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Thermodynamic properties of solutions: enthalpy of mixing of 2,4-lutidine + *n*-alkanes

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Abstract

The main purpose of this work is the determination of the excess heat of mixing H^E for binary mixtures of 2,4-lutidine and C_6 to C_{10} *n*-alkanes at 298.15 K. Prigogine–Flory–Patterson theory and the extended real associated solutions (ERAS) method are applied to describe the excess heat of mixing of the mixtures investigated.

INTRODUCTION

In our previous works we have presented the experimental values of excess heat of mixing H^E for binary systems: pyridine + C_6 to C_{10} *n*-alkanes [1, 2], α-picoline + C_6 to C_{10} *n*-alkanes [3], β-picoline + C_6 to C_{10} *n*-alkanes [4], γ-picoline + C_6 to C_{10} *n*-alkanes [5].

In this paper we present the experimental H^E values for the systems 2,4-lutidine + C_6 to C_{10} *n*-alkanes and a comparison of these H^E_{exp} values with results obtained using Prigogine–Flory–Patterson theory and the extended real associated solutions (ERAS) method. These methods successfully describe the change of magnitude of the excess enthalpy and its change with the size of the alkane molecule.

EXPERIMENTAL

The reagents used for the investigations and the methods of purification were the same as those described previously [1, 2].

2,4-Lutidine and *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane were purified in accordance with ref. 6. The final purities, as determined by GLC, were better than 99.95% for *n*-alkanes and 99.99% for 2,4-lutidine.

The measurements of the enthalpies of mixing were carried out using a calorimeter described previously [1].

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RESULTS AND DISCUSSION

The measurements of H^E for all mixtures are given in Table 1. The results were fitted to an expression of the form

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

where x_1 is the mole fraction of 2,4-lutidine. The parameters A_i, together with the standard deviations δ are given in Table 2. The H^E values for all five investigated binary systems are positive and increase with increasing chain length of *n*-alkanes.

We reinvestigated mixtures of 2,4-lutidine + C_6, C_7 and C_8 *n*-alkanes. The difference between the results reported in ref. 7 and ours might have arisen from our use of high purity materials, particularly 2,4-lutidine, without isomers. In ref. 7 the purity of 2,4-lutidine (obtained from Aldrich Chemical Co.) was stated as 99%. It seems that it was not pure enough, because the isomers 2,3-, 2,5- and 2,6-lutidine have similar densities and refractive indexes to 2,4-lutidine and only the precise distillation process can separate them. In this work we made use of differences between vapour pressures of these isomers. That purification process was carried on a 45-plate rectifying column and the purity of 2,4-lutidine was determined by GLC.

We used Prigogine–Flory–Patterson theory and the ERAS method to describe the mixtures investigated. The relations and notation are the same as in our earlier publication [2].

The compressibility coefficient k and the expansibility coefficient α for 2,4-lutidine were obtained by the group contribution method. The thermodynamic association constant K and enthalpy of self-association h_{ass} for 2,4-lutidine were obtained as in ref. 4. In this case the homomorph was *m*-xylene.

The parameters of pure components are given in Table 3 and association parameters of 2,4-lutidine in Table 4. In Table 5 the χ_{12} parameters obtained by Prigogine–Flory–Patterson and ERAS calculations are given with standard errors $\delta(H^E)$.

Both of the methods used successfully described the change of excess heat of mixing H^E for the systems investigated. However the ERAS method gave lower values of H^E and shifted their maximum values to the *n*-alkane rich region. Figure 1 shows, for example, the chemical contribution to the ERAS method, which helps to state the part that association takes in the development of H^E. The S-shaped curve shows that in high densities of pyridine base $0.5 < x_1 < 1.0$ the association effect dominates the dissociation effect. It seems that the assumption of a dimerization type of association leads to an exaggeration of the importance of this effect as a component of H^E for investigated systems.

TABLE 1

Excess molar heats of mixing H^E for binary mixtures of 2,4-lutidine with *n*-alkanes (C_6–C_{10}) at 298.15 K

Mole fraction of 2,4-lutidine	H^E (J mol^{-1})	Mole fraction of 2,4-lutidine	H^E (J mol^{-1})
$(CH_3)_2C_5H_3N + C_6H_{14}$		$(CH_3)_2C_5H_3N + C_8H_{18}$	
0.0893	281.3	0.0943	354.1
0.1348	415.8	0.1354	499.7
0.1484	442.5	0.1974	693.5
0.1972	568.6	0.2429	816.4
0.2959	766.7	0.2977	930.3
0.3470	850.6	0.3994	1098.1
0.4497	934.2	0.4599	1144.4
0.5005	942.5	0.5102	1172.0
0.5229	956.6	0.5274	1168.6
0.5507	943.8	0.5274	1165.1
0.6139	916.4	0.5671	1161.1
0.6675	857.4	0.6043	1143.5
0.7166	777.4	0.6596	1077.1
0.7412	734.4	0.7031	1006.4
0.8226	558.2	0.7616	876.5
0.9152	304.2	0.8372	668.3
		0.8656	577.4
$(CH_3)_2C_5H_3N + C_7H_{16}$		0.9008	452.7
0.0936	333.0		
0.1394	484.5	$(CH_3)_2C_5H_3N + C_9H_{20}$	
0.1904	635.5	0.1030	437.1
0.2450	783.2	0.1988	760.4
0.2450	775.6	0.3173	1048.7
0.3028	898.8	0.3512	113.5
0.3630	1002.0	0.4214	1198.2
0.4110	1060.8	0.4363	1202.0
0.4581	1095.0	0.4827	1225.5
0.4581	1092.2	0.5087	1229.3
0.5102	1107.4	0.5087	1231.5
0.5102	1106.1	0.5502	1220.4
0.5480	1114.5	0.5685	1214.2
0.5860	1103.8	0.6082	1181.2
0.6182	1080.5	0.6287	1159.8
0.6515	1036.1	0.6476	1136.3
0.6515	1039.5	0.7070	1039.8
0.6801	1002.5	0.8055	807.9
0.7152	948.8	0.9031	446.5
0.7375	897.9		
0.7756	810.7	$(CH_3)_2C_5H_3N + C_{10}H_{22}$	
0.7756	812.5	0.0999	446.9
0.7756	818.8	0.0999	448.8
0.8303	668.4	0.0999	450.6
0.8376	648.3	0.2129	841.5
0.8622	579.0	0.3167	1091.1
0.9044	419.4	0.3838	1198.7

