ELSEVIER

Thermochimica Acta 268 (1995) 37–43

thermochimica
acta

Excess enthalpies for binary systems containing 2,4,6-trimethylpyridine and normal alkanes (C_6H_{14}–$C_{10}H_{22}$) at 298.15 K

H. Wilczura *, T. Kasprzycka-Guttman

Department of Chemistry, University of Warsaw, 02-093 Warsaw, Pasteura 1, Poland

Received 17 January 1995; accepted 27 April 1995

Abstract

The experimental data of excess enthalpies for binary systems formed by 2,4,6-trimethylpyridine and *n*-alkanes (C_6H_{14}–$C_{10}H_{22}$) at 298.15 K have been reported.

The results of the computation of $H^E = f(x)$ by the Prigogine–Flory–Patterson and Extended Real Associated Solution models are compared with the experimental values of H^E.

Keywords: Excess enthalpy; Extended Real Associated Solution model (ERAS); Normal alkanes; Prigogine–Flory–Patterson model (PFP); 2,4,6-Trimethylpyridine

1. Introduction

As an extension of our investigation of the intermolecular interactions in pure pyridine bases, the excess enthalpies $H^E = f(x)$ for the binary systems of 2, 4, 6-trimethylpyridine with aliphatic hydrocarbons (C_6H_{14}–$C_{10}H_{22}$) at 298.15 K have been measured.

The binaries formed by 2, 4, 6-trimethylpyridine and normal alkanes are representatives of associated systems with the 2, 4, 6-trimethylpyridine as a self-associated component. There is information on the self-association of pyridine and its methyl derivatives in the literature [1–5]. However, the problem of self-association of the pyridine bases is very complicated and is not yet solved.

---

* Corresponding author.

SSDI 0040-6031(95)02461-1

We have already reported [6–10] experimental results for $H^E = f(x)$ and their theoretical descriptions for pyridine, 2-, 3- and 4-methylpyridine, and 2,4- and 2,6-dimethylpyridine.

This paper reports experimental data for $H^E = f(x)$ and also the results of excess enthalpy representation for 2,4,6-trimethylpyridine + *n*-alkane binaries using two theoretical models of non-electrolyte solutions: the Prigogine–Flory–Patterson model [11–13] and the Extended Real Associated Solution model [14].

2. Experimental

The measurements of the excess enthalpies of mixing were carried out using the UNIPAN 600 flow microcalorimeter (Poland) with a separate dosage system [15]. The accuracy of the H^E value was $\pm 2\ \mathrm{J\,mol^{-1}}$. All substances used for the investigations were thoroughly purified as described previously [16]. The final purities checked by GLC were better than 99.9% for aliphatic hydrocarbons and better than 99.6% for 2,4,6-trimethylpyridine.

3. Results and discussion

The experimental values of H^E are given in Table 1. All the results were fitted using the Redlich–Kister polynomial

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

where x_1 is the mole fraction of 2,4,6-trimethylpyridine. The parameters A_i and the standard deviations δ are also given in Table 1.

For all the investigated binaries, the excess enthalpies are endothermic and the $H^E_{\max}$ values are within the range 808.3–1043.2 J mol^{-1}. The H^E curves are symmetrical and the values of the excess enthalpies increase with the chain length of the hydrocarbon component.

A theoretical description of the experimental results has been made using two non-electrolyte solution models, the Prigogine–Flory–Patterson (PFP) [11–13] and the Extended Real Associated Solution (ERAS) [14].

The PFP model takes into account only the physical interactions with the excess properties of mixtures. The ERAS model considers the PFP physical contribution and also the chemical term H^E_{ch} which describes the contribution of association to the excess properties according to the Kretschmer–Wiebe model [17].

In the investigated systems, the chemical term reflects the self-association of 2,4,6-trimethylpyridine.

