Vapour-liquid equilibrium for n-alkane binary mixtures: prediction through the corresponding states principle

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Abstract. An extended corresponding-states principle for chain molecules has been used to calculate isothermal vapour-liquid equilibrium phase diagrams for binary mixtures of normal alkanes. The calculated results were compared with experimental results from the literature for n-hexane + n-hexadecane at 293.15, 303.15, 313.15, 323.15 and 333.15 K, n-hexane + n-decane, + n-undecane, + n-dodecane at 308.15 K, and n-heptane + dotriacontane at 346.15 K. Excellent agreement was found in every case.

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1. Introduction

The study of vapour-liquid equilibria (VLE) of pure fluids and mixtures is of great importance for both theoretical and practical purposes. In the first case VLE data are necessary for developing models to reproduce the experimental behaviour. It is of particular interest to have binary data available to determine the interaction parameters required in equations used to predict the phase behaviour of multi-component systems. From the practical point of view, knowledge of VLE data is important for many industrial processes, specially for mixtures of hydrocarbons of various molecular weight.

The normal alkanes have been the object of a great number of studies to determine their thermodynamic behaviour. This is due to the great importance of the n-alkanes in industrial processes, either as raw materials or as products. Furthermore, the thermodynamic properties have been used widely to test theories of the liquid state or solution models. Hence, in this work we make use of the corresponding-states principle (CSP) as applied to the thermodynamic excess properties of mixtures of n-alkanes [1] to predict isothermal vapour-liquid phase diagrams for binary mixtures of n-alkanes. Previous results from this laboratory on the thermodynamics of n-alkane mixtures include predictions of the CSP for excess heat capacity [1–3], excess enthalpy [1], excess Gibbs free energy [1], excess

entropy [1], activity coefficients at finite concentration [1], activity coefficients at infinite dilution [1,4], Henry's law constant [4,5] and excess volumes [3,6].

2. The corresponding states principle

The basic concepts and equations of the CSP were developed in previous works [1,7]. Thus, we include in the present work only the relevant equations for the calculation of vapour-liquid equilibrium data.

The quantity which is directly obtained from the CSP is the activity coefficient, γ, for each one of the components of the binary mixtures of n-alkanes. The γ is derived by differentation of the residual excess Gibbs free energy ΔG_R^E, as given by the CSP

$$\Delta G_R^E = U^* \tilde{G}_R(\tilde{T}) - x_1 U_1^* \tilde{G}_R(\tilde{T}_1) - x_2 U_2^* \tilde{G}_R(\tilde{T}_2), \tag{1}$$

where U^* is the energy reduction parameter for the mixture, taken to be a linear function of those for the pure components 1 and 2 (*i.e.* $U^* = x_1 U_1^* + x_2 U_2^*$); $\tilde{G}_R(\tilde{T})$, $\tilde{G}_R(\tilde{T}_1)$ and $\tilde{G}_R(\tilde{T}_2)$ are the reduced Gibbs energies for the mixture and the pure components, respectively. The reduction parameters for the pure n-alkanes were derived from equation-of-state data [8], whereas the universal reduced function $\tilde{G}_R(\tilde{T})$ was obtained from application of the CSP to ΔC_p^E, ΔH^E and ΔG^E experimental data for n-alkane binary mixtures [1].

After differentiation of Eq. (1), γ is given by

$$\ln \gamma_i(\text{residual}) = \frac{U_i^*}{RT} \left[\tilde{G}_R(\tilde{T}) - \tilde{G}_R(\tilde{T}_i) - (\tilde{T}_i - \tilde{T}) \tilde{S}_R(\tilde{T}) \right], \tag{2}$$

where $\tilde{S}_R(\tilde{T})$ is the reduced entropy for the mixture and calculated from the corresponding universal reduced function [1].

For completeness, we reproduce the functions for $\tilde{G}_R(\tilde{T})$ and $\tilde{S}_R(\tilde{T})$

$$\tilde{G}_R = A_0 \ln \tilde{T} - A_1 \tilde{T}(\ln \tilde{T} - 1) - \sum_{i=2}^{4} \frac{A_i \tilde{T}^i}{i(i-1)}, \tag{3}$$

$$\tilde{S}_R = -\frac{A_0}{\tilde{T}} + A_1 \ln \tilde{T} + \sum_{i=2}^{4} \frac{A_i \tilde{T}^{i-1}}{(i-1)}, \tag{4}$$

with the following values for the constants, $A_0 = 284000$, $A_1 = -3336.3$, $A_2 = 15.3172$, $A_3 = -31.3094 \times 10^{-3}$, and $A_4 = 24.387 \times 10^{-6}$.

