EXCESS ENTHALPIES OF BINARY MIXTURES OF 2-, 3-, 4-PICOLINE + n-ALKANE (C₆H₁₄–C₁₀H₂₂) AT 298.15 K. COMPARISON WITH THEORY

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The molar excess enthalpies measured for binary mixtures of 2-, 3-, 4-picolone + n-alkane (C₆H₁₄–C₁₀H₂₂) 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 C₆–C₁₀ 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-
cess properties. In the investigated systems chemical term reflects a self-association of picolines. Denoting the physical and chemical contributions to excess enthalpy by $H_{ph}^E$ and $H_{ch}^E$ respectively, the PFP expression for excess enthalpy $H^E$ is given by:

$$H^E = H_{ph}^E = \left( \phi_1 P_1^* + \phi_2 P_2^* - \rho M \right) x_1 x_2$$

with characteristic pressure of mixture

$$p_M^* = \phi_1^* + \phi_2^* - \phi_1 \theta_2 x_1$$

where $x_{12}$ is the interaction energy parameter and $\theta_2$ the surface fraction:

$$\theta_2 = \frac{\phi_2 s_2}{\phi_1 s_1 + \phi_2 s_2}$$

with $s$ – the molecular surface-to-volume ratio and the hard core volume fraction:

$$\phi_1 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*}$$

The remaining symbols are $v_1^*$ – hard core volumes, $P_1^*$ – characteristic pressures, $\bar{v}_1$ – reduced volumes, all related to components, and $\bar{v}_M$ – reduced volume of mixture.

The ERAS expression for $H^E$ is given by:

$$H^E = H_{ph}^E + H_{ch}^E = H_{ph}^E + K \Delta h^* x_1 (\theta_1 - \theta_1^*) - x_1 \frac{p_M^*}{\bar{v}_M} K \Delta v^* (\theta_1 - \theta_1^*)$$

where the main parameters of association are: $K$ – the association constant, $\Delta h^*$, $\Delta v^*$, – the enthalpy and volume of formation of hydrogen bond, respectively.

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

$$p_1^* = \frac{\alpha - \alpha^*}{k - \alpha^* \frac{\Delta v^*}{\Delta h^*} T}$$

where $\alpha$ – thermal expansion coefficient and $\alpha^*$ – a contribution to $\alpha$ arising from association effects

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

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