The PFP expression for excess enthalpy $H^E = H^H_{\mathrm{ph}}$, is given by

$$H^E = (v_1^* x_1 + v_2^* x_2)\left[\frac{\varphi_1 p_1^*}{\tilde{v}_1} + \frac{\varphi_2 p_2^*}{\tilde{v}_2} - \frac{p_M^*}{\tilde{v}_M}\right] \tag{1}$$

Table 1

Experimental H^E data for 2,4,6-trimethylpyridine with normal alkanes (C_6H_{14}–$C_{10}H_{22}$) at 298.15 K: x_1, mole fraction of 2,4,6-trimethylpyridine; A_i, coefficients of the Redlich–Kister polynomial; δ, standard deviation

x_1	H^E J mol^{-1}	x_1	H^E J mol^{-1}
2,4,6-Trimethylpyridine + C_6H_{14}			
0.1035	303.1	0.5600	788.0
0.2032	531.8	0.6060	757.8
0.2504	616.7	0.6540	717.2
0.3008	691.6	0.7035	655.2
0.3490	740.4	0.7633	564.9
0.4214	788.2	0.8115	475.1
0.4680	805.0	0.8814	323.6
0.5117	808.3		
$A_1 = 3221.3$	$A_2 = -150.2$	$A_3 = -61.7$	$\delta = 2.4$
2,4,6-Trimethylpyridine + C_7H_{16}			
0.1030	322.6	0.5524	919.6
0.2056	592.0	0.6129	890.4
0.2497	682.4	0.6489	858.4
0.2940	760.5	0.7008	786.4
0.3503	839.6	0.7504	712.6
0.3928	886.9	0.7989	616.0
0.4475	926.5	0.9017	345.6
0.4971	939.0	0.9502	185.7
$A_1 = 3775.9$	$A_2 = 155.4$	$A_3 = -53.1$	$\delta = 5.5$
2,4,6-Trimethylpyridine + C_8H_{18}			
0.1112	361.8	0.5544	956.1
0.2131	629.1	0.6089	924.1
0.2502	708.4	0.6452	891.6
0.3026	804.6	0.7024	813.4
0.3592	890.1	0.7498	735.8
0.4088	938.8	0.7970	634.9
0.4467	956.5	0.8980	366.4
0.4990	971.7		
$A_1 = 3880.1$	$A_2 = 126.1$	$A_3 = -115.5$	$\delta = 5.1$
2,4,6-Trimethylpyridine + C_9H_{20}			
0.1207	424.8	0.5424	1007.7
0.2019	646.7	0.5949	981.3
0.2506	754.8	0.6458	943.8
0.3019	850.5	0.6991	862.6
0.3585	935.3	0.7494	780.2
0.4178	990.7	0.7959	679.3
0.4551	1008.7	0.8845	443.6
0.5053	1017.3	0.9249	307.8
$A_1 = 4063.3$	$A_2 = 136.2$	$A_3 = 153.0$	$\delta = 6.0$
2,4,6-Trimethylpyridine + $C_{10}H_{22}$			
0.1289	450.7	0.5482	1033.7
0.2019	669.3	0.5984	1012.2
0.2487	769.1	0.6470	967.3
0.3032	873.2	0.6978	905.6
0.3425	930.4	0.7503	810.7

Table 1 (*Continued*)

x_1	H^E J mol^{-1}	x_1	H^E J mol^{-1}
0.3940	978.4	0.8021	701.2
0.4517	1025.8	0.8986	401.3
0.5127	1043.2		
	$A_1 = 4163.9$ $A_2 = 218.7$	$A_3 = 211.1$ $\delta = 5.7$	

where p_M^* and $\tilde{v}_M$ denote the characteristic pressure of the mixture and the reduced volume of the mixture respectively. The characteristic pressure of the mixture is given by

$$p_M^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \Theta_2 \chi_{12} \tag{2}$$

where χ_{12} is the interaction energy parameter and Θ_2 the surface fraction

$$\Theta_2 = \frac{\varphi_2 s_2}{\varphi_1 s_1 + \varphi_2 s_2} \tag{3}$$

with s being the molecular surface-to-volume ratio, and the hard core volume fraction given by

$$\varphi_1 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \tag{4}$$

The remaining symbols are: v_i^*, hard core volumes; p_i^*, characteristic pressures; and $\tilde{v}_i$, reduced volumes, all related to the components ($i = 1, 2$). The ERAS expression for excess enthalpy $H^E = H^E_{ph} + H^E_{ch}$ is

$$H^E = H^E_{ph} + K \Delta h^* x_1 (\Theta_1 - \Theta_1^0) - x_1 \frac{p_M^*}{\tilde{v}_M} K \Delta \vartheta^* (\Theta_1 - \Theta_1^0) \tag{5}$$

where the main parameters of association are K, the association constant, and Δh^* and $\Delta\vartheta^*$, the enthalpy and volume of formation of the hydrogen bond respectively.