For the calculation of the combinatorial contribution to γ we have used only the Flory approximation, since it has been shown [1] that this and the Guggenheim-Huggins-Miller-Orr approximation gives values which are essentially identical. The

Flory approximation is

$$\ln \gamma_i(\text{comb}) = \ln\left(\frac{\psi_i}{x_i}\right) + \left(1 - \frac{1}{r_i}\right)\psi_j, \tag{5}$$

where ψ_i is a segment or 'hard-core' volume fraction, defined as

$$\psi_i = 1 - \psi_j = \frac{x_i V_i^*}{(x_i V_i^* + x_j V_j^*)}, \tag{6}$$

x_i is the mole fraction, and r_i is the ratio of molecular segments of component j to component i. This ratio is calculated here as $r_i = (n_j + 1)/(n_i + 1)$, with n_i as the number of carbon atoms in the molecule.

3. Thermodynamic framework

The condition of equilibrium for a two component vapour-liquid system at temperature T and total pressure P is given by

$$f_i^V = f_i^L, \qquad i = 1, 2 \tag{7}$$

where f stands for fugacity and superscripts V and L designate, respectively, the vapour phase and liquid phase.

The component fugacities f_i are functions of temperature, pressure, and mixture composition; thus

$$f_i^V(T, P, y_i) = \phi(P, T, y)P y_i \tag{8}$$

$$f_i^L(T, P, x_i) = \gamma(P^0, T, x)x_i f_i^0(P^0, T), \tag{9}$$

where ϕ_i is the fugacity coefficient, y_i is the vapour phase mole fraction, x_i is the liquid phase mole fraction and f_i^0 is the liquid phase reference fugacity.

4. Prediction of phase equilibria

The method used for the prediction of isothermal vapour-liquid equilibrium data calculates the total pressure P and the vapour y_i and liquid x_i compositions. It may be briefly presented as follows.

A bubble-point calculation is performed with the aid of Eq. (7). The vapour phase composition was calculated by

$$y_i = \frac{\gamma_i x_i f_i^0}{\phi_i P}.$$

The Poynting term which should appear in this expression has been omitted, since it is negligible at the low pressures of this work.

An iterative procedure was employed in the calculations [9], since the total pressure was calculated by

$$P = \frac{\gamma_i x_i f_i^{0,L}}{\phi_i y_i}.$$

At the final stage of the iteration, the relation

$$\sum_{i=1}^{2} y_i = 1 \tag{10}$$

must be fulfilled while the pressure was no longer changed within a desired tolerance (in this investigation $|P_{i+1} - P_i| < 3$ kPa).

Values of $\gamma_i(P^0 = 0, T, x)$ were evaluated with Eqs. (2) and (5) using relations (3) and (4) for $\tilde{G}_R$ and $\tilde{S}_R$, respectively. The reference fugacity $f_i^{0,L}(P = 0, T)$ was calculated, as in previous work [4,5], with the correlation of Prausnitz *et al.* [10], namely,

$$\ln f^{0,L} = C_1 + \frac{C_2}{T} + C_3 T + C_4 \ln T + C_5 T^2, \tag{11}$$

where the constants C_i are characteristic of each n-alkane for a given temperature range.

The fugacity coefficients ϕ_i were evaluated from the virial equation truncated after the second coefficient

$$\ln \phi = \frac{B_i P}{RT}, \tag{12}$$

where B_i is obtained from

$$B_i = 2 \sum_{i=1}^{2} y_i B_{ij} - B, \tag{13}$$

and the second virial coefficient for the mixture is

$$B = \sum_{i=1}^{2} \sum_{j=1}^{2} y_i y_j B_{ij}(T), \tag{14}$$

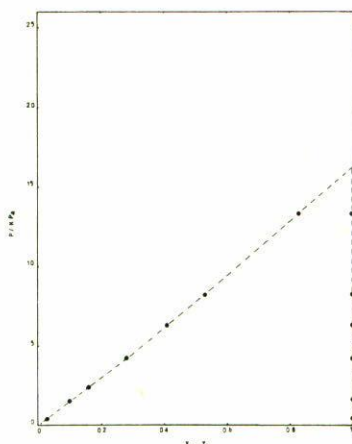with B_{ij} calculated from a relation from the literature [11].

