Experimental and predicted vapour-liquid equilibrium of the binary mixtures n-heptane + chlorobutane isomers

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ABSTRACT

The study of the isothermal vapour-liquid equilibrium (VLE) of the binary mixtures n-heptane plus chlorobutane isomers (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane) at three different temperatures, T = 288.15, 298.15 and 308.15 K, is presented in this contribution. The experimental results were correlated using Wilson equation and the thermodynamic consistency of the data was checked by the van Ness method. Furthermore, two different methods have been used to predict the phase equilibrium in isothermal conditions: a pure group contribution method (modified-UNIFAC) and a group contribution equation of state (VTPR).

1.   Introduction

The study of the phase equilibrium of binary mixtures provides information of great interest for many industrial applications, especially in separation processes like distillation or extraction. To get an accurate knowledge of the phase equilibrium it is desirable to have a reliable and complete set of experimental data. However, this kind of information is not always available and it is necessary to use prediction methods, for the development and improvement of these methods [1-7] it is necessary to dispose of a phase equilibria database as large as possible.

With the aim of increasing the vapour-liquid equilibrium database and following our systematic study on vapour-liquid equilibrium of systems containing an alkane and a chloroalkane [8-10] we present here the vapour-liquid equilibrium of the four binary mixtures n-heptane plus chlorobutane isomers (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane) at T = 288.15, 298.15 and 308.15 K. These experimental vapour-liquid equilibrium data were checked for thermodynamic consistency and they were correlated using the Wilson equation [11].

Additionally, using our experimental data, two different predictions models were tested: modified-UNIFAC method and volume translated Peng–Robinson group contribution equation of state (VTPR model) that combines the VTPR equation of state with the group contribution concept.

A survey of the literature shows that there are some papers reporting the isothermal vapour-liquid equilibrium for the systems: n-heptane + 1-chlorobutane at T = 298.15 K and 323.15 K [12], and at T = 303.15 K, 323.15 K and 353.15 K [13], n-heptane + 2-chlorobutane at T = 323.15 K and 333.15 K [14], and n-heptane + 2-chloro-2-methylpropane at T = 323.15 K [14].

2. Experimental section

The information about the commercial source of the liquids used in this work, together with their purities and water contents, are shown in Table 1. The water content of the liquids was determined by using an automatic titrator Crison KF 1S-2B.

Table 1

Provenance, water content and purity of the compounds

Compound	Source	Water content (ppm)	Purity (mass %)	Analysis Method
n-Heptane	Sigma-Aldrich	150	99	GC
1-Chlorobutane	Sigma-Aldrich	308	99	GC
2-Chlorobutane	Aldrich	269	99	GC
1-Chloro-2-methylpropane	Fluka	277	99	GC
2-Chloro-2-methylpropane	Aldrich	223	99	GC

An all-glass dynamic recirculating type still equipped with a Cottrell pump has been used for the determination of the VLE. This is a Labodest model from Fischer. The equilibrium pressure is measured with a Digiquartz 735-215A-102 pressure transducer connected to a Digiquartz 735 display unit and the equilibrium temperature is obtained with a thermometer from Automatic Systems Laboratories, model F25 with a PT100 probe. The uncertainty in the pressure and temperature measurements is $\pm$ 0.05 kPa and $\pm$ 0.01 K, respectively. The following procedure was used in the study of the VLE: once the temperature and pressure are constant, the system was left to recirculate for about 45 min; time enough to consider that the equilibrium is reached. After this time, samples of the liquid and vapour phases are analysed by densitometry to know their composition by means of an Anton Paar DMA 5000 densimeter. The uncertainty in the determination of the mole fraction of the liquid and vapour phases is estimated to be 0.001.

The vapour pressure values of the pure liquids at T= 298.15 K obtained from literature [12, 15-18] and the experimental vapour pressures at working temperatures are given in Table 2.

