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# Isobaric Vapor−Liquid Equilibrium for the Binary Systems 1-Pentanol + Cyclohexane and 1-Pentanol + *n*-Hexane at Low Alcohol Compositions

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Isobaric vapor−liquid equilibrium at 101.3 kPa has been measured for the systems 1-pentanol + cyclohexane and 1-pentanol + *n*-hexane, at low alcohol mole fractions. These data were satisfactorily correlated with Wilson, NRTL, and UNIQUAC activity coefficient models to obtain the binary interaction parameters of both mixtures. With these parameters, an accurate knowledge of vapor−liquid equilibrium for both mixtures can be reached in a range of 1-pentanol mole fractions less than 0.1.

## Introduction

Processes based on distillation operations are extensively used for the separation of a great number of liquid mixtures. For this reason, knowledge of vapor−liquid equilibrium data is of great importance, to accurately design the required equipment. Furthermore, it is very important to obtain the equilibrium data in the range of compositions in which the separation is being developed.

Cyclohexane and *n*-hexane are solvents employed in many processes, and equilibrium data with both compounds have been obtained. 1-Pentanol belongs to one of the most important additive groups, called polar modifiers. High and medium molecular weight alcohols have been demonstrated to act properly as polar modifiers, due to their hydroxyl group at the end of a hydrocarbon chain.

Equilibrium data for 1-pentanol with other alcohols such as 1-propanol[1] and ethanol[2] have been determined previously in binary or ternary systems, but there is no reported work dealing with equilibrium data of the binary system proposed here. The most similar publication[3] works deal with a quaternary mixture of benzene + cyclohexane + 1-pentanol + anisole.

This paper reports the results of measurements of vapor−liquid equilibrium for the binary systems 1-pentanol + cyclohexane and 1-pentanol + *n*-hexane at low alcohol concentrations and atmospheric pressure. In most of the processes, the higher concentration of polar modifiers is always below 10 % mole fraction; for this reason, only this zone of the equilibrium curve has been taken into account, to obtain higher resolution on the curve.

All equilibrium data were fit to Wilson,[4] NRTL,[5] and UNIQUAC[6] activity coefficient models, to obtain the binary interaction parameters of these models and to introduce them in the simulation model. The data fit was done using ASPEN PLUS commercial software because this is the same software employed to develop the simulation model. No measurements of vapor−liquid equilibrium of this system have been previously reported.

**Table 1. Vapor−Liquid Equilibrium Data for 1-Pentanol (1) + Cyclohexane (2) at $P$ = 101.3 kPa**

| $x_1$ | $y_1$ | $T_b$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| 0.0059 | 0.0057 | 353.8 | 9.538 | 1.003 |
| 0.0095 | 0.0083 | 353.9 | 8.535 | 1.002 |
| 0.0106 | 0.0090 | 353.9 | 8.323 | 1.002 |
| 0.0157 | 0.0125 | 354.0 | 7.780 | 1.001 |
| 0.0222 | 0.0155 | 354.1 | 6.804 | 1.002 |
| 0.0272 | 0.0184 | 354.3 | 6.493 | 0.998 |
| 0.0335 | 0.0204 | 354.4 | 5.820 | 1.000 |
| 0.0436 | 0.0238 | 354.3 | 5.254 | 1.010 |
| 0.0457 | 0.0239 | 354.5 | 4.983 | 1.007 |
| 0.0496 | 0.0250 | 354.4 | 4.824 | 1.013 |
| 0.0554 | 0.0268 | 354.6 | 4.590 | 1.011 |
| 0.0654 | 0.0284 | 354.7 | 4.099 | 1.018 |
| 0.0680 | 0.0292 | 354.7 | 4.055 | 1.020 |

