

APPLICATION OF THE PRIGOGINE–FLORY–PATTERSON AND EXTENDED REAL ASSOCIATED SOLUTION METHODS TO EXCESS MOLAR VOLUMES OF PYRIDINE BASE WITH *n*-ALKANE MIXTURES

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ABSTRACT

The binary excess molar volumes, V^E , of γ -picoline–*n*-alkane mixtures were measured at 25°C. The Prigogine–Flory–Patterson and extended real associated solution models have been fitted to the experimental results.

INTRODUCTION

As an extension of our investigation of the effect of chain length of an *n*-alkane, as well as the number and position of methyl groups in a pyridine ring, excess molar volumes, V^E , for a γ -picoline + a C_6 to C_{10} *n*-alkane have been measured at 25°C. For these systems no V^E values were available in the literature.

EXPERIMENTAL

γ -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. 1. The final purity, as determined by GLC, was better than 99.95% for *n*-alkanes and 99.99% for γ -picoline.

The excess molar volume was measured using dilatometry as described by Duncan et al. [2]. The precision of the determination of V^E was better than $0.0045 \text{ cm}^3 \text{ mol}^{-1}$.

RESULTS

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

TABLE 1

Excess molar volume of mixing V^E , for binary mixtures of γ -picoline with C_6 - C_{10} n -alkanes at 25°C

Mole fraction of γ -picoline	V^E ($\text{cm}^3 \text{mol}^{-1}$)	Mole fraction of γ -picoline	V^E ($\text{cm}^3 \text{mol}^{-1}$)
$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_6\text{H}_{14}$		$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_8\text{H}_{18}$ (continued)	
0.0351	0.0175	0.4800	0.2488
0.0504	0.0221	0.5887	0.1896
0.0630	0.0246	0.6280	0.1655
0.0904	0.0290	0.7240	0.1064
0.1294	0.0213	0.8100	0.0588
0.1963	-0.0040	0.8800	0.0280
0.2014	-0.0066	0.9203	0.0147
0.2507	-0.0355	0.9547	0.0063
0.2904	-0.0623	0.9701	0.0035
0.2960	-0.0663	0.9812	0.0019
0.3922	-0.1359		
0.4278	-0.1606	$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_9\text{H}_{20}$	
0.5208	-0.2149	0.0824	0.1780
0.6100	-0.2454	0.1452	0.2775
0.6896	-0.2488	0.2135	0.3536
0.7320	-0.2400	0.2987	0.4069
0.7965	-0.2116	0.3467	0.4190
0.8993	-0.1276	0.3548	0.4199
0.9640	-0.0505	0.4029	0.4188
		0.4394	0.4114
$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_7\text{H}_{16}$		0.4501	0.4082
0.0581	0.0772	0.4916	0.3919
0.1037	0.1180	0.5602	0.3531
0.1477	0.1430	0.6293	0.3025
0.1567	0.1466	0.6720	0.2671
0.1960	0.1567	0.7414	0.2058
0.2858	0.1517	0.8245	0.1312
0.3124	0.1444	0.8731	0.0895
0.3442	0.1329	0.9349	0.0415
0.4321	0.0904		
0.4556	0.0774	$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_{10}\text{H}_{22}$	
0.5455	0.0265	0.0512	0.1214
0.5546	0.0214	0.0602	0.1408
0.6664	-0.0321	0.1428	0.2937
0.7310	-0.0524	0.2252	0.4023
0.8377	-0.0612	0.2899	0.4589
0.8475	-0.0602	0.3480	0.4897
0.8710	-0.0565	0.3803	0.4991
0.9393	-0.0345	0.4223	0.5036
0.0600	-0.0243	0.4399	0.5030
		0.4464	0.5024
$\text{CH}_3\text{C}_5\text{H}_4\text{N} + \text{C}_8\text{H}_{18}$		0.4847	0.4952
0.0502	0.0931	0.4929	0.4928
0.0840	0.1440	0.5455	0.4712
0.0860	0.1467	0.6518	0.3976
0.1680	0.2339	0.7022	0.3510
0.2286	0.2706	0.7423	0.3098
0.2960	0.2885	0.8107	0.2326
0.3600	0.2871	0.8997	0.1242
0.4210	0.2724	0.9499	0.0617

TABLE 2

Smoothing coefficients, A_i , and standard deviations, s , for γ -picoline-(C_6 - C_{10}) n -alkane 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

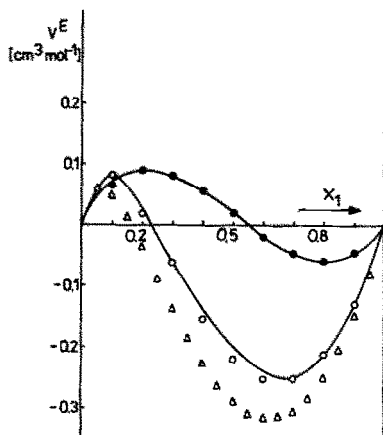


Fig. 1. Excess molar volumes V^E versus molar fraction of γ -picoline for γ -picoline- n -hexane at 25°C. \circ , Experimental data; \bullet , data from Prigogine-Flory-Patterson method; Δ , data from ERAS method.