Table 2

Properties of the pure compounds and comparison of vapour pressures with literature data at T = 298.15 K.[a]

Compound	T/ K	p / kpa		V / cm^3·mol^{-1}	B / cm^3·mol^{-1}
		Exptl.	Lit.		
	288.15	3.630		145.585	-3493
n-Heptane	298.15	6.095	6.101 [12]	147.405	-3086
	308.15	9.865		149.274	-2749
	288.15	8.400		103.891	-1914
1-Chlorobutane	298.15	13.515	13.499 [15]	105.088	-1722
	308.15	21.035		106.462	-1560
	288.15	13.360		105.340	-1815
2- Chlorobutane	298.15	20.905	20.969 [16]	106.710	-1641
	308.15	31.550		108.135	-1492
	288.15	13.000		104.808	-1896
1-Chloro-2-methylpropane	298.15	20.350	19.85 [17]	106.176	-1691
	308.15	30.450		107.597	-1522
	288.15	26.420		109.000	-1209
1-Chloro-2-methylpropane	298.15	40.130	40.054 [18]	110.582	-1140
	308.15	59.520		112.234	-1076

[a] Standard uncertainties u are $u(T) = 0.01$ K, and $u(p) = 0.05$ kPa.

3. Results and discussion

The Wilson equation [11] was used to correlate the activity coefficients, γ_i, with the temperature, T, and the mole fraction of liquid phase, x_i.

$$ln\gamma_1 = -ln\left(x_1 + \Lambda_{12} x_2\right) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right) \tag{1}$$

$$ln\gamma_2 = -ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{2}$$

$$\Lambda_{ij} = \frac{V_j^\circ}{V_i^\circ}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{3}$$

where V_i° is the molar volume of component i in the liquid phase at $T = 298.15$ K, (λ_{ij}-λ_{ii}) are the Wilson parameters, T is the absolute temperature and R is the gas constant.

Wilson parameters have been calculated by minimizing the objective function [19] in terms of experimental and calculated pressures:

$$F = \sum_{i=1}^{n}\left(\frac{p^{exp} - p^{cal}}{p^{exp}}\right)_i^2 \tag{4}$$

The calculated pressure is obtained considering the non-ideality of the vapour phase, the second virial coefficients, and the variation of the Gibbs energies of the pure liquids with pressure.

$$p^{cal} = \sum_{i=1}^{2}x_i\gamma_i p_i^\circ \exp\left[\frac{\left(V_i^\circ - B_{ii}\right)\left(p - p_i^\circ\right) - \left(1 - y_i\right)^2 p\delta_{ij}}{RT}\right] \tag{5}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{6}$$

where y_i and p_i° are the vapour phase mole fraction and the vapour pressure of the component i, respectively, p is the total pressure and B_{ii} is the second virial coefficient of compound i that for n-heptane, 1-chlorobutane, 2-chlorobutane, and 2-chloro-2-methylpropane were obtained from TRC tables [20,21] and for 1-chloro-2-methylpropane was estimated with Tsonopoulos method [22,23], B_{ij} is the cross second

virial coefficient and it can be obtained as the average of the second virial coefficients of the pure compounds.

The estimated parameters of the Wilson equation together with the corresponding average deviations in pressure, Δp, and vapour-phase composition, Δy, for each system are gathered in Table 3. The consistency of the experimental data was examined trough the van Ness method, described by Fredenslund et al. using the excess Gibbs energies fitted with the Wilson equation. According to this test, if the average deviation in vapour composition, Δy, is less than 0.01, experimental data can be considered consistent. All the systems studied satisfied this condition as it can be seen in Table 3, where the resulting Δy values are given.

Experimental VLE data, the correlated activity coefficients and the calculated excess Gibbs energies are given in the supplementary material. The pressure-composition diagrams, p-x_1-y_1 are shown in Figures 1 to 4, and the excess Gibbs energies at $T = 298.15$ K are represented in Figure 5.