**Table 2. Vapor−Liquid Equilibrium Data for 1-Pentanol (1) + *n*-Hexane (2) at $P$ = 101.3 kPa**

| $x_1$ | $y_1$ | $T_b$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| 0.0106 | 0.0072 | 341.9 | 12.967 | 1.004 |
| 0.0207 | 0.0102 | 342.0 | 9.293 | 1.008 |
| 0.0278 | 0.0130 | 342.4 | 8.672 | 1.002 |
| 0.0288 | 0.0131 | 342.4 | 8.469 | 1.003 |
| 0.0354 | 0.0142 | 342.2 | 7.545 | 1.015 |
| 0.0395 | 0.0150 | 342.4 | 7.043 | 1.013 |
| 0.0467 | 0.0159 | 342.5 | 6.272 | 1.016 |
| 0.0518 | 0.0172 | 342.4 | 6.174 | 1.024 |
| 0.0657 | 0.0193 | 342.6 | 5.380 | 1.031 |
| 0.0694 | 0.0197 | 342.9 | 5.115 | 1.025 |
| 0.0835 | 0.0204 | 342.7 | 4.446 | 1.045 |
| 0.0904 | 0.0209 | 342.7 | 4.208 | 1.052 |
| 0.0958 | 0.0214 | 342.7 | 4.062 | 1.058 |

## Experimental Section

***Materials.*** All chemical reagents used were analytical grade and were purchased from Aldrich.

***Apparatus and Procedure.*** The experiments were carried out in an apparatus, which had been previously used before.[7−9] In this apparatus, entirely made out of glass, both the liquid and vapor phases are continuously recirculated to provide proper mixing of the phases and to ensure that equilibrium was established. The vapor condenser is connected to a constant-pressure system controlled by a Cartesian manostat. Pressure was kept constant at (101.32 ± 0.1) kPa. The equilibrium temperatures were measured with a certified thermocouple type J. with a precision of ± 0.1 °C.

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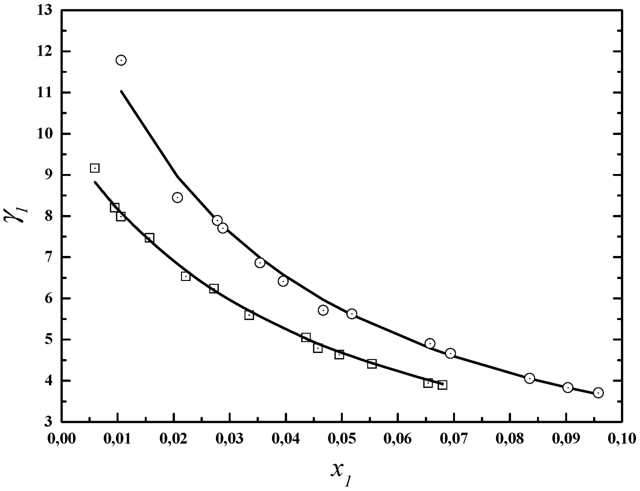

**Figure 1.** 1-Pentanol activity coefficients as a function of 1-pentanol mole fraction: □, experimentally determined for the 1-pentanol + cyclohexane system at $P = 101.32$ kPa; ○, experimentally determined for the 1-pentanol + *n*-hexane system at $P = 101.32$ kPa; -, values obtained with the Wilson model.

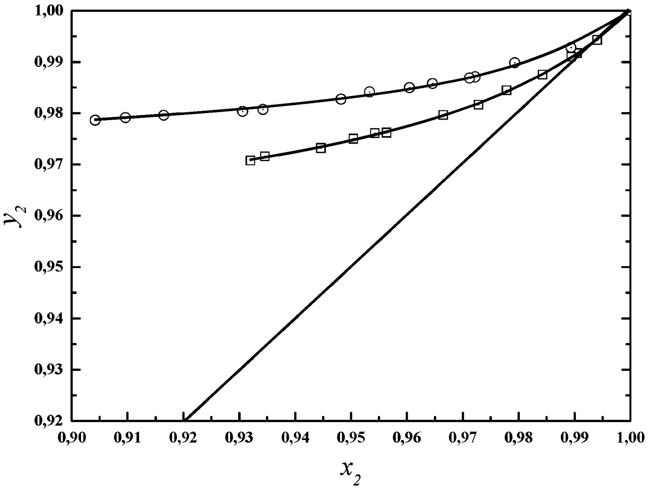

**Figure 2.** Vapor mole fractions as a function of liquid mole fractions at $P = 101.32$ kPa. □, liquid cyclohexane mole fraction as a function of vapor cyclohexane mole fraction for the 1-pentanol + cyclohexane system; ○, liquid *n*-hexane mole fraction as a function of vapor *n*-hexane mole fraction for the 1-pentanol + *n*-hexane system; -, values regressed with the Wilson model.

