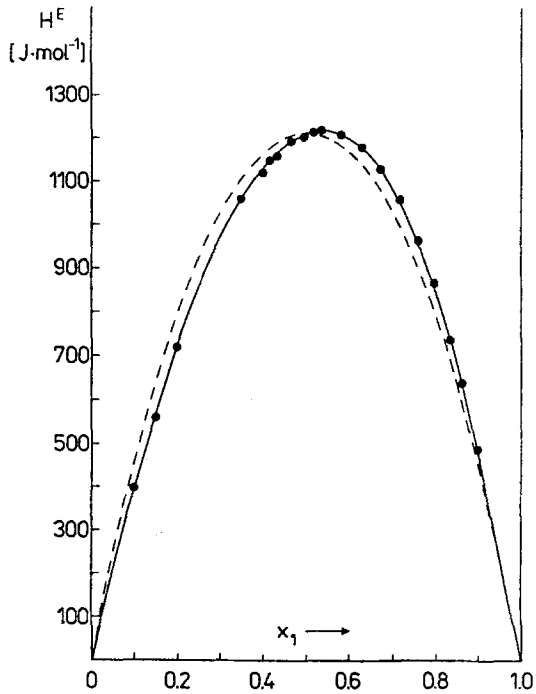

Fig. 2 Excess molar enthalpy H^E for binary mixture of α–picoline with *n*–heptane at 298.15 K, x_1 mole fraction of α–picoline: • experimental data, (——) calculated from P-F-P theory, (— — —) calculated from ERAS method

Ait–Kaci measured H^E for α–picoline +*n*–hexane, *n*–heptane, *n*–octane and *n*–decane at 298.15 K [3, 12]; the results reported here for the systems α–picoline +*n*–hexane, *n*–heptane and *n*–octane are significantly different from their data. The present results for these systems in the equimolar regions are of the order of 200 J·mol^{-1} higher than those of Ait–Kaci [3, 12]. For α–picoline +*n*–decane, our results are similar within experimental error to the data from [3, 12].

Our experimental data have been fitted to the Prigogine–Flory–Patterson theory and the extended real associated solution (ERAS) method [13–15]. The properties of the pure components are given in Table 2. The values of parameter X_{12} in the Prigogine–Flory–Patterson theory and the ERAS method, together with the standard error of the fit, are given in Table 3.

The present results of Prigogine–Flory–Patterson theory calculations are very similar to those obtained experimentally, especially in the systems α–picoline +*n*–hexane and *n*–heptane (Figs 1 and 2). This theory is very successful in fitting H^E data for binary systems of differing molecular size and nature. The application of this theory to α–picoline +*n*–octane, *n*-nonane and *n*–decane mixtures is also remarkably good (Figs 3–5).

Table 1 Excess enthalpies for α–picoline + C_6 to C_{10} *n*–alkane at 298.15 K, x_1 - mole fraction of α–picoline, s – standard error

x_1	H^M / J·mol^{-1}	x_1	H^M / J·mol^{-1}	x_1	H^M / J·mol^{-1}
		α–picoline +*n*–hexane			
0.0449	168.08	0.4350	999.25	0.6360	969.77
0.1856	598.28	0.4574	1012.06	0.6843	912.42
0.2315	707.04	0.4873	1023.50	0.7459	809.35
0.2520	750.57	0.5102	1026.30	0.7916	710.50
0.2760	799.56	0.5362	1025.53	0.8363	594.75
0.2997	839.75	0.5639	1018.35	0.8794	462.00
0.3489	911.60	0.6159	987.72	0.9227	315.35
0.3822	955.90				
A_1 =4102.05		A_2 =292.35		A_3 =101.02	s =2.2
		α–picoline +*n*–heptane			
0.1026	400.48	0.4657	1193.58	0.7163	1058.86
0.1521	567.44	0.4951	1210.13	0.7573	971.61
0.2000	712.30	0.5148	1216.73	0.7974	866.37
0.3478	1050.69	0.5354	1219.69	0.8351	748.65
0.3988	1127.10	0.5832	1210.57	0.8663	636.93
0.4252	1147.01	0.6293	1179.76	0.9037	485.24
0.4325	1165.50	0.6731	1129.47		
A_1 =4848.47		A_2 =763.20		A_3 =170.51	s =4.9
		α–picoline +*n*–octane			
0.0512	217.54	0.3900	1172.74	0.6684	1181.14
0.1010	412.42	0.4514	1242.01	0.6872	1151.51
0.1532	598.06	0.4903	1267.15	0.7281	1072.62
0.2076	770.17	0.5238	1276.68	0.7681	975.82
0.2635	923.09	0.5454	1276.73	0.8500	714.45
0.3183	1048.22	0.5988	1255.67	0.9093	469.73
0.3531	1114.36	0.6235	1235.44	0.9417	315.48
A_1 =5084.32		A_2 =712.60		A_3 =41.66	s =3.8
		α–picoline +*n*–nonane			
0.0560	244.16	0.4021	1235.59	0.7392	1114.09
0.0620	269.06	0.4742	1312.79	0.7962	957.37
0.1168	483.20	0.4926	1324.27	0.8347	825.63
0.1898	738.69	0.5461	1337.68	0.8712	680.56
0.2460	906.55	0.5968	1321.74	0.9061	522.75
0.3000	1044.01	0.6440	1280.46	0.9399	351.46
0.3392	1128.45	0.6930	1209.19	0.9711	176.66
A_1 =5311.67		A_2 =908.02		A_3 =143.79	s =2.9