Table 3
Correlation parameters for the Wilson Equation, average deviation in vapour pressure, Δp, and average deviation in vapour-phase composition, Δy

System	λ_{12}-λ_{11} (J mol^{-1})	λ_{21}-λ_{22} (J mol^{-1})	Δp (kPa)	Δy
n-Heptane + 1-chlorobutane	-412.07	1700.21	0.023	0.0047
n-Heptane + 2-chlorobutane	-702.71	1906.24	0.068	0.0070
n-Heptane + 1-chloro-2-methylpropane	-718.44	1784.52	0.073	0.0079
n-Heptane + 2-chloro-2-methylpropane	74.48	1092.25	0.042	0.0062

The p-x_1 diagram of Sayegh et al. [12] for the mixture n-heptane + 1-chlorobutane at $T = 298.15$ K have been also plotted in Figure 1. The average deviation in pressure between their results and ours is 0.069 kPa.
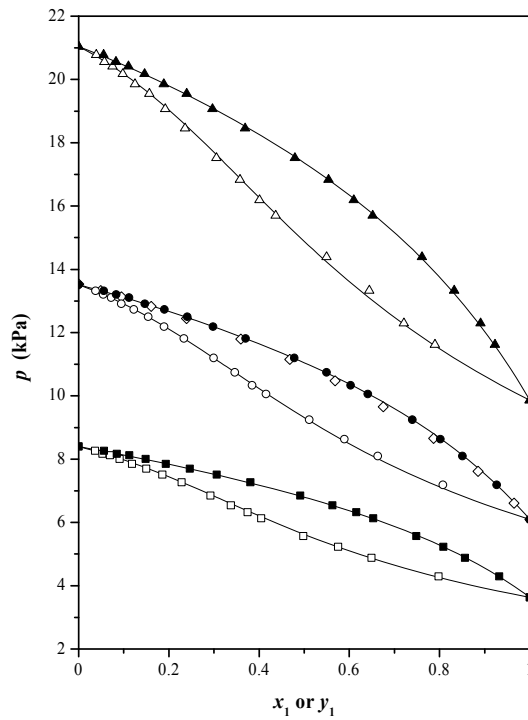
Figure 1. *p-x₁-y₁* diagrams for the binary mixture n-heptane (1) + 1-chlorobutane (2): (□,■) experimental data at T = 288.15 K; (○,●) experimental data at T = 298.15 K; (◇) ref. [12]; (Δ,▲) experimental data at T = 308.15 K; (——) Wilson correlation.