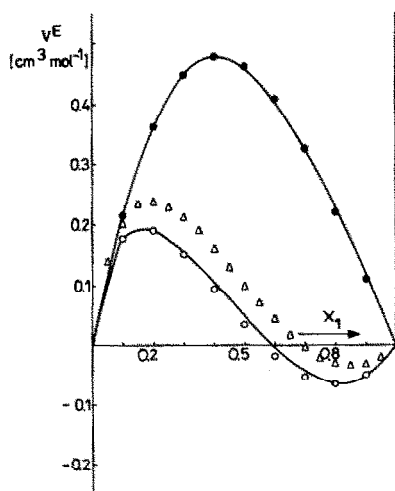


Fig. 2. Excess molar volumes V^E versus molar fraction of γ -picoline for γ -picoline- n -heptane at 25°C. \circ , Experimental data; \bullet , data from Prigogine-Flory-Patterson method; Δ , data from ERAS method.

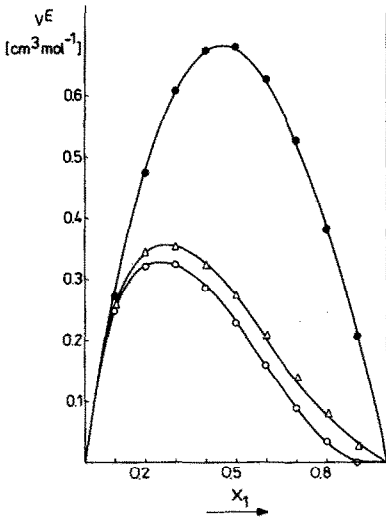


Fig. 3. Excess molar volumes V^E versus molar fraction of γ -picoline for γ -picoline-*n*-octane at 25°C. ○, Experimental data; ●, data from Prigogine-Flory-Patterson method; △, data from ERAS method.

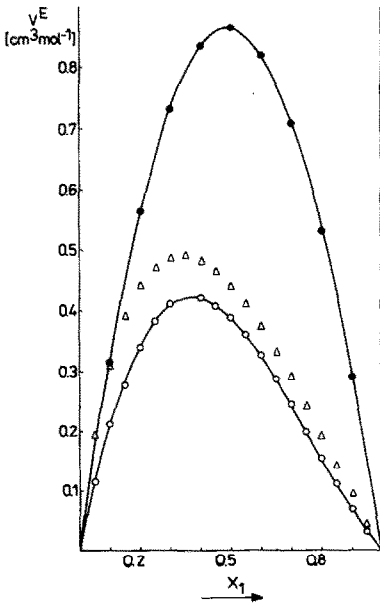


Fig. 4. Excess molar volumes V^E versus molar fraction of γ -picoline for γ -picoline-*n*-nonane at 25°C. ○, Experimental data; ●, data from Prigogine-Flory-Patterson method; △, data from ERAS method.

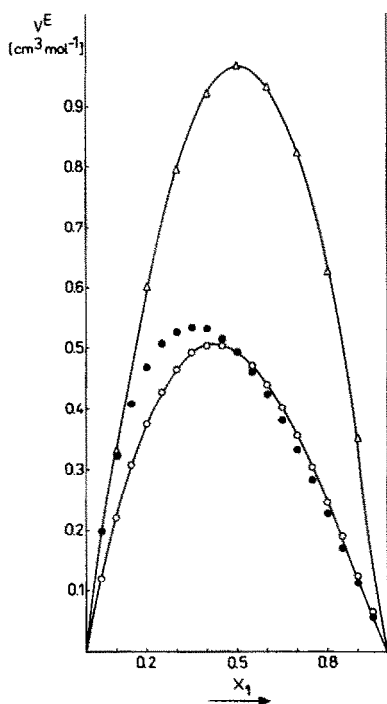


Fig. 5. Excess molar volumes V^E versus molar fraction of γ -picoline for γ -picoline- n -decane at 25°C. \circ , Experimental data; \bullet , data from Prigogine-Flory-Patterson method; Δ , data from ERAS method.

fitted to the data using

$$V^E \text{ (cm}^3 \text{ mol}^{-1}\text{)} = x_1 x_2 \sum_{i=1}^3 A_i (2x - 1)^{i-1} \quad (1)$$

where x_1 is the mole fraction of γ -picoline. The smoothing coefficients A_i for γ -picoline + (C_6 - C_{10}) n -alkanes determined from the results in Table 1 are given in Table 2, together with the standard deviations s . For the systems comprising γ -picoline + n -hexane or n -heptane the values of V^E are positive for the n -alkane rich region and negative for the γ -picoline rich region. For the systems of γ -picoline + n -octane, n -nonane or n -decane V^E is positive.

No excess molar volumes of mixing were available in the literature. Figures 1-5 show the experimental excess molar volumes V^E as a function of the composition for γ -picoline + the respective n -alkanes.

