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EXCESS ENTHALPIES OF BINARY MIXTURES OF 2-, 3-, 4-PICOLINE + *n*-ALKANE (C_6H_{14}–$C_{10}H_{22}$) AT 298.15 K. COMPARISON WITH THEORY

H. Wilczura, B. Semeniuk, A. Myslinski and T. Kasprzycka-Guttman

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WARSAW, 02-093 WARSAW,
PASTEURA 1, POLAND

The molar excess enthalpies measured for binary mixtures of 2-, 3-, 4-picoline + *n*-alkane (C_6H_{14}–$C_{10}H_{22}$) at 298.15 K have been compared with the Prigogine-Flory-Patterson theory and the Extended Real Associated Solution model estimations.

Keywords: Extended Real Associated Solution model (ERAS), Prigogine-Flory-Patterson theory (PFP), pyridine base+alkane mixtures, thermodynamic properties

Introduction

The present study is a part of the research on thermodynamic properties of pyridine base + alkane mixtures. They are representatives of associated systems with the pyridine base as a self-associated component. Experimental method and detailed results of excess enthalpy determination for binary mixtures of 2-, 3-, 4-picolines with C_6–C_{10} *n*-alkanes at 298.15 K are published separately [1, 2]. This paper reports the results of excess enthalpy representation for the above picoline + *n*-alkane binaries using two theoretical models, that derived from Prigogine-Flory-Patterson theory (PFP) [3–7] and the Extended Real Associated Solution model (ERAS) [8]. Comparison of both model estimations with experiment is given.

Theory

The PFP model considers only a contribution of physical interactions to the excess properties of mixtures. In the ERAS model the PFP physical contribution is supplemented by the chemical term, directly expressing a contribution of association to the ex-

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cess properties. In the investigated systems chemical term reflects a self-association of picolines. Denoting the physical and chemical contributions to excess enthalpy by $H^{\mathrm{E}}_{\mathrm{ph}}$ and $H^{\mathrm{E}}_{\mathrm{ch}}$ respectively, the PFP expression for excess enthalpy H^{E} is given by:

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

with characteristic pressure of mixture

$$p_{\mathrm{M}}^* = \varphi_1^* + \varphi_2 p_2^* - \varphi_1 \theta_2 x_{12} \tag{2}$$

where x_{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 – the molecular surface-to-volume ratio and the hard core volume fraction:

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

The remaining symbols are v_1^* – hard core volumes, p_1^* – characteristic pressures, $\tilde{v}_1$ – reduced volumes, all related to components, and $\tilde{v}_{\mathrm{M}}$ – reduced volume of mixture.

The ERAS expression for H^{E} is given by:

$$H^{\mathrm{E}} = H^{\mathrm{E}}_{ph} + H^{\mathrm{E}}_{ch} = H^{\mathrm{E}}_{ph} + K\,\Delta h^*\, x_1\,(\theta_1 - \theta_1^{\circ}) - x_1 \frac{p_{\mathrm{M}}^*}{\tilde{v}_{\mathrm{M}}} K \Delta v^*\,(\theta_1 - \theta_1^{\circ})\,. \tag{5}$$

where the main parameters of association are: K – the association constant, Δh^*, Δv^*, – the enthalpy and volume of formation of hydrogen bond, respectively.

Remaining individual parameters of the associated component, marked with subscript '1', take the form:

$$p_1^* = \frac{\alpha - \alpha^*}{\kappa - \alpha^* \dfrac{\Delta v^*}{\Delta h^*} T}\, T \tilde{v}_1^2 \tag{6}$$

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

$$\alpha^* = \frac{\Delta v^*}{v_{1\mathrm{m}}^*} \frac{\Delta h^*}{RT^2} \frac{1}{2K}\,[\,\sqrt{4K+1} - 2K\sqrt{4K+1} - 1\,]; \tag{7}$$

$$v_1^* = v_{1m}^* + \Delta v^* K \theta_1, \tag{8}$$

$$\varphi_1 = \frac{\theta_1}{(1 - K\theta_1)^2}, \tag{9}$$

with v_{1m}^* – the characteristic volume of monomer species and their volume fraction:

$$\theta_1 = \frac{2K\Phi_1 + 1 - \sqrt{4K\Phi_1 + 1}}{2K^2\Phi_1} \tag{10}$$

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 components – v_1, v_2

Procedures, results and discussion

In both PFP and ERAS calculations the reduced and characteristic quantities were estimated, using Flory's reduced equation of state [3], from the pure component properties, given in Table 1.