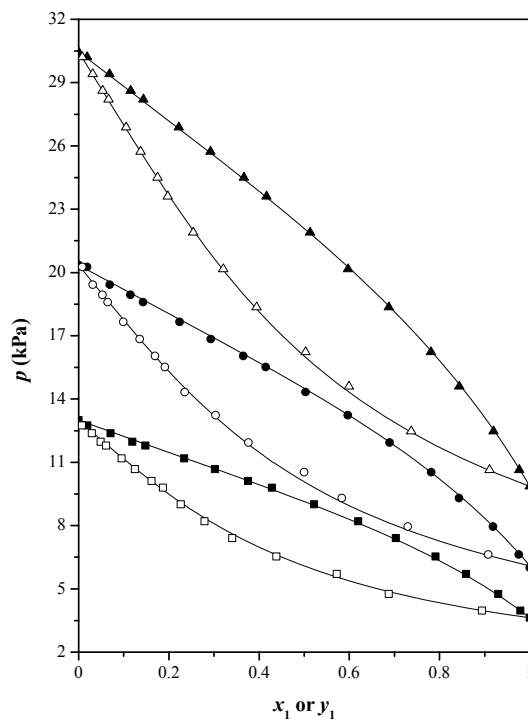**Figure 2.** *p-x₁-y₁* diagrams for the binary mixture n-heptane (1) + 2-chlorobutane (2): (□,■) experimental data at T = 288.15 K; (○,●) experimental data at T = 298.15 K; (Δ,▲) experimental data at T = 308.15 K; (——) Wilson correlation.
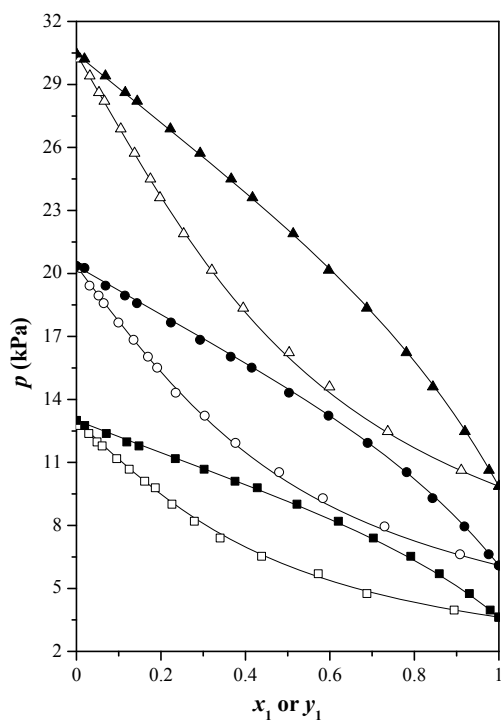
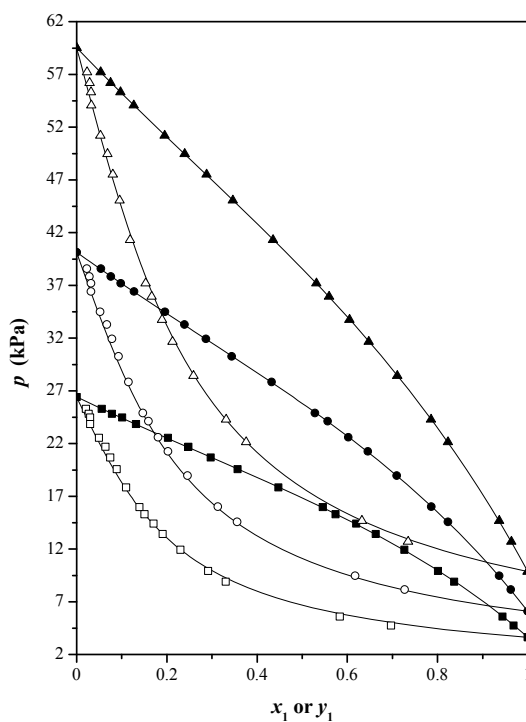**Figure 3.** p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 1-chloro-2-methylpropane (2): ($\square$,$\blacksquare$) experimental data at T = 288.15 K; ($\circ$,$\bullet$) experimental data at T = 298.15 K; ($\triangle$,$\blacktriangle$) experimental data at T = 308.15 K; (——) Wilson correlation.

Figure 4. p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 2-chloro-2-methylpropane (2): ($\square$,$\blacksquare$) experimental data at T = 288.15 K; ($\circ$,$\bullet$) experimental data at T = 298.15 K; ($\triangle$,$\blacktriangle$) experimental data at T = 308.15 K; (——) Wilson correlation.

For all mixtures, the excess Gibbs energies are positive and G^E values increase with temperature, although this temperature effect is very small. At $T = 298.15$ K, the excess Gibbs energies follow the sequence: 1-chlorobutane > 2-chloro-2-methylpropane ≈ 2-chlorobutane > 1-chloro-2-methylpropane. This sequence is similar to that of the mixtures containing n-hexane and the isomeric chlorobutanes, but the G^E values are now bigger, around 20 J·mol^{-1}.
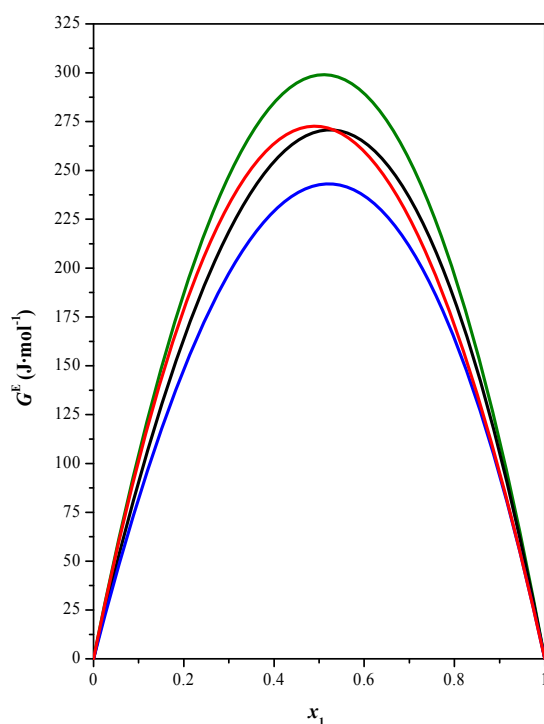