Table 1 Continued

x_1	H^M / J·mol^{-1}	x_1	H^M / J·mol^{-1}	x_1	H^M / J·mol^{-1}
		α–picoline +*n*–decane			
0.0601	274.50	0.3959	1305.27	0.5893	1407.77
0.1133	497.50	0.4238	1345.21	0.6180	1385.95
0.1711	716.73	0.4400	1364.70	0.6628	1331.10
0.2224	889.70	0.5140	1417.78	0.7109	1242.93
0.2470	965.01	0.5298	1421.19	0.7559	1131.87
0.3093	1132.33	0.5474	1421.59	0.8470	817.89
0.3299	1179.95	0.5676	1417.56	0.8735	703.13
				0.9077	538.76
				0.9697	192.55
A_1 =5649.56		A_2 =929.09		A_3 =35.32	s =2.9

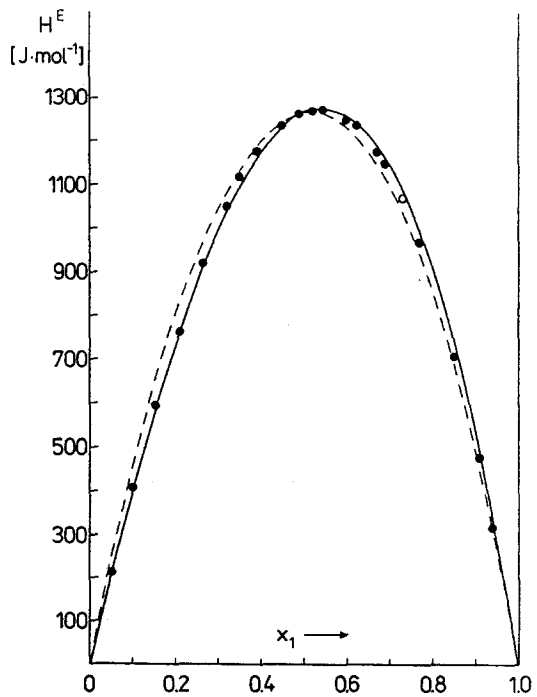

Fig. 3 Excess molar enthalpy H^E for binary mixture of α–picoline with *n*–octane at 298.15 K, x_1 mole fraction of α–picoline:: • experimental data, (——) calculated from)P-F-P, theory, (— — —) calculated from ERAS method

Table 2 Component properties and parameters used in calculations H^E for(α–picoline + *n*–alkine) at 298.15 K by the P–F–P theory and ERAS model

Component	d / g·cm^{-3}	p^* / J·cm^{-3}	$10^3 \cdot \alpha$ / K^{-1}	s / A^{-1}	$10^3 \cdot \kappa$ / J·cm^{-3}	K	Δh^* / J·mol^{-1}	Δv^* / cm^3·mol^{-1}
α–picoline	0.9395 [7]	617.7 [7]	1.002 [7]	1.09 [10]	0.7533 [7]	1.53 [10]	–7743 [10]	–5.30 [10]
n–hexane	0.6550 [8]	423 [9]	1.391 [8]	1.04 [9]	1.7039 [11]	–	–	–
n–heptane	0.6793 [8]	432 [9]	1.253 [8]	1.02 [9]	1.4606 [11]	–	–	–
n–octane	0.6983 [8]	439 [9]	1.165 [8]	0.99 [9]	1.3024 [11]	–	–	–
n–nonane	0.7139 [8]	443 [9]	1.090 [8]	0.97[d]	1.1754 [11]	–	–	–
n–decane	0.7263 [8]	448 [9]	1.050 [8]	0.96 [9]	1.1096 [11]	–	–	–