Table 1 Parameters of pure components at 298.15 K

Component	M	d / g·cm^{-3}	p^* / J·cm^{-3}	α / kK^{-1}	κ / MPa^{-1}	s / A^{-1}
2-Picoline	93.130	0.93948	617.7	1.002	0.7533	1.09
3-Picoline	93.130	0.95268	629.6	0.9720	0.7100	1.09
4-Picoline	93.130	0.95065	642.5	0.9680	0.6919	1.09
Reference			[10]	[10]	[10]	a
n-Hexane	86.178	0.6550	423.0	1.3910	1.7039	1.04
n-Heptane	100.205	0.6793	432.0	1.2530	1.4606	1.02
n-Octane	114.232	0.6983	439.0	1.1650	1.3024	0.99
n-Nonane	128.259	0.7139	443.0	1.09	1.1754	0.97
n-Decane	142.286	0.7263	448.0	1.05	1.1096	0.96
Reference		[12]	[11]	[10]	[13]	[11]

a) Authors own data, estimated by group contribution method

The parameters of association for ERAS H^{E}_{ch} term, listed in Table 2, were estimated as follows: the association constant K – from vapour pressures of pure picolines and that of toluene, taken as a homomorphic substance [9], the enthalpies of association Δh^{*} – from the $K(T)$ values by van't Hoff's formula, the volume of association Δv^{*} – as a difference of characteristic volumes of picoline and the $K(T)$ values by van't Hoff's formula, the volume of association Δv^{*} – as a difference of characteristic volumes of picoline and the homomorph. In all calculation procedures for both PFP and ERAS methods the only adjustable parameter was the interaction energy parameter χ_{12}.

Table 2 Association parameters of picolines

Component	K_{298}	Δh^{*} / J·mol^{-1}	Δv^{*} / cm^{3}·mol^{-1}
2-Picoline	4.16	–7743	–5.30
3-Picoline	10.28	–8748	–6.01
4-Picoline	10.87	–8721	–5.79

In all systems investigated the experimental excess enthalpy H^{E} has large positive values, increasing with the chain length of hydrocarbon component [1, 2].

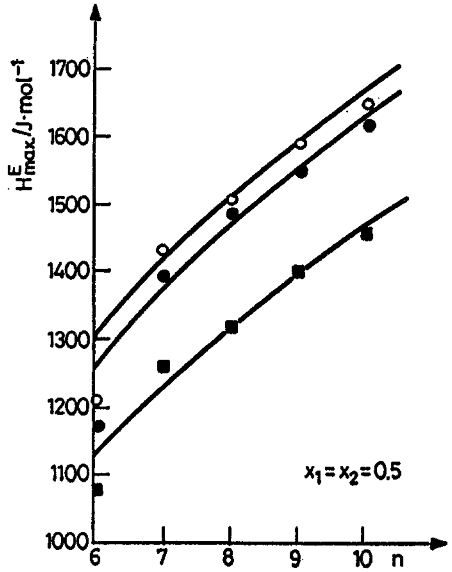

Fig. 1 Maximum H^{E} values for picolines viz. carbon atom number of hydrocarbon components: 2-picoline, 3-picoline, 4-picoline

For the series of binaries with particular picolines the following order of the maximum values H^{E}_{max} (Fig. 1) is observed:

2-picoline < 3-picoline < 4-picoline.

Calculated excess enthalpies, as well by PFP as by ERAS methods, give a good representation of both H^{E} magnitude and its concentration dependence, however some systematic shift of both calculated H^{E} curves toward experimental ones is observed. The best values of adjustable χ_{12} parameter and corresponding standard deviations of calculated H^{E} from the experiment are listed in Table 3.

Table 3 Parameters x_{12} in PFP and ERAS calculations with corresponding standard errors $\delta(H^{E})$

System		PFP		ERAS	
		x_{12} / J·cm^{-3}	$\delta(H^{E})$ / J·mol^{-1}	x_{12} / J·cm^{-3}	$\delta(H^{E})$ / J·mol^{-1}
2-Picoline	+ Hexane	46.33	3.8	27.29	58.7
	+ Heptane	51.50	7.9	31.24	66.9
	+ Oxtane	51.51	15.7	29.11	52.4
	+ Nonane	51.88	21.7	28.17	46.5
	+ Decane	53.31	40.5	28.50	36.8
3-Picoline	+ Hexane	51.41	17.6	32.53	62.9
	+ Heptane	57.50	11.5	37.58	64.1
	+ Oxtane	58.75	43.3	36.03	41.0
	+ Nonane	59.21	61.1	34.79	35.0
	+ Decane	59.51	74.8	34.62	24.1
4-Picoline	+ Hexane	52.77	5.9	34.96	73.4
	+ Heptane	59.04	8.0	38.85	80.1
	+ Octane	59.43	29.8	37.01	49.7
	+ Nonane	60.63	45.2	36.63	36.9
	+ Decane	60.79	55.1	34.98	35.1

The course of calculated total H^{E} – curves for P–F–P and ERAS models with H^{E}_{ch} contribution to the latter model is exemplified in Fig. 2 by the results for chosen system.