Figure 5. Excess Gibbs functions, G^E, at $T = 298.15$ K for n-heptane (1) + isomeric chlorobutane (2): (——) 1-chlorobutane; (——) 2-chlorobutane; (——) 1-chloro-2-methylpropane; (——) 2-chloro-2-methylpropane.

4.   UNIFAC and VTPR predictions

In this work, two different methods (modified-UNIFAC and VTPR) have been used to predict the vapour-liquid equilibrium of binary mixtures n-heptane + chlorobutane isomers.

The group interaction parameters for both methods [24,25], needed for the estimation of vapour-liquid equilibrium, are given in the supplementary material, on the

other hand all the properties of pure compounds required for the VTPR model calculations have been taken directly from Dortmund Data Bank [26] and they are also given in the supplementary material.

The accuracy of the predictions of both methods was tested by comparing the experimental VLE data with the calculated ones. The results are graphically represented in Figures 6 to 9 and numerically shown in Table 4. For modified-UNIFAC method the overall average deviations are $\Delta p = 0.565$ kPa and $\Delta y = 0.0100$, the predictions are slightly better at lower temperatures; the best results correspond to the system n-heptane + 1-chloro-2-methylpropane, with $\Delta p = 0.0759$ kPa and $\Delta y = 0.0022$, while the biggest deviations are obtained for the binary system n-heptane + 2-chloro-2-methylpropane, with $\Delta p = 1.545$ kPa and $\Delta y = 0.0195$. It can be outlined that the predictions using the new parameters, NIST-modified-UNIFAC parameters, provided by Kang et al. [24] are better than those obtained with the original modified-UNIFAC parameters [4] (overall average deviations: $\Delta p = 0.786$ kPa, $\Delta y = 0.00162$).

Table 4
Modified-UNIFAC and VTPR predictions: average deviation in vapour pressure, Δp, and average deviation in vapour phase composition, Δy.

System	UNIFAC		VTPR	
	Δp (kPa)	Δy	Δp (kPa)	Δy
n-Heptane + 1-chlorobutane	0.147	0.0051	0.288	0.0123
n-Heptane + 2-chlorobutane	0.491	0.0132	0.353	0.0109
n-Heptane + 1-chloro-2-methylpropane	0.076	0.0022	0.272	0.0082
n-Heptane + 2-chloro-2-methylpropane	1.545	0.0195	0.751	0.0085
Overall average	0.565	0.0100	0.416	0.0100

For the VTPR model the overall average deviations are lower than for the modified-UNIFAC method being the VTPR values Δp = 0.416 kPa and Δy = 0.0100, for this model the predictions are also slightly better at lower temperatures. The smallest deviations, with a difference between experimental and predicted values, Δp = 0.272 kPa and Δy = 0.0082, are obtained for the binary mixture n-heptane + 1-chloro-2-methylpropane, the highest deviations correspond to the binary system n-heptane + 2-chloro-2-methylpropane with Δp = 0.751 kPa and Δy = 0.0116.

