Vapor-liquid equilibria for binary and ternary systems composed of acetone, 1-butanol, and ethanol at atmospheric pressure

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Abstract. The experimental vapor-liquid equilibrium data for three binary systems of acetone + 1-butanol, ethanol + 1-butanol, acetone + ethanol and a ternary system of ethanol + acetone + 1-butanol at atmospheric pressure were measured using an ebulliometer. The binary experimental data were correlated using the Wilson, NRTL, and UNIQUAC models to obtain the binary interaction parameters of the models. These parameters were used to predict the ternary equilibrium data. The average absolute deviations of temperature (AAD T) between the experimental and correlation data of the three models are the same, 0.63, for the acetone + 1-butanol system, 0.72, 0.65, and 0.70, for the ethanol + 1-butanol system, and 0.15, 0.30, and 0.19, for the acetone + ethanol system, respectively. The AAD T values for the ternary system of ethanol + acetone + 1-butanol by comparing the experimental data with the data calculated using the three models were 0.28, 0.56, and 0.67, respectively.

1. Introduction
Diesel engines are widely used in everyday life such as transportation equipment, heavy equipment, and industrial equipment. The need for diesel fuel can be measured by the large number of these tools, which are increasing every day. Most of these diesel engines still use petroleum-based fuels (petrodiesel). In fact, the need for diesel fuel is not supported by the availability of petrodiesel which is increasingly scarce because it is a non-renewable fossil fuel. The most likely way to overcome the scarcity of fuel is to develop alternative fuels. For diesel engines, the use of biodiesel is one of the answers.

Biodiesel is a mono-alkyl ester from vegetable oil or animal fat. The best advantage of biodiesel compared to petrodiesel is that biodiesel is an environmentally friendly fuel. The emission resulted from a burning process of biodiesel are less than that of petrodiesel. Biodiesel is able to reduce the dependence on fossil fuels. The availability of fossil fuels such as petroleum, coal and natural gas are limited. In the next few years, this energy sources will run out [1].

Types of alcohol that can be used as a standard for producing biodiesel through the transesterification process include primary and secondary alcohols. The primary alcohols include methanol, ethanol, propanol, 1-butanol, and isobutanol whereas the secondary alcohols are isopropanol and 2-butanol. Biodiesel production using primary and secondary alcohols give conversions of 94.8-98.5% and 61.2-83.8% respectively, with soybean oil and hexane as raw material [2]. Methanol and ethanol as alcohols which are often used in making biodiesel give yields of 79.3%
and 66.9% respectively, whereas 1-butanol and isopropanol yields 88.4% and 45.3%. In biodiesel production, 2-butanol is less reactive than 1-butanol because the formation of alkenes in the dehydration reaction is greater [3]. Therefore 1-butanol is the alternative alcohol for producing biodiesel.

Butanol can be produced from the fermentation process of ABE (Acetone – Butanol – Ethanol) using Clostridium acetobutylicum bacteria which can convert glucose and other simple sugars into acetone, butanol, and ethanol. These bacteria can also convert large amounts of carbohydrates, including hexose and pentose, hemicellulose, and cellulose under suitable conditions for their growth. The fermentation process lasts 36 - 48 hours. The product ratio of ABE is 30% acetone, 60% butanol, and 10% ethanol respectively and can be separated by distillation and fractionation to increase the purity of butanol [4]. Therefore, the vapor-liquid equilibrium data are needed in the design of the distillation column.

In this study, the measurement of the binary vapor-liquid equilibrium data of ethanol + 1-butanol, acetone + 1-butanol, and acetone + ethanol systems as well as the ternary system of ethanol + acetone + 1-butanol at atmospheric pressure were conducted. The experimental data obtained were correlated using the Wilson, NRTL and UNIQUAC models.

2. Experimental section

2.1. Materials
In this work, acetone used was supplied from SmartLab, whereas ethanol and 1-butanol were supplied from Merck. The characteristics of each material can be seen in table 1.

| Table 1. Material description of pure components |
|-----------------------------------------------|
| Components | Supplier | Purity* |
| Acetone    | SmartLab | 99.9%   |
| 1-Butanol  | Merck    | 99.0%   |
| Ethanol    | Merck    | 99.8%   |

* Purity obtained from the Supplier

2.2. Apparatus and procedures
The vapor-liquid equilibrium data were measured by a simple static ebulliometer which consists of an ebulliometer cell, that is a flat bottom flask for boiling the mixtures, equipped with a magnetic stirrer, a heating system, a condenser, a temperature indicator, and a thermocouple. The mixtures of binary and ternary systems in various compositions prepared using analytical balance were put into the ebulliometer cell. The magnetic stirrer was turned on to distribute evenly the mixture. Furthermore, the cooling water was flowed into the condenser before turning the heating system on. The heating process was marked by the formation of vapor that flows from the boiling chamber to the condenser. The equilibrium condition was reached when the temperature was constant. The equilibrium temperatures were then recorded, and the liquid phase samples were taken from the valve of boiling chamber to be analyzed using a Gas Chromatography (GC).