The remaining parameters of the associated component, marked with subscript "1", take the form

$$p_1^* = \frac{\alpha - \alpha^*}{K - \alpha^* \dfrac{\Delta\vartheta^*}{\Delta h^*} T} T(\tilde{v}_1)^2 \tag{6}$$

where α is the thermal expansion coefficient and α^* is a contribution to α arising from association effects

$$\alpha^* = \frac{\Delta\vartheta^*}{v_{1m}^*} \frac{\Delta h^*}{RT^2} \frac{1}{2K} (4K + 1)^{0.5} - 2K(4K + 1)^{0.5} \tag{7}$$

$$v_1^* = v_{1m}^* + \Delta\vartheta^* K \Theta_1 \tag{8}$$

$$\varphi_1 = \frac{\Theta_1}{(1 - K\Theta_1)^2} \tag{9}$$

with v^*_{1m} the characteristic volume of the monomer species and their volume fraction being

$$\Theta_1 = \frac{2K\phi_1 + 1 - (4K\phi_1 + 1)}{2K^2\phi_1} \tag{10}$$

where ϕ_1 is the analytical volume fraction of the associated component

$$\phi_1 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \tag{11}$$

expressed by molar volumes of the components v_1 and v_2.

In both the PFP and ERAS calculations, the reduced and characteristic quantities were estimated using Flory's reduced equation of state [13] from the pure component properties, which are given in Table 2.

The self-association parameters of 2,4,6-trimethylpyridine have been computed using the relationships reported earlier [8]. Mesitylene was choosen as the homomorphic substance. Values of these were the following: the thermodynamic association constant $K_{298.15} = 2.2$; the enthalpy of association $\Delta h^* = -12889\ \mathrm{J\,mol^{-1}}$; the volume of association $\Delta\vartheta^* = -6.51\ \mathrm{cm^3\,mol^{-1}}$.

The results of H^E calculation according to the PFP and ERAS models are compared with the experimental data in Figs. 1 and 2 for the choosen systems.

In both of these models, the only adjustable parameter is the interaction energy parameter χ_{12}. Its values, together with the standard deviations $\delta(H^E)$, are given in Table 3.

For the mixtures of 2,4,6-trimethylpyridine with *n*-alkanes, the PFP model gives a better description of $H^E = f(x)$ than the ERAS model. The Kretschmer–Wiebe model [17] of the continuous association of 2,4,6-trimethylpyridine included in the ERAS model is, in our opinion, unsatisfactory for reproducing its behaviour in mixtures with

Table 2
Properties of pure components: density *d*, characteristic pressure p^* obtained from the Flory formalism, isobaric thermal expansivity α, isothermal compressibility κ for *n*-alkanes and 2,4,6-trimethylpyridine at 298.15 K, and the molecular surface-to volume-ratio *s*

Component	$d/\mathrm{g\,cm^{-3}}$	$p^*/\mathrm{J\,cm^{-3}}$	$\alpha/\mathrm{kK^{-1}}$	$\kappa/\mathrm{TPa^{-1}}$	$s/\mathrm{Å^{-1}}$
C_6H_{14}	0.6550	423.0	1.3910	1703.9	1.04
C_7H_{16}	0.6793	432.0	1.2530	1460.6	1.02
C_8H_{18}	0.6983	439.0	1.1650	1302.4	0.99
C_9H_{20}	0.7139	443.0	1.09	1175.4	0.97
$C_{10}H_{22}$	0.7263	448.0	1.05	1109.6	0.96
Ref.	[18]	[19]	[18]	[20]	[19]
2,4,6-Trimethyl-pyridine	0.9103	606.6	1.0094	774.7	0.85
Ref.	[16]	[16]	[16]	a	[16]

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

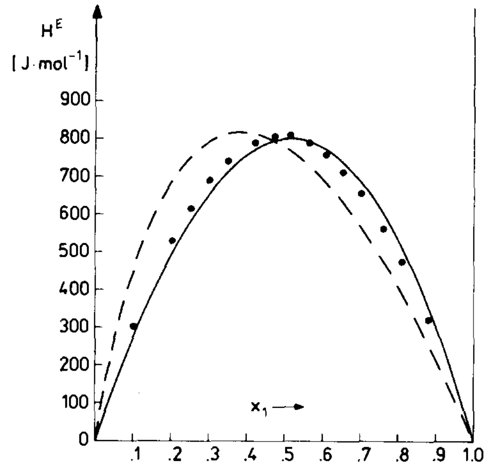

Fig. 1. Excess enthalpy for the 2,4,6-collidine (1) + *n*-hexane system at 298.15 K: ●, experimental points; ——, PFP model; — —, ERAS model.