The predictions with the VTPR model are better than the modified-UNIFAC ones for the systems containing n-heptane and a secondary or tertiary chlorobutane.
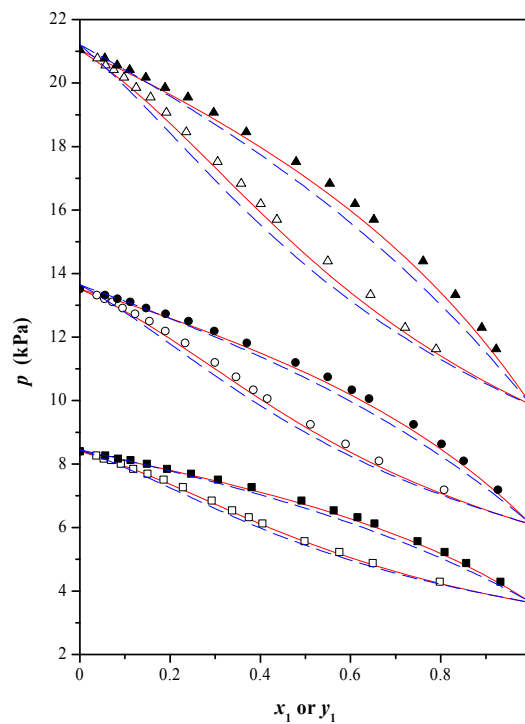

Figure 6. p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 1-chlorobutane (2): (■, □) experimental data at T = 288.15 K; (●, ○) experimental data at T = 298.15 K; (▲, △) experimental data at T = 308.15 K; (——) mod-UNIFAC prediction; (— —) VTPR prediction.
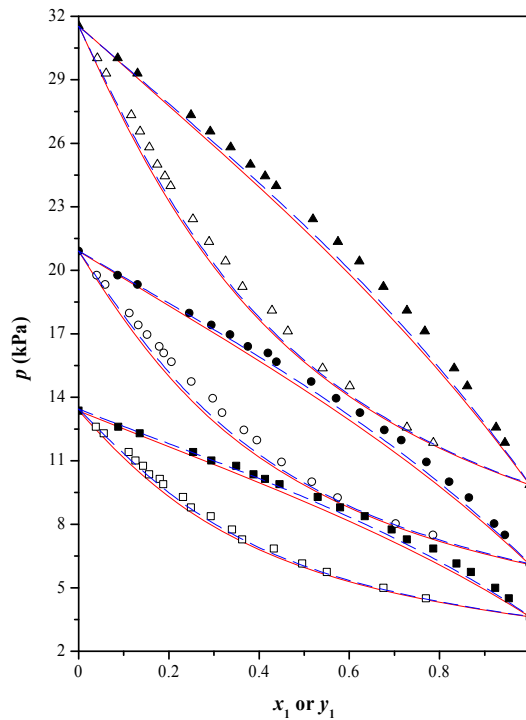
Figure 7. p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 2-chlorobutane (2): (■, □) experimental data at T = 288.15 K; (●, ○) experimental data at T = 298.15 K; (▲, △) experimental data at T = 308.15 K; (——) mod-UNIFAC prediction; (— —) VTPR prediction.
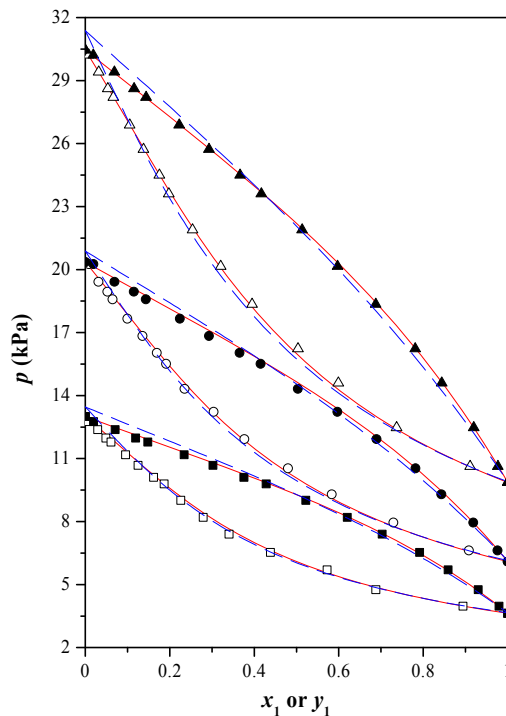