Values of H^{E}_{ch} exhibit a rather small dependence on the chain length of hydrocarbon component (Figs 3 –5). The S-shaped H^{E}_{ch} curves suggest that in the range of high concentrations of picolines, $0.50 < x_1 < 1.00$, association, dominates over disassociation. In the ERAS model dimerisation has been assumed as the only form of association, which seems to be also the most probable mode of self-association of picolines by hydrogen bond with the pyridine-ring nitrogen atom. Position of the methyl group in picoline molecule influences its dimerisation ability. Thus, the CH_3-group in position 2 attenuates the association of 2-picoline compared with 3- and 4-isomers. This can be ex-

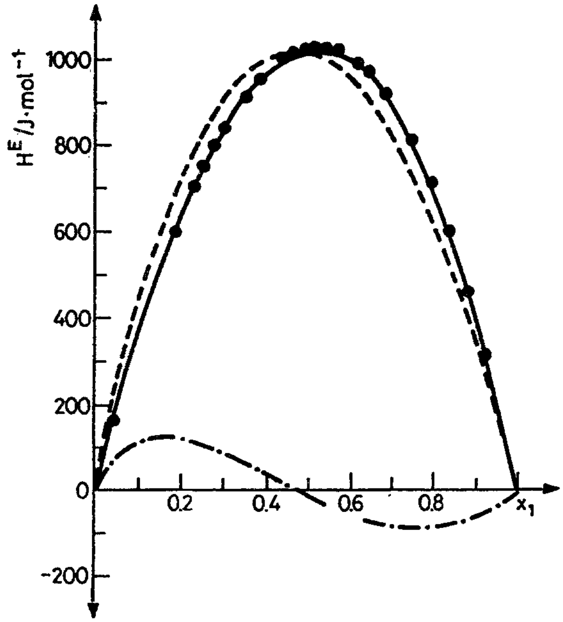

Fig. 2 2-picoline + *n*-hexane. o experimental — PFP theory - - - ERAS method —·—·— H_{ch}^E

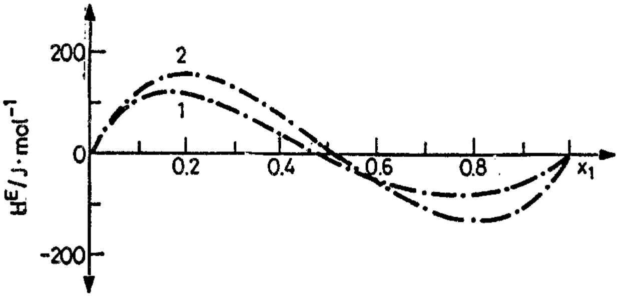

Fig. 3 H_{ch}^E for mixtures: (1) 2-picoline + *n*-hexane; (2) 2-picoline + *n*-decane

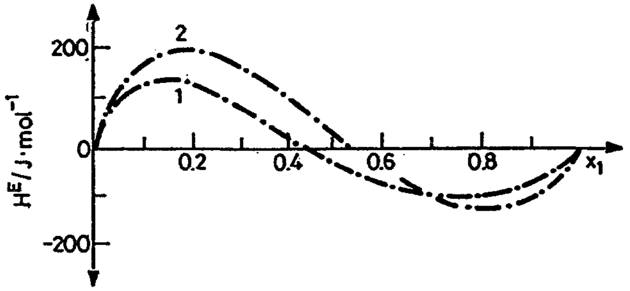

Fig. 4 H_{ch}^E for mixtures: (1) 3-picoline + *n*-hexane; (2) 3-picoline+ *n*-decane

plained by two effects. The first, according to Marcom [14] is the influence of CH_3-group position on the alone electron pair of nitrogen atom. The second is the steric hindrance at the nitrogen atom caused by the 2-positioned CH_3-group. Therefore, the degrees of association of 3- and 4-picoline should be nearly equal and both distinctly greater than that one of 2-picoline [13, 15]. The same conclusion can be drawn from the values of association constants estimated in this work (Table 2). It should be also noted that the sequence of H^E_{max} values for series of systems with particular picolines (Fig. 1) corresponds to the order of pure picolines dipol moments [16]: 2-picoline 1.97D, 3-picoline 2.4D, 4-picoline 2.6D.

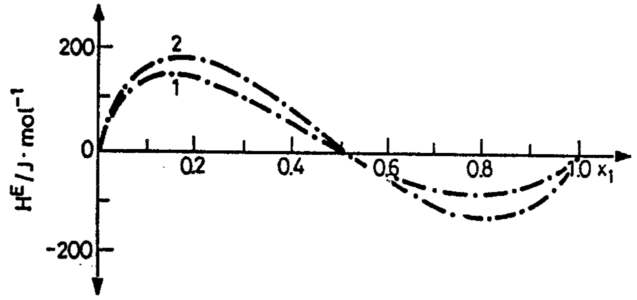

Fig. 5 H^E_{ch} for mixtures: (1) 4-picoline + *n*-hexane

Magnitudes of the H^E_{ch} terms alone, as well as rather small differences between the PFP and ERAS estimations allow to conclude, that self-association of picolines inconsiderably contributes to the total excess enthalpy of their mixtures with alkanes. Within the limits of this small differences, however, the PFP estimations are better for systems with lower alkanes, and these of ERAS – for systems with higher alkanes.

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Zusammenfassung — Die bei 298.15 K gemessenen molaren Zusatzenthalpien binärer Mischungen aus 2-,3-,4-Picolin und einem *n*-Alkan (C_6H_{14}-$C_{10}H_{22}$) wurden mit den nach der Prigonine-Flory-Patterson-Theorie und den nach dem erweiterten Modell real assoziierter Lösungen (ERAS) berechneten Werten verglichen.