FIGURE 1. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-hexadecane at 293.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [12].

5. Results and discussion

Calculated total pressure-vapour phase composition-liquid phase composition curves at constant-temperature conditions were compared with experimental data for n-hexane + n-hexadecane at 293.15, 303.15, 313.15, 323.15 and 333.15 K, n-hexane + n-decane, + n-undecane, + n-dodecane at 308.15 k, and n-heptane + dotriacontane at 346.15 K. The results obtained are shown in Figs. 1–9.

The n-hexane + n-hexadecane system has been the most intensively studied of the n-alkane mixtures, and it is therefore used to test the predictions in a large temperature range. Figs. 1–5 include experimental data of Ref. [12] and the p-y-x predictions for each one of the temperatures considered. It may be observed that there exists excellent agreement between both sets of data.

In Figs. 6–8 we illustrate experimental and predicted p-y-x data for the three systems formed by n-hexane as common component mixed individually with n-decane [13], n-undecane [14] and n-dodecane [15] at 308.15 K. It is clear that the agreement here is also remarkable.

We show results for an asymmetric mixture in Fig. 9, that is, one which contains components with large difference in molecular size. The predictions obtained in this work agree very well with the experimental data [16].

The comparison of results carried out in this work has shown that the CSP is capable of giving accurate values of the activity coefficients for mixtures of n-alkanes. Evidence from other works has also shown that the CSP predicts a wide variety of thermodynamic properties of liquid n-alkane mixtures with high accuracy.
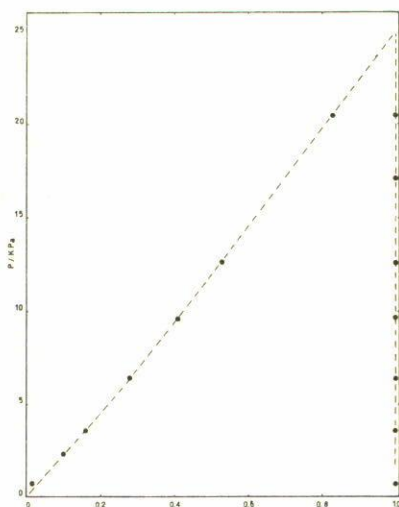
FIGURE 2. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-hexadecane at 303.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [12].
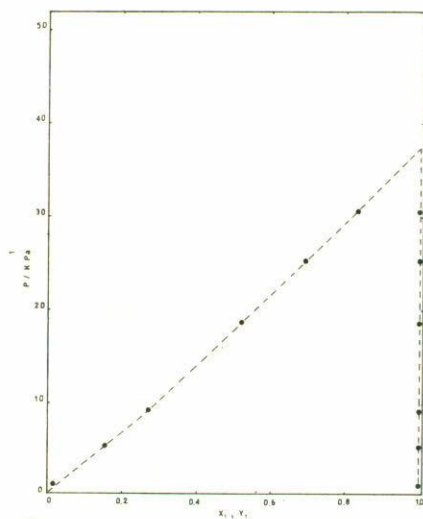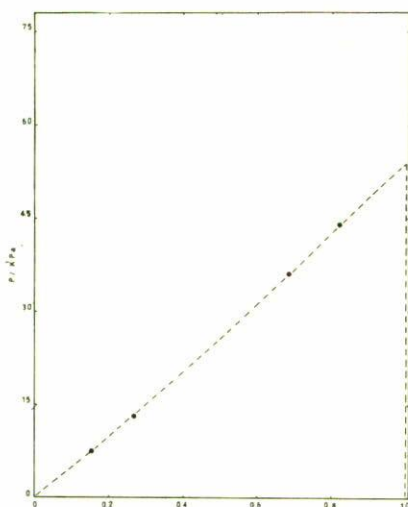