2.3. Sample Analysis
The liquid phase samples were analyzed for all systems using GC Shimadzu plus 2010 with a flame ionization detector (FID) and the Stabil-Wax column. A carrier gas used was helium (He) UHP gas with a flow rate of 30 mL/min. The analysis was conducted by setting the isothermal temperature of the oven (column temperature) to 130°C (403.15 K) with a split ratio of 20. The detector used was calibrated by plotting the percent areas versus the mole fractions of the components in the calibration curve prepared for the system studied to get the mole fraction of each sample from the area fraction.
For calibration, each mixture composition with interval mole fraction of 0.1 was used to ensure a high degree of accuracy in the GC analysis. The accuracy of the experimental results was obtained by fitting the calibration curve by using a four-degree polynomial to find out the equation and the good consistency shown by giving $R^2$ value of 1.

3. Results and discussion
Before the ebulliometer was used in this work, it was validated first to determine its accuracy by measuring the equilibrium temperatures of a binary system of ethanol + water at atmospheric pressure. The experimental data obtained was compared with the literature data of Lai, et al [5]. The experimental data ($T$ and $x$) were also correlated with the Wilson, NRTL, and UNIQUAC models to obtain the interaction parameters and to be used for comparing with literature data. This comparison gives the average deviation in temperature less than 0.5 and show that the measured equilibrium temperatures were in good agreement with the literature data.

The experimental results of the vapor-liquid equilibrium data for three binary systems at atmospheric pressure were presented in table 2. In this study, the operating condition was at atmospheric pressure, so that the vapor phase can be assumed to be an ideal gas and equation (1) can be used to calculate vapor-liquid equilibrium data,

$$y_i P = P_i^{sat} y_i x_i$$  \hspace{1cm} (1)

where $x_i$ and $y_i$ are the liquid phase and vapor phase mole fractions of component $i$, $y_i$ is the activity coefficient of component $i$, $P$ is the total pressure, and $P_i^{sat}$ is the vapor pressure of the pure component $i$ that can be calculated using the Antoine equation [6]. The Antoine constants used in this research can be seen in table 3.

| Table 2. The experimental data of the binary systems at atmospheric pressure |
|-----------------------------|-----------------------------|-----------------------------|
| $T$ (°C) | $x_1$ | $T$ (°C) | $x_1$ | $T$ (°C) | $x_1$ |
| ethanol (1) + 1-butanol (2) | 117.8 | 0 | 117.8 | 0 | 78.3 | 0 |
| | 110.1 | 0.0847 | 101.6 | 0.0924 | 73.3 | 0.1019 |
| | 104.6 | 0.1897 | 93.8 | 0.1917 | 69.9 | 0.1837 |
| | 99.9 | 0.2958 | 85.6 | 0.2723 | 66.8 | 0.2965 |
| | 96.3 | 0.4028 | 78.6 | 0.3675 | 64.5 | 0.3941 |
| | 92.6 | 0.5084 | 73.2 | 0.4854 | 62.7 | 0.4802 |
| | 89.1 | 0.6100 | 69.0 | 0.5794 | 61.3 | 0.5914 |
| | 86.2 | 0.7118 | 65.8 | 0.6904 | 60.0 | 0.6905 |
| | 83.7 | 0.8071 | 62.6 | 0.7970 | 58.9 | 0.7667 |
| | 81.2 | 0.9022 | 60.0 | 0.9012 | 57.8 | 0.8998 |
| | 78.3 | 1 | 56.1 | 1 | 56.1 | 1 |

| Table 3. Antoine equation constants for pure components |
|-----------------------------|-----------------------------|-----------------------------|
| Components | A | B | C |
| Ethanol | 16.8958 | 3795.17 | 230.918 |
| Acetone | 14.3145 | 2756.22 | 228.06 |
| 1-Butanol | 15.3144 | 3212.43 | 182.739 |
The binary vapor-liquid equilibrium experimental data were correlated with the Wilson, NRTL, and UNIQUAC models to obtain the binary interaction parameters for three pairs of binary systems. The binary parameters of each model were used to calculate the vapor fraction of the ternary system. The value of structural parameters data of pure components [7] are necessary for correlating with UNIQUAC model, and that are shown in table 4.