Figure 8. p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 1-chloro-2-methylpropane (2): (■, □) experimental data at T = 288.15 K; (●, ○) experimental data at T = 298.15 K; (▲, △) experimental data at T = 308.15 K; (——) mod-UNIFAC prediction; (— —) VTPR prediction.
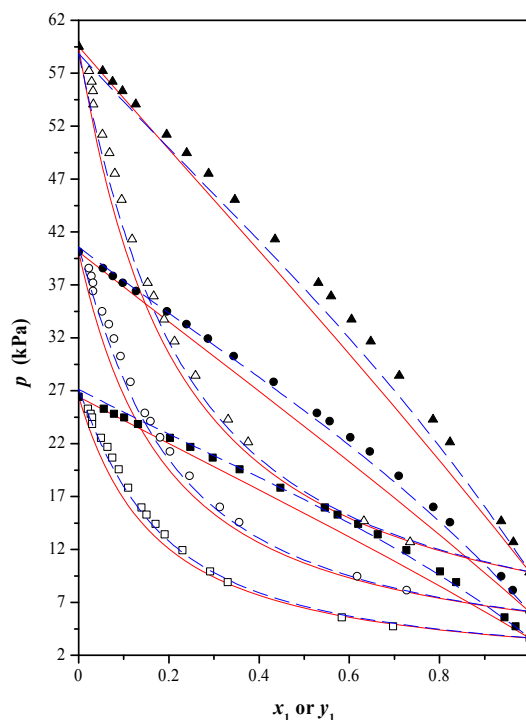
Figure 9. p-x_1-y_1 diagrams for the binary mixture n-heptane (1) + 2-chloro-2-methylpropane (2): (■, □) experimental data at T = 288.15 K; (●, ○) experimental data at T = 298.15 K; (▲, △) experimental data at T = 308.15 K; (——) mod-UNIFAC prediction; (— —) VTPR prediction.

5.   Conclusions

The vapour-liquid equilibrium for binary mixtures containing n-heptane and chlorobutane isomers (1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane and 2-chloro-2-methylpropane) has been studied at three temperatures: T = 288.15, 298.15 and 308.15 K, activity coefficients and excess Gibbs energies have been obtained from experimental data. G^E are positive for all the systems and at T = 298.15 K show this tendency: 1-chlorobutane > 2-chloro-2-methylpropane ≈ 2-chlorobutane ⪢ 1-chloro-2-methylpropane.

Experimental data have been used to test the accuracy of two prediction methods: modified-UNIFAC and VTPR; being the modified-UNIFAC results slightly better for the systems n-heptane + 1-chlorobutane and n-heptane + 1-chloro-2-

methylpropane, while for the systems n-heptane + 2-chlorobutane and n-heptane + 2-chloro-2-methylpropane the VTPR predictions are more accurate.

Acknowledgements

List of symbols

B_{ii} second virial coefficient of component i ($cm^3 \cdot mol^{-1}$)

B_{ij} cross second virial coefficient ($cm^3 \cdot mol^{-1}$)

G^E excess Gibbs function ($J \cdot mol^{-1}$)

p total pressure (kPa)

p_i° vapour pressure of component i (kPa)

R molar gas constant (= 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$)

T temperature (K)

V_i° molar volume of component i ($m^3 \cdot mol^{-1}$)

x_i mole fraction of component i in the liquid phase

y_i mole fraction of component i in the vapour phase

Greek letters

Δ average deviation

γ_i activity coefficient of component i

$\Lambda_{12}, \Lambda_{21}$ parameters for Wilson equation

$\lambda_{ij} - \lambda_{ii}$ adjustable parameters for Wilson equation ($J \cdot mol^{-1}$)

Subscripts

cal calculated

exp experimental

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