Abstract

The present work goals the study of vapor-liquid equilibrium (VLE) of binary system composed by heptane and dodecane. The importance of VLE study lies on its applications on industrial processes, such as separation and also for the description of vapor-liquid coexistence loci. The experimental stage of this work consists on the obtainment of a calibration curve, which correlates the mixture density with the molar fraction of the components. Afterwards many experiments are performed using an ebulliometer, model VLE-602 FISCHER with pressure control. Each experiment provides two samples, which contains liquid and condensed vapor phases. The molar fraction of components in each phase is determined by a calibration curve. The ebulliometer also provides the vapor and liquid temperatures and the pressure in which the experiment was taken.

The data obtained on the experimental stage of this work are used for the estimation of binary interaction parameters of the Wilson model. The determination of these parameters appears as an optimization task through the minimization of an objective-function (or fitness function). For such, a stochastic method known as Differential Evolution was applied. This method consists in a simple and very efficient algorithm. Finally, it is possible to plot the phases diagram with the experimental points and the Wilson model prediction for the mixture. Keywords: vapor-liquid equilibrium; Differential evolution; Wilson model; Parameter estimation and ebulliometer.

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1 Introduction

The study of VLE presents many industrial applications, such as separation process in oil and chemistry industries. Occasionally, substances separation might be an impracticable process due to certain similarities of substances, or even because of the high costs involved. Therefore, the estimation of binary interaction parameters and understanding the behavior of vapor and liquid phases show great importance at the optimization of purification processes of these substances.

This work presents experimental and also the computational procedures. The experiments were taken at the pressure of 20 kPa, and a calibration curve was obtained in order to correlate molar fraction and density of each phase. After generating all the experimental data it is possible to analyse how the Wilson model prediction will fit it.

2 Materials and Methods

2.1 Experimental Procedures

The first step on the experimental procedures is the obtainment of a calibration curve, which correlates the molar fraction of the components with the density of the phases obtained in the experiments taken in the ebulliometer. For such, many solutions composed by heptane and dodecane were prepared, in which the quantity of each substance varied from 0 to 100% (in molar amount). After the solution is prepared, it is placed in a thermostatic bath at 10°C (this low temperature is due to high volatility of heptane). When the solution reaches the desired temperature, the it is placed in a picnometer (a very precise glassware for measuring small volumes). Afterwards, the picnometer is placed in an analytical
balance in order to determine the mass of each solution. With these information (mass and volume) it is possible to determine the density of the solution.

After this first stage (obtainment of the calibration curve), it is time to obtain the VLE data. These data are obtained with the aid of a Labodest VLE 602 ebulliometer, produced by Fischer Engineering. The experiments are taken at 200 kPa, in order to reduce the temperature in the ebulliometer. The heating power must be adjusted to reach the ideal condensed vapor flow (1 or 2 drops per second) and to ensure that the liquid will flow to the liquid chamber. The equilibrium is reached when the vapor and liquid temperatures do not vary over 0.1°C, which takes about 1.5 hours. Through this experiment, it is possible to obtain two samples (liquid and condensed vapor). Then, the samples are placed in a thermostatic bath at 10°C (same temperature that the calibration curve was obtained). Similarly the calibration curve, the samples are placed in a picnometer, and its weight is determined by an analytical balance. All these procedures, make possible to determine the density of each sample. At last, the molar fraction of each component is determined using the calibration curve.

2.2 Thermodynamic modeling and numerical methods

This subsection aims the description of the objective function obtainment, and also to describe the thermodynamic models used during the development of this work. The condition for equilibrium is described in the following equation.

\[ f_i^l = f_i^v \]  

In this equation, \( f_i^l \) represents the fugacity of component \( i \) in liquid phase, and \( f_i^v \) represents the fugacity of component \( i \) in vapor phase.

The experimental data generated in the ebulliometer are substituted in the calibration curve. Afterwards, applying the modified Raoult’s equation, it is possible to determine the activity coefficient for each component. The equation (2) represents how the experimental activity coefficient is obtained.

\[ \gamma_i^{exp} = \frac{P y_i}{x_i P_{sat}^i} \]  

In this equation, \( x_i \) and \( y_i \) represent the molar fraction of component \( i \) in liquid and vapor phases, respectively. \( P \) is the pressure in which the experiment was taken (in this case, 200 mbar), and \( \gamma_i^{exp} \) represents the experimental activity coefficient.

The pressure \( P_{sat}^i \) is a temperature function and is determined by the Antoine equation.

\[ \ln(P_{sat}^i) = A_i - \frac{B_i}{T + C_i} \]  

Where, \( A_i, B_i, C_i \) represent the Antoine constants, and \( T \) is the temperature in Celsius degrees. After all these steps, it is possible to calculate the experimental activity coefficient, and to compare with the prediction of Wilson model, determined by the following equations.

\[ \ln(\gamma_1) = -\ln(x_1 + x_2A_{12}) + x_2 \left( \frac{A_{12}}{x_1 + x_2A_{12}} - \frac{A_{21}}{x_2 + x_2A_{21}} \right) \]  

\[ \ln(\gamma_2) = -\ln(x_2 + x_1A_{21}) - x_1 \left( \frac{A_{12}}{x_1 + x_2A_{12}} - \frac{A_{21}}{x_2 + x_2A_{21}} \right) \]  

The parameter \( A_{ij} \) is determined by equation (6).

\[ A_{ij} = \frac{V_i}{V_j} \exp(-\frac{A_{ij}}{RT}) \]  

In this equation \( V_i \) is the molar volume of substance \( i \), \( R \) is the universal gas constant, \( T \) is the temperature in Kelvin.
The parameters $A_{12}$ and $A_{21}$ are known as parameters of binary interaction. With all the data from the experiments, there is an optimization problem to be solved through the minimization of the objective function, as shown in equation (7).

$$FO(A_{12}, A_{21}) = \sum_{j=1}^{n_p} \sum_{i=1}^{c} \left( \frac{\gamma_{ij}^{exp} - \gamma_{ij}^{calc}}{\gamma_{ij}^{exp}} \right)^2$$

(7)

In equation (7), $n_p$ represents the number of experimental data, $c$ is the number of components in the system ($c = 2$, in this case), $exp$ refers to the experimental activity coefficient (estimated by the modified Raoult’s equation), and $calc$ refers to the calculated activity coefficient (through the Wilson model - equations (4) and (5) in this work).