DISCUSSION

We have compared the experimental data with the results calculated by applying Prigogine-Flory-Patterson theory and the extended real associated solution (ERAS) model, as reported earlier [3-6].

The expression for V^E from Prigogine-Flory-Patterson theory, which separates the three contributions, is

$$\begin{aligned} \frac{V^E}{x_1V_1^* + x_2V_2^*} = & \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}}{[(4/3)\tilde{V}^{-1/3} - 1]} \varphi_1\theta_2 \frac{x_{12}}{P_1^*} \\ & - \frac{(\tilde{V}_1 - \tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3} - 1]}{[(4/3)\tilde{V}^{-1/3} - 1]\tilde{V}} \varphi_1\varphi_2 \\ & + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{P_1^*\varphi_1 + P_2^*\varphi_2} \varphi_1\varphi_2 \end{aligned} \quad (2)$$

where the surface fraction θ_2 is given by

$$\theta_2 = \frac{x_2V_2^*s_2}{(x_1V_1^*s_1 + x_2V_2^*s_2)} = \frac{\phi_2s_2}{\phi_1s_1 + \phi_2s_2} \quad (3)$$

where s is the molecular surface/volume ratio for the components, φ is a composition variable given by

$$\varphi_1 = \frac{\phi_1P_1^*}{\phi_1P_1^* + \phi_2P_2^*} = 1 - \varphi_2 \quad (4)$$

and the hard core volume fraction is given by

$$\phi_1 = \frac{x_1V_1^*}{x_1V_1^* + x_2V_2^*} \quad (5)$$

The ERAS model proposed by Heintz and Lichtenhalter [6] expresses V^E in the form

$$V_m^E = \tilde{V}_M x_1 K \Delta v^* (\phi_1 - \phi_1^0) + (V_1^* x_1 + V_2^* x_2) (\tilde{V}_M - \phi_1 V_1 - \phi_2 V_2) \quad (6)$$

The first term represents the chemical contribution to V_m^E , which is essentially identical with V^E in ref. 8, of the additional factor V_M . The second term of eqn. (6) is identical with V_{Flory}^E , representing the physical contribution to V_{comb}^E .

TABLE 3

Values of the parameters χ_{12} , Δh^* and Δv^* for the mixtures

Mixture	χ_{12} (J cm ⁻³)	Δh^* (J mol ⁻¹)	Δv^* (cm ³ mol ⁻¹)
γ -Picoline + <i>n</i> -hexane	9.3		
<i>n</i> -heptane	13.6		
<i>n</i> -octane	11.9	-18.58	-5.79
<i>n</i> -nonane	11.7		
<i>n</i> -decane	10.6		

TABLE 4

Parameters for pure components at 298.15 K. Characteristic values of V^* , K and $10^4\alpha$ obtained from the ERAS formalism

Component	V_{mol} (cm^3 mol^{-1})	V^* (cm^3 mol^{-1})	p^* (J cm^{-3}) ^a	$10^4\alpha$ (K^{-1}) ^a	$10^4\alpha^*$ (K^{-1})	$10^{-5}\mathcal{H}$ ^b (Pa^{-1}) ^a	K	s (A^{-1}) ^a
γ -Picoline	97.96	82.1	642.5 [5]	9.68 [11]	2.22	6.92 [10]	8.41	1.09 [5]
<i>n</i> -Hexane	131.57	99.5	423 [7]	13.91 [9]	—	—	—	1.04 [7]
<i>n</i> -Heptane	147.50	114.0	432 [12]	12.53 [9]	—	—	—	1.02 [8]
<i>n</i> -Octane	163.54	128.0	439 [7]	11.65 [9]	—	—	—	0.99 [7]
<i>n</i> -Nonane	178.79	142.0	443 [9]	10.65 [10]	—	—	—	0.97 [9]
<i>n</i> -Decane	195.92	156.0	448 [7]	10.50 [9]	—	—	—	0.96 [7]

^a References given in square brackets.

^b $\mathcal{H} = \frac{\alpha}{\gamma}$.

The interaction parameter χ_{12} in Prigogine–Flory–Patterson theory, obtained from the equimolar value of enthalpy of mixing, was used to predict the V^E values. The initial K value and Δh^* value for γ -picoline were calculated from the properties of pure substances by the procedure described by Nath and Bender [13]. The parameters χ_{12} , Δh^* and K (Tables 3 and 4) in the ERAS model were determined by a fitting procedure applied simultaneously to the experimental H^E data and V^E data for all mixtures under consideration.

The reaction volume of the hydrogen bonding, Δv^* , is independent of the chain length of the alkane and was calculated from the difference between the hard core volume v^* of γ -picoline and that of its inert homomorph toluene.

All parameters needed for the calculations are given in Tables 3 and 4. Figures 1–5 show the V^E values calculated by Prigogine–Flory–Patterson theory and the ERAS model.

Data prediction of the V^E value based on Prigogine–Flory–Patterson free volume theory leads to some qualitative disagreement with experimental findings, whereas the ERAS model predicts our experimental values of V^E quite well.

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