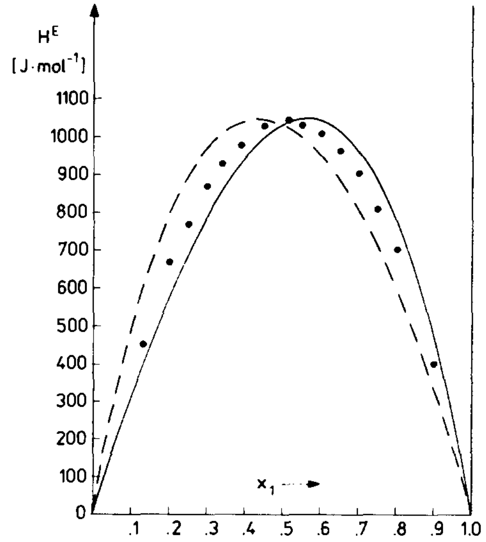

Fig. 2. Excess enthalpy for the 2,4,6-collidine (1) + *n*-decane system at 298.15 K: ●, experimental points; ——, PFP model; — —, ERAS model.

n-alkanes. This remark corresponds with discussion [21] on intermolecular interactions in pure pyridine bases, suggesting that non-specific intermolecular interactions are predominant in pure pyridine and its methyl derivatives, as well as in their mixtures with aliphatic hydrocarbons.

Table 3
Values of parameters χ_{12} in the PFP and ERAS calculations with standard errors $\delta(H^E)$ respectively

System	PFP		ERAS	
	χ_{12}/J cm^{-3}	$\delta(H^E)$/J mol^{-1}	χ_{12}/J cm^{-3}	$\delta(H^E)$/J mol^{-1}
2,4,6-Trimethylpyridine				
$+C_6H_{14}$	27.8	26.0	10.1	92.8
C_7H_{16}	30.1	21.2	11.6	106.8
C_8H_{18}	29.8	36.7	9.9	99.2
C_9H_{20}	30.2	49.7	9.4	89.4
$C_{10}H_{22}$	29.9	58.7	8.2	90.2

References

[1] Y. Yukawa, Handbook of Organic Structural Analysis, W. A. Benjamin Inc., 1965.
[2] I. Wawer and S. Warycha, Pol. J. Chem., 59 (1985) 565.
[3] R. Smets and P. Huyskens, Bull. Soc. Chim. Fr., (5–6) (1978) 173.
[4] S. Warycha and J. C. Rytting, J. Sol. Chem., 13(8) (1984) 585.
[5] S. Warycha and I. Wawer, Adv. Mol. Relaxation and Interaction Processes, 14 (1979) 29.
[6] T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 158 (1990) 1.
[7] T. Kasprzycka-Guttman, H. Wilczura and A. Myslinski, J. Therm. Anal., 38 (1992) 1357.
[8] T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 198 (1992) 405.
[9] T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 184 (1991) 321.
[10] T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 209 (1992) 25.
[11] E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64 (1968) 2035.
[12] P. J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
[13] P. J. Flory, R. A. Orwoll and A. Vrij, J. Am. Chem. Soc., 86 (1964) 3507; 86 (1964) 3515.
[14] A. Heintz, Ber. Bunsenges. Phys. Chem., 89 (1985) 172.
[15] H. Wilczura, T. Kasprzycka-Guttman and S. Randzio, Bull. Pol. Acad. Sci. Ser. Chim., 34 (11–12) (1986) 483.
[16] H. Wilczura, T. Kasprzycka-Guttman and E. Megiel, Thermochim. Acta, 247 (1994) 237.
[17] C. B. Kretschmer and R. Wiebe, J. Chem. Phys., 22 (1954) 1697.
[18] R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc., 89 (1967) 6814.
[19] M. Costas and D. Patterson, J. Sol. Chem., 11 (11) (1982) 807.
[20] A. Treszczanowicz, D. Patterson, G. Benson and T. Kasprzycka-Guttman, Fluid Phase Equilibria, 50 (1989) 235.
[21] H. Wilczura, T. Kasprzycka-Guttman, M. Jarosz-Jarszewska and A. Myslinski, J. Therm. Anal. in press.