**Table 3. Antoine Equation Parameters[a] of the Pure Substances**

| compound | *A* | *B* | *C* | temp range/K |
|---|---|---|---|---|
| cyclohexane | 13.74 | −2766.63 | −50.5 | 280 to 380 |
| *n*-hexane | 13.82 | −2697.55 | −48.78 | 245 to 370 |
| 1-pentanol | 14.51 | −3026.89 | −105.0 | 310 to 411 |

[a] $\ln P_i^0(\text{kPa}) = A + B/[T/\text{K} + C]$.

**Table 4. Temperature, $\sigma(T) = [T(\text{exptl}) - T(\text{calcd})]^2$, 1-Pentanol Vapor Mole Fraction, $\sigma(y_1) = [y_1(\text{exptl}) - y_1(\text{calcd})]^2$, and Root-Mean-Square Deviations for the Methods Tested**

| 1-pentanol (1) + cyclohexane (2) | | | 1-pentanol (1) + *n*-hexane (2) | | |
|---|---|---|---|---|---|
| method | $100\cdot\sigma(T)$ | $100\cdot\sigma(y_1)$ | method | $100\cdot\sigma(T)$ | $100\cdot\sigma(y_1)$ |
| Wilson | 0.22 | 1.35 | Wilson | 0.18 | 2.95 |
| NRTL | 0.22 | 1.42 | NRTL | 0.16 | 4.00 |
| UNIQUAC | 0.22 | 1.75 | UNIQUAC | 0.17 | 4.15 |

**Table 5. $b_{12}$ and $b_{21}$ Coefficients of the Binary Interaction Parameters of the Wilson, NRTL, and UNIQUAC Models for 1-Pentanol (1) + Cyclohexane (2)**

| | Wilson | NRTL | UNIQUAC |
|---|---|---|---|
| $b_{12}$ | −878.96 | 359.25 | 227.58 |
| $b_{21}$ | 60.30 | 663.43 | −536.59 |

**Table 6. $b_{12}$ and $b_{21}$ Coefficients of the Binary Interaction Parameters of the Wilson, NRTL, and UNIQUAC Models for 1-Pentanol (1) + *n*-Hexane (2)**

| | Wilson | NRTL | UNIQUAC |
|---|---|---|---|
| $b_{12}$ | −928.53 | 303.67 | 230.36 |
| $b_{21}$ | 15.96 | −304.32 | −571.31 |

The liquid and condensed vapor analyses were carried out by gas chromatography on a Perkin-Elmer A/S gas chromatograph with a flame ionization detector. The capillary column was a J&W DB-23. The estimated uncertainty for mole fractions was estimated as ± $3\cdot10^{-4}$.

## Results and Discussion

In Tables 1 and 2 vapor−liquid equilibrium data ($x_1$, $y_1$, $T$) and experimental liquid phase activity coefficients are presented for both the mixtures studied in the work. These coefficients were calculated from eqs 1 and 2.

$$\gamma_i = \frac{y_i P}{x_i P_i^0}\cdot\exp\left[\frac{(B_{ij} - v_i)(P - P_i^0) + (1 - y_i)P\delta_{ij}}{RT}\right] \quad (1)$$

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

where $\gamma_i$ is the activity coefficient; $x_1$ and $y_1$ are the liquid and vapor equilibrium mole fractions; $P$ is the total pressure; $P_i^0$ is the pure component vapor pressure; $v_i$ is the liquid molar volume; $R$ is the universal gas constant; $T$ is the absolute temperature; $B_{ii}$ is the second virial coefficient of the pure gas; and $B_{ij}$ is the cross second virial coefficient; both coefficients were calculated according to the Tsonopoulos correlation.[10] To calculate the vapor pressure of the pure components, the Antoine equation was employed. The Antoine constants taken from Reid and Prausnitz[11] are shown in Table 3. As can be seen in Tables 1 and 2, the two systems present a positive deviation of ideality.