TABLE 1 (continued)

Mole fraction of 2,4-lutidine	H^E (J mol^{-1})	Mole fraction of 2,4-lutidine	H^E (J mol^{-1})
$(CH_3)_2C_5H_3N + C_{10}H_{22}$			
0.4296	1246.8	0.6094	1235.4
0.4296	1253.6	0.6476	1192.9
0.4595	1267.9	0.6677	1168.8
0.4885	1277.6	0.7247	1061.8
0.4995	1284.6	0.7950	889.2
0.5310	1281.0	0.8187	817.6
0.5310	1280.3	0.8276	789.1
0.5388	1280.4	0.8527	704.2
0.5552	1271.2	0.8527	685.1
0.5552	1268.6	0.9105	454.5
0.5924	1251.3	0.9105	458.1

TABLE 2

Smoothing coefficients A_i and standard deviations δ for mixtures of 2,4-lutidine with *n*-alkanes (C_6–C_{10}) at 298.15 K

Mixture	A_1	A_2	A_3	δ
2,4-Lutidine +				
n-hexane	3805.1	205.4	−232.4	5.4
n-heptane	445.2	477.9	−41.2	5.3
n-octane	4664.9	451.4	−101.6	5.0
n-nonane	4919.2	232.4	56.8	4.9
n-decane	5121.2	352.2	305.7	5.0

TABLE 3

Parameters of pure components at 298.15 K

Component	d (g cm^{-3})	P^* (J mol^{-1})	α (kK^{-1})	$\chi \times 10^3$ (MPa^{-1})	s (A^{-1})
2,4-Lutidine	0.92664 [a]	596.0 [b]	0.9544 [b]	0.7380 [b]	0.97 [c]
n-Hexane	0.6550 [d]	423.0 [e]	1.3910 [d]	1.7039 [f]	1.04 [e]
n-Heptane	0.6793 [d]	432.0 [e]	1.2530 [d]	1.4606 [f]	1.02 [e]
n-Octane	0.6983 [d]	439.0 [e]	1.1650 [d]	1.3024 [f]	0.99 [e]
n-Nonane	0.7139 [d]	443.0 [e]	1.09 [d]	1.1754 [f]	0.97 [e]
n-Decane	0.7263 [d]	448.0 [e]	1.05 [d]	1.1096 [f]	0.96 [e]

[a] Ref. 9.

[b] Authors' own data, estimated by group contribution method.

[c] Authors' own data, unpublished.

[d] Ref. 10.

[e] Ref. 11.

[f] Ref. 12.

TABLE 4

Association parameters of pyridine base at 298.15 K

Component	K	Δh^* (J mol^{-1})	Δv^* (cm^3 mol^{-1})
2,4-Lutidine	4.59	−7414	−3.77

TABLE 5

Parameters χ_{12} in Prigogine–Flory–Patterson and ERAS calculations with corresponding standard errors $\delta(H^E)$

	P–F–P		ERAS	
	χ_{12} (J cm^{-3})	$\delta(H^E)$ (J mol^{-1})	χ_{12} (J cm^{-3})	$\delta(H^E)$ (J mol^{-1})
2,4-Lutidine + hexane	37.14	9.4	26.19	88.8
+ heptane	40.70	5.9	29.60	83.4
+ octane	40.66	19.3	27.39	69.1
+ nonane	41.26	43.8	26.81	32.9
+ decane	41.25	52.9	26.47	27.1

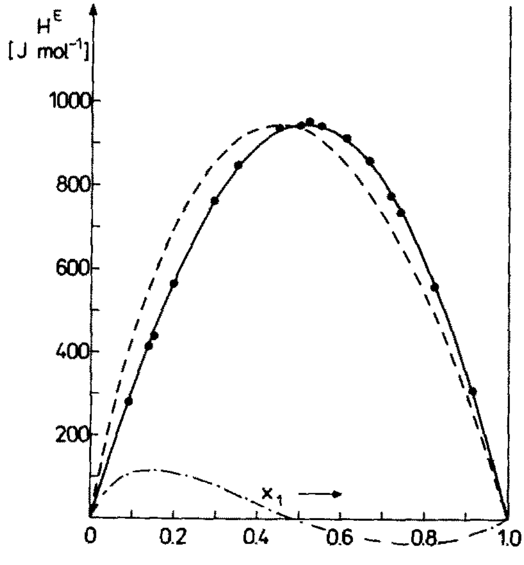

Fig. 1. $H^E = f(x_1)$ for 2,4-lutidine$_{(1)}$ + n-hexane at 298.15 K: ● experimental data; —— P–F–P theory data; – – – ERAS method data; –·–·– $H^E_{chem.}$ term data.

The highest values of H^E seem to be caused mainly by nonspecific interactions, so except for dispersion interactions, especially strong are the effects of n–π and π–π (whose existence was noted by Kiehiaian [8]) and orientation interactions. The energy effect connected with dissociation of pyridine base is a minor part of the total H^E values for the investigated systems.

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