



# 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).

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## 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.

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

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**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              |

**Table 2**Properties of the pure compounds and comparison of vapour pressures with literature data at  $T = 298.15 \text{ K}^a$ 

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

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.01 \text{ K}$ , and  $u(p) = 0.05 \text{ kPa}$ .

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 density-meter. 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  $T = 298.15 \text{ K}$  obtained from literature [12,15–18] and the experimental vapour pressures at working temperatures are given in Table 2.

### 3. Results and discussion

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

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

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

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

where  $V_i^\circ$  is the molar volume of component  $i$  in the liquid phase at  $T = 298.15 \text{ K}$ ,  $(\lambda_{ij} - \lambda_{ii})$  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:

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

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.

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

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (6)$$

where  $y_i$  and  $p_i^\circ$  are the vapour phase mole fraction and the vapour pressure of the component  $i$ , respectively,  $p$  is the total pressure and

**Table 3**Correlation parameters for the Wilson Equation, average deviation in vapour pressure,  $\Delta p$ , and average deviation in vapour-phase composition,  $\Delta y$ .

| System                               | $\lambda_{12} - \lambda_{11} \text{ (J mol}^{-1}\text{)}$ | $\lambda_{21} - \lambda_{22} \text{ (J mol}^{-1}\text{)}$ | $\Delta p \text{ (kPa)}$ | $\Delta y$ |
|--------------------------------------|---|---|--------------------------|------------|
| 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     |

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