[d] – interpolated from the values for the other *n*–alkanes

Table 3 Numerical values of parameters X_{12} of Prigogine–Flory–Patterson and equations Extended Real Associated Solution and the standard error of the fit δ at 298.15 K

Mixture	X_{12}		δ / J·mol^{-1}	
	P–F–P	ERAS	P–F–P	ERAS
α–picoline + *n*–hexane	46.3	26.5	3.8	43.8
α–picoline +*n*–heptane	51.5	30.4	7.9	50.2
α–picoline +*n*–octane	51.5	28.4	15.7	30.6
α–picoline +*n*–nonane	51.9	27.6	21.6	23.0
α–picoline +*n*–decane	53.3	28.0	40.4	17.3

A direct comparison of the measurements in this work with those from the Prigogine-Flory-Patterson theory and the ERAS method shows excellent agreement between our results and those from the P-F-P theory for small molecules of *n*–alkane and good agreement for the P-F-P theory for the longer *n*–alkanes. The

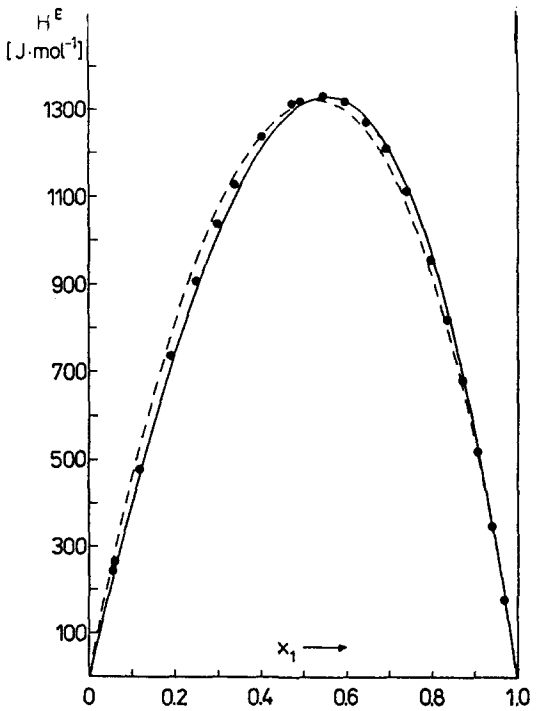

Fig. 4 Excess molar enthalpy H^E for binary mixture of α–picoline with *n*–nonane at 298.15 K, x_1 mole fraction of α–picoline: • experimental data, (——) calculated from P-F-P theory, (— — —) calculated from ERAS method

ERAS method reproduced the main features of the experimental data, but quantitative agreeement was not achieved.

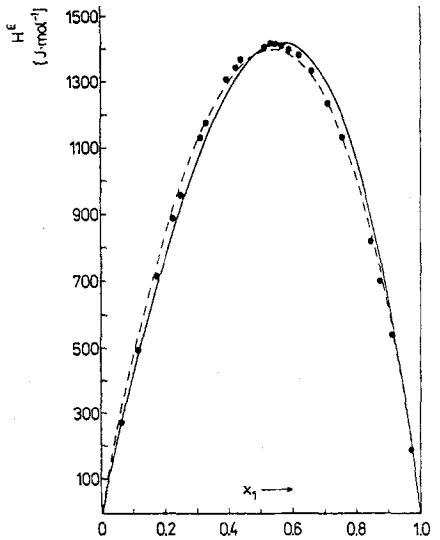

Fig. 5 Excess molar enthalpy H^E for binary mixture of α–picoline with *n*–decane at 298.15 K, x_1 mole fraction of α–picoline: (– – –) calculated from ERAS method , (———) calculated from P-F-P theory, : • experimental data

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Zusammenfassung — Die molaren Überschubenthalpien binärer Mischungen von α–Picolin mit C_6C_{10} *n*–Alkanen wurden bei 298.15 K im ganzen Zusammensetzungsbereich gemessen. Die gemessenen H^E Werte wurden mit denen verglichen, die mit Hilfe von Prigogine–Flory–Patterson Theorie und nach der ERAS-Methode berechnet wurden.