FIGURE 3. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-hexadecane at 313.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [12].
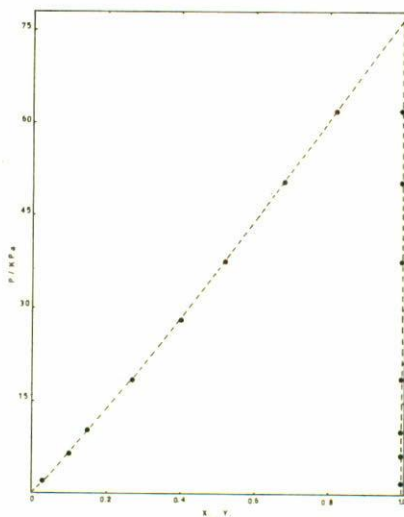
FIGURE 4. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-hexadecane at 323.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [12].
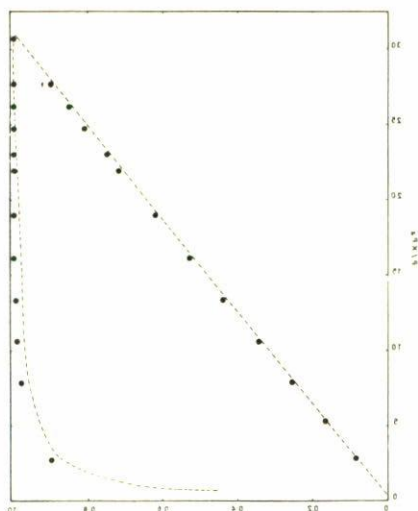

FIGURE 5. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-hexadecane at 333.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [12].

FIGURE 6. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-decane at 308.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [13].
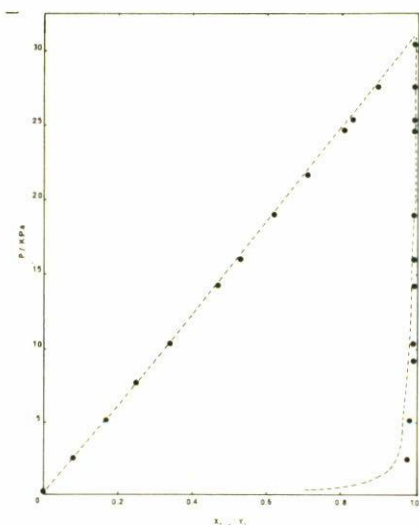

FIGURE 7. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-undecane at 308.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [14].

FIGURE 8. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-hexane + n-dodecane at 308.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [15].
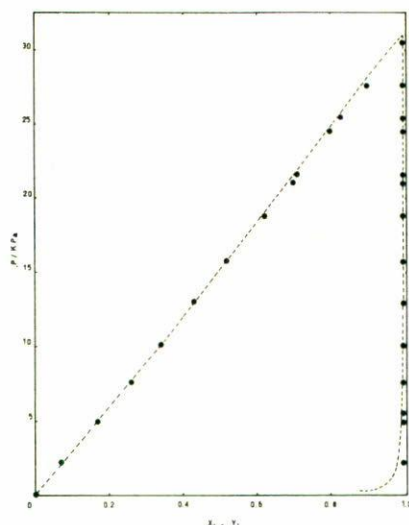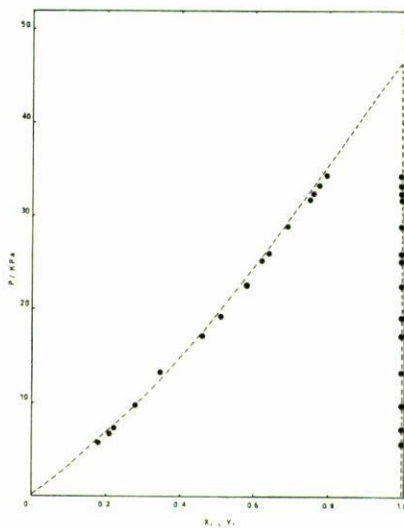

FIGURE 9. Comparison of pressure (p)-vapour phase composition (y)-liquid phase composition (x) for n-heptane + dotriacontane at 346.15 K. Full lines, calculated data of this work; points, experimental data from Ref. [16].

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Resumen. Se ha utilizado una forma extendida del Principio de Estados Correspondientes para calcular diagramas de fases vapor-líquido isotérmicos para mezclas binarias de alcanos normales. Estos resultados son comparados con datos experimentales de la literatura para n-hexano + n-hexadecano a 293.15, 303.15, 313.15, 323.15 y 333.15 K, n-hexano + n-decano, + n-undecano, + n-dodecano a 308.15 K, y n-heptano + dotriacontano a 346.15 K. En todos los casos existe excelente concordancia entre los resultados calculados y los datos experimentales.