### Table 4. Structural parameter data of pure components

| Component       | r    | q    |
|-----------------|------|------|
| Ethanol (1)     | 2.5755 | 2.588 |
| Acetone (2)     | 2.5735 | 2.3360 |
| 1-Butanol (3)   | 3.9235 | 3.664 |

To obtain the optimal parameters for each model, the temperature deviation value between the experimental and the calculation data must be as minimum as possible using Average Absolute Deviation (AAD) defined in equation (2).

\[
AAD T = \frac{1}{n} \sum_{i=1}^{n} |T_{\text{exp}} - T_{\text{calc}}|
\]  

The interaction parameters for each binary system at atmospheric pressure using the Wilson, NRTL, and UNIQUAC models along with the AAD T can be seen in tables 5.

### Table 5. Interaction parameters of the binary systems at atmospheric pressure.

| Models               | Interaction parameters* | AAD T |
|----------------------|-------------------------|-------|
|                      | \(A_{12}\) (cal/mole)    | \(A_{21}\) (cal/mole) | \(\alpha\) |       |
| Ethanol (1) + 1-butanol (2) | -83.24                  | 94.02  | 0.72  |
| Wilson               | -239.38                 | -124.26 | 0.4   | 0.65  |
| NRTL                 | 144.12                  | -133.71 | 0.70  |
| UNIQUAC              | 273.75                  | -48.06  | 0.63  |
| acetone (1) + 1-butanol (2) | -21.18                  | 253.53  | 0.3   | 0.63  |
| Wilson               | -65.49                  | 126.07  | 0.63  |
| NRTL                 | 157.88                  | 218.86  | 0.15  |
| UNIQUAC              | 147.95                  | 255.13  | 0.30  |
| acetone (1) + ethanol (2) | 31.12                   | 32.28  | 0.19  |

*) \(A_{12}\) and \(A_{21}\) are the interaction parameters:
Wilson: \(a_{12}, a_{21}\) ; NRTL: \(b_{12}, b_{21}\) ; UNIQUAC: \(u_{12}, u_{21}\)
Based on the AAD T, the Wilson, NRTL, and UNIQUAC models have good results to correlate the experimental data. The experimental and the calculation results of each model for the binary systems along with the literature data were plotted on the T-x-y diagrams as shown in figures 1-3.

**Figure 1.** Vapor-liquid equilibria for ethanol (1) + 1-butanol (2) system at atmospheric pressure compared with literature data [8]

**Figure 2.** Vapor-liquid equilibria for acetone (1) + 1-butanol (2) system at atmospheric pressure compared with literature data [9]
Figure 3. Vapor-liquid equilibria for acetone (1) + ethanol (2) system at atmospheric pressure compared with literature data [10]

The experimental vapor-liquid equilibrium data for ternary systems of ethanol (1) + acetone (2) + 1-butanol (3) at atmospheric pressure are presented in Table 6. These data were also correlated with the Wilson, NRTL and UNIQUAC models to calculate the activity coefficients of the components using the binary interaction parameters obtained. The average deviations from each model can be seen in Table 7. It shows that the three models correlate well for the ternary system. The Wilson model gives the smallest deviation compared with the NRTL and the UNIQUAC models. The AAD T value obtained by the Wilson model was 0.2839. The experimental and the calculated data of ternary system for all models are shown graphically in Figure 4. The tie-lines connected the liquid phases and the vapor phases calculated by the correlation models with.

Table 6. Experimental results for ethanol (1) + acetone (2) + 1-butanol (3) system.

| T (°C) | x₁   | x₂   |
|--------|------|------|
| 94.8   | 0.0489 | 0.1480 |
| 87.7   | 0.0849 | 0.2006 |
| 84.6   | 0.1150 | 0.2276 |
| 81.8   | 0.1387 | 0.2662 |
| 77.3   | 0.1988 | 0.3002 |
| 75.2   | 0.2241 | 0.3300 |
| 75.0   | 0.3810 | 0.2697 |
| 74.7   | 0.5354 | 0.2031 |
| 74.6   | 0.6785 | 0.1504 |
| 75.3   | 0.8175 | 0.1011 |
Table 7. Average deviations for ethanol (1) + acetone (2) + 1-butanol (3) system

| Model      | AAD T  |
|------------|--------|
| Wilson     | 0.2839 |
| NRTL       | 0.5586 |
| UNIQUAC    | 0.6683 |

Figure 4. Vapor-liquid equilibria for ethanol (1) + acetone (2) + 1-butanol (3) system at atmospheric pressure for a) Wilson model, b) NRTL model, c) UNIQUAC model
4. Conclusion
The experimental vapor-liquid equilibrium data for the binary systems of ethanol + 1-butanol, acetone + 1-butanol, and ethanol + acetone and for the ternary system of ethanol + acetone + 1-butanol at atmospheric pressure have been presented. The ebulliometer was validated well by using the ethanol + water system. The experimental data were correlated well with the Wilson, NRTL, and UNIQUAC models. The Wilson model gives the smallest deviation for the ternary system compared with the others.

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