### 2.3 The differential Evolution Algorithm

In this work, the minimization task was solved applying the differential evolution method, which is a stochastic optimization method (Storn & Price, 1997). The method is presented in a summarized scheme in the following steps:

1. **Generation of a Population**

   Generating a population of pairs of candidates within a real interval. Then, the generated points are:

   $$X_{i,G}, i = 1, ..., pop$$

   (8)

   In this equation, $X_{i,G}$ represents the vector $i$ (element of the population), from a generation $G$, and $pop$ is the size of the population ($pop$ does not change during the minimization process).

2. **Mutation**

   For each target vector, $X_{i,g}, i = 1, ..., pop$, a mutant vector is generated as proposes the following equation:

   $$V_{i,G+1} = X_{R1,G} + F(X_{R2,G} - X_{R3,G})$$

   (9)

   Where $R1$, $R2$ and $R3$ are random integers, $F$ is a real and constant factor $\in [0, 2]$ which controls the amplification of the differential variation ($X_{R2,G} - X_{R3,G}$), and $V_{i,G+1}$ is the mutant vector.

3. **Crossover**

   The crossover is introduced to increase the diversity of the perturbed parameter vectors. The parameter $C$, in the following equation, is known as crossover constant and must be in the interval $[0, 1]$. The integer $rnbr(i)$ is randomly chosen in the problems dimension. Then, each element of the trial vector $u_{i,G+1}$ is given by the following equation:

   $$u_{ji,G+1} = \begin{cases} V_{ji,G+1}, & \text{if } rand[0,1] \leq C, \text{ or } j = rnbr(i) \\ X_{ji,G+1}, & \text{if } rand[0,1] > C, \text{ or } j \neq rnbr(i) \end{cases}$$

   (10)

4. **Selection**

   This step tests whether the trial vector $u_{i,G+1}$ yields a smaller objective function value compared to $X_{i,G}$, so $X_{i,G+1}$ is set to $u_{i,G+1}$; otherwise $X_{i,G}$ is retained. Equation (11) summarizes the selection step.

   $$X_{i,G+1} = \begin{cases} u_{i,G+1}, & \text{if } FO(u_{i,G+1}) < FO(X_{i,G}) \\ X_{i,G}, & \text{otherwise} \end{cases}$$

   (11)
3 Results

3.1 Experimental Results

The first experimental result obtained is this work is the calibration curve for the n-heptane + n-dodecane mixture. An important factor is that the mixtures were at 10°C, as presented in the experimental procedures subsection. The curve was obtained by a quadratic fitting with a correlation coefficient of $R = 0.997$. The figure (1) represents the calibration curve (molar fraction versus density) obtained for heptane + dodecane mixture.

![Figure 1: Calibration curve for n-heptane + n-dodecane](image)

The ebulliometer provides the the liquid and vapor temperatures and the pressure (in this case, controlled pressure at 200mbar). With the vapor temperature and the density of each sample (determined with the aid of an analytical balance), it is possible to calculate the molar fraction of the samples applying the polynomial obtained for the calibration curve. The experimental data is presented in table (1) and figure (2).
Table 1: Experimental results.

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>$x_1$</th>
<th>$y_1$</th>
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</thead>
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<tr>
<td>331.49</td>
<td>0.7837</td>
<td>0.9869</td>
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<tr>
<td>332.40</td>
<td>0.7300</td>
<td>0.9857</td>
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<td>343.01</td>
<td>0.5165</td>
<td>0.9721</td>
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<td>363.73</td>
<td>0.2924</td>
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</tr>
<tr>
<td>364.27</td>
<td>0.2821</td>
<td>0.9776</td>
</tr>
<tr>
<td>405.24</td>
<td>0.0692</td>
<td>0.7644</td>
</tr>
<tr>
<td>428.7</td>
<td>0.0131</td>
<td>0.0644</td>
</tr>
</tbody>
</table>

Figure 2: Experimental equilibrium data for n-heptane + n-dodecane

3.2 Numerical Results for Parameters Estimation

After all the procedures presented previously in this are completed and the experimental data is already generated, then it is time to apply the differential evolution method to estimate the binary interaction parameters, through the minimization of the objective function, represented in equation (7). The values estimated were $A_{12} = 668.86\, \text{cal/mol}$ and $A_{21} = -726.33\, \text{cal/mol}$, which generated an objective function value of 4.36.
Finally, the final step in this work is to obtain the Wilson model prediction and how it fits the experimental data. In Figure 3 it is possible to see the experimental data (represented in blue circles and crosses), the Wilson model prediction with parameters estimated by the differential evolution (represented in dotted line) and also the prediction for null parameters (represented in continuous line).

![Figure 3: Experimental equilibrium data for n-heptane + n-dodecane and Wilson model prediction](image)

4 Conclusions

This work presents the experimental and numerical procedures for the VLE problem for a binary mixture. It also presents the steps for the parameters estimation with the experimental data obtained in the ebulliometer.

The Wilson model prediction fitted very well the experimental data, and most importantly, it is possible to see that a better fit is obtained using the parameters estimated by the differential evolution algorithm in comparison with null parameters.
5 References