The experimental data were tested to evaluate the thermodynamic consistency using the method described by Fredenslund et al.[12] and the L−W method of Wisniak.[13] Both tests were performed using PRO-VLE 2.0.[14]

To develop the first test, a four-term Legendre polynomial was used to correlate the excess Gibbs energy. According this criterion, the experimental data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, $\Delta y$, is less than 0.01. For the two mixtures studied in this work, the results obtained are $\Delta y = 0.0003$ for the 1-pentanol + cyclohexane system and $\Delta y = 0.0009$ for the 1-pentanol + *n*-hexane system. The results of the test indicate that data obtained for both systems are thermodynamically consistent.

Concerning the L−W method, the values obtained of $D = 100(L - W)/(L + W)$[13] were less than 3 in both mixtures (1.8 for cyclohexane + 1-pentanol and 2.6 for *n*-hexane + 1-pentanol), indicating that the data were thermodynamically consistent.

The equilibrium data were correlated with the Wilson,[4] NRTL,[5] and UNIQUAC[6] activity coefficient models, by using ASPEN PLUS commercial software. This software uses an objective function called "maximum likelihood" which minimizes the difference between the experimental and fitted data for all the variables that appear in adjustment (pressure, temperature, and liquid and vapor composition of both components).

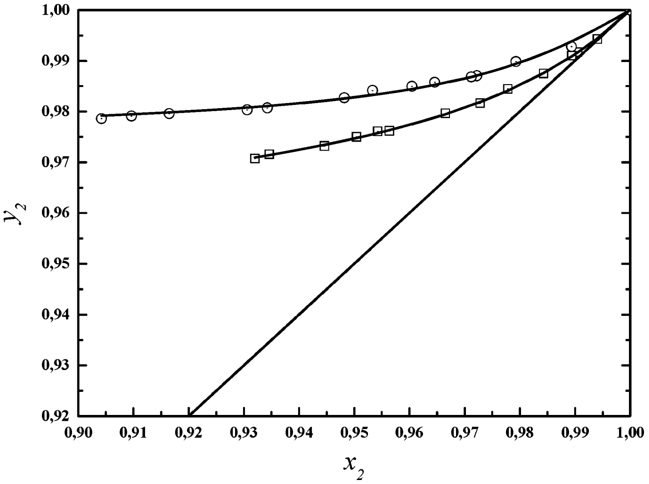

**Figure 3.** Vapor mole fractions as a function of liquid mole fractions at $P = 101.32$ kPa. □, liquid cyclohexane mole fraction as a function of vapor cyclohexane mole fraction for the 1-pentanol + cyclohexane system; ○, liquid *n*-hexane mole fraction as a function of vapor *n*-hexane mole fraction for the 1-pentanol + *n*-hexane system; -, values regressed with the NRTL model.

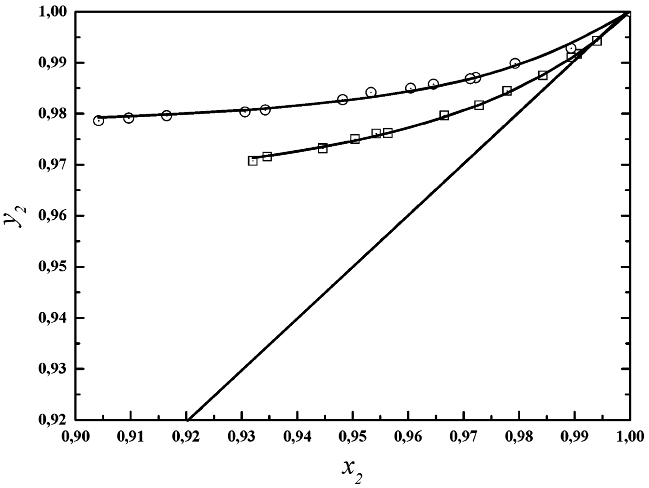

**Figure 4.** Vapor mole fractions as a function of liquid mole fractions at $P = 101.32$ kPa. □, liquid cyclohexane mole fraction as a function of vapor cyclohexane mole fraction for the 1-pentanol + cyclohexane system; ○, liquid *n*-hexane mole fraction as a function of vapor *n*-hexane mole fraction for the 1-pentanol + *n*-hexane system; -, values regressed with the UNIQUAC model.

The equation type of the Wilson model, which this software employs to calculate the activity coefficient in a multicomponent mixture, is described in eq 3.

$$\ln \gamma_{ij} = 1 - \ln(\sum_j A_{ij}x_j) - \sum_j \frac{A_{ji}x_j}{\sum_k A_{jk}x_k} \tag{3}$$

In this expression, $x_i$ represents liquid mole fraction of component $i$, and the binary interaction parameters ($A_{ij}$, $A_{ji}$) are defined as a function of temperature in eq 4.

$$\ln A_{ij} = \ln\left(\frac{v_j}{v_i}\right) + \frac{b_{ij}}{T} \tag{4}$$

where $v_i$ and $v_j$ are the liquid molar volumes at the system temperature calculated using the Rackett[15] model.

For the NRTL model, the equation type employed by ASPEN PLUS is described in eq 5.

$$\ln \gamma_{ij} = \frac{\sum_{j=1}^{C} \tau_{ji}G_{ji}x_j}{\sum_{k=1}^{C} x_kG_{ki}} + \sum_{j=1}^{C} \frac{x_jG_{ij}}{\sum_{k=1}^{C} x_kG_{kj}}\left[\tau_{ij} - \frac{\sum_{n=1}^{C} \tau_{nj}G_{nj}x_n}{\sum_{k=1}^{C} x_kG_{kj}}\right] \tag{5}$$

As before, $x_i$ represents liquid mole fraction of component $i$, and the binary interaction parameters ($\tau_{ij}$, $\tau_{ji}$) are defined as a function of temperature in eq 6.

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad \alpha_{ij} = c_{ij} \tag{6}$$

The "nonrandomness factor", α, values range from 0.2 to 0.47.[5] In this work, a constant value of 0.3, which is adequate for nonpolar substances,[5] has been used.

For the UNIQUAC model, the equation type employed by ASPEN PLUS is described in eq 7.

$$\ln \gamma_{ij} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2}q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) - q'_i \ln t'_i - q'_i \sum_j \frac{\theta'_j\tau_{ij}}{t'_i} + l_i + q'_i - \frac{\Phi_i}{x_i}\sum_j x_jl_j \tag{7}$$

In this case, the binary interaction parameters are defined as a function of temperature as

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} + c_{ij}\ln T + d_{ij}T\right) \tag{8}$$

and the other parameters are structural ones, defined for each component.[6]

In Tables 5 and 6, the Wilson, NRTL, and UNIQUAC $b_{12}$ and $b_{21}$ adjusted constants of the binary interaction parameters are shown. As an example, Figure 1 shows the experimental activity coefficients along with the regressed ones obtained for the Wilson model. Figures 2, 3, and 4 show the $x-y$ graphs to compare experimental and regressed data. As can be seen, all three models fit accurately the experimental data for both mixtures by considering only the $b_{ij}$ constants of the binary interaction parameters; for this reason, it was not necessary to introduce more adjusting constants. To support this statement, in Table 4, the mean percentage deviations of temperature and 1-pentanol vapor mole fraction are presented.

With the obtained parameters, an accurate knowledge of vapor−liquid equilibrium for both mixtures can be made in the range of less than 0.01 mole fractions of 1-pentanol.

## Conclusion

Consistent VLE data at $P = 101.3$ kPa have been determined for the binary systems 1-pentanol + cyclohexane and 1-pentanol + *n*-hexane at low alcohol mole fractions. Wilson, NRTL, and UNIQUAC models fit accurately the experimental data, which allow the use of the binary interaction parameters obtained to develop vapor−liquid equilibrium calculations of both mixtures.

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