Isobaric Vapor-Liquid Equilibria for Binary System of Ethanol (1) + Eugenol (2) at 400 and 760 mmHg

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Abstract—Eugenol is the main component of clove oil, while the main impurities of it is β-caryophyllene. Eugenol with a purity higher than 98% has a higher price than low purity eugenol. Thus, further eugenol purification process is needed. Common purification processes are extraction and distillation. In the design and simulation of the distillation process it requires a knowledge of Vapor-Liquid Equilibrium (VLE) data from a mixture of components to be separated (eugenol and ethanol) as the result of extraction process. In this work, the experimental VLE data were measured for binary mixtures of ethanol(1) + eugenol(2) at 400 and 760 mmHg. The apparatus used for this experiment is an othmer still equipped with a vacuum pump and a manometer. The experiments were performed to obtain equilibrium data (T), component concentrations in liquid phase (x), and in vapor phase (y). The binary VLE data were correlated with the Wilson, NRTL and UNIQUAC models to obtain the binary parameters. The reliability of these models were tested by comparing with experimental results using Root Mean Square Deviation (RMSD). For the system and the operation condition studied, the Wilson, NRTL and UNIQUAC models suited well and give satisfactory results based on the RMSD values.

Keywords—Ethanol, Eugenol, Vapor-Liquid Equilibrium, Wilson, NRTL, UNIQUAC

I. INTRODUCTION

Clove oil is a kind of essential oil that produced in Indonesia. Eugenol is the main compound of the clove oil, it is valuable and widely used in flavor and fragrance industry due to its distinctive scent. In commercial production by farmer, the content of eugenol in clove oil is approximately 70-90 % [1], [2]. Higher purity eugenol more than 98% is more expensive, the price is about three times higher rather than low purity eugenol with 70 % purity [3]. In order to obtain eugenol with desired purity, extraction and distillation steps (vacuum distillation was preferred) should be included in the production process. In the extraction process, alcohol compounds especially ethanol is commonly used as solvent to separate eugenol from their impurities [4]. Eugenol purification from ethanol as the result of the extraction process through vacuum distillation is needed to avoid eugenol degradation. In the design and simulatin of the purification of ethanol and eugenol mixture, the VLE data at low pressures were necessary. Some VLE data for the binary mixture at vacuum condition were already reported [5], [6]. Unfortunately, as our knowledge, the VLE data for ethanol and eugenol were not available in literature at the moment.

In order to obtain the data for engineering and industrial applications, the isobaric VLE data for ethanol and eugenol at low pressure 400 mmHg and atmospheric pressure 760 mmHg were conducted.

These binary VLE data from experimental results were correlated with the Wilson [7], the Non-random Two-Liquid (NRTL) [8], and the Universal Quasichemical Activity Coefficient (UNIQUAC) [9] equations to obtain the binary interaction parameters for each models and its pressures.

II. METHOD

A. Materials

The materials used were eugenol and ethanol supplied by Merck Co. and PT. Indesso Niagatama, respectively. All the chemicals were used without further purification and their description appears in Table 1.

| Chemicals | Purity* | Source | Purification Method |
|-----------|---------|--------|---------------------|
| Eugenol   | 99.9 %  | PT. Indesso Niagatama | None |
| Ethanol   | 99.8 %  | Merck Co | None |

*Mol fraction purity

B. Apparatus

In this work, the apparatus of Vapor-Liquid Equilibrium data at constant pressure were measured using an Othmer still. It was composed of a boiler cell, a condenser, two sample ports (for the liquid and vapor phases), a vacuum pump, heater wire, a magnetic stirrer, thermcouple and temperature sensors. The pressure was controlled using a valve and was kept constant through a desire pressure line with a manometer that connected to stabilizer tank. The experimental apparatus were shown in Figure 1.

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C. Procedure

To obtain the phase equilibrium data, the liquid binary mixtures with known composition were introduced into the boiler cell. The total volume occupied by the liquid solution in the boiler cell was around 500 cm$^3$. The vacuum pump was started to reach the desired pressure then the sample was heated by the heating wire and both vapor and liquid phases were continuously circulating in the still to provide intimate contact of the phases. The equilibrium state was reached when the temperature remained constant for about 15 minutes and then both liquid and vapor phases were sampled. To change the mixture composition, the different amounts of ethanol or eugenol were introduced into the still, the mixture was stirred and the procedure was repeated. After that, the liquid and vapor phases were analyzed by measuring the refractive index using an Abbe-Type Refractometer by ATAGO NAR-1T [10], with an uncertainty of measurement ± 0.0002. A calibration curve of the refractive index was obtained using the binary systems.

III. RESULTS AND DISCUSSION

A. Validation of Experiment

In order to validate the reliability and the accuracy of the apparatus used in this work, the vapor pressures of pure ethanol at various compositions were measured and compared with the reported data calculated with the Antoine equation. The deviations of the experimental and reported data were calculated using Eqs. 1 and 2 [11].

$$AD = [T_{exp}^{sat} - T_{lit}^{sat}]$$

$$RMSD = \sum_{i=1}^{n} \left(\frac{(T_{exp}^{sat} - T_{lit}^{sat})^2}{n}\right)^{0.5}$$

where superscripts $lit$ and $exp$ represent reported values and the experimental data, respectively. $n$ is the number of data points. The results are presented in Figure 2. It shows that the measured data agree with the literature data. The Root Mean Square Deviation (RMSD) of ethanol with lit a and b [12], [13] are 0.880 and 0.633, respectively. Thus, these values indicate that the measurements applied in this apparatus are reliable.
TABLE 2. EXPERIMENTAL VLE DATA AND ACTIVITY COEFFICIENTS OF SYSTEM ETHANOL(1) + EUGENOL(2) AT 400 AND 760 MMHG

| P (mmHg) | T (K) | x1 | y1 | γ1 | y1 | γ2 |
|----------|-------|----|----|----|----|----|
| 400      | 354.5 | 1.000 | 1.000 | 1.00 | 339.8 | 1.000 | 1.000 | 1.00 |
| 357.6 | 0.902 | 0.980 | 0.96 | 23.05 | 360.0 | 0.762 | 0.979 | 1.04 |
| 369.2 | 0.558 | 0.979 | 1.02 | 7.89 | 373.6 | 0.418 | 0.979 | 1.17 |
| 380.6 | 0.321 | 0.978 | 1.20 | 3.12 | 380.6 | 0.321 | 0.978 | 1.20 |
| 414.8 | 0.176 | 0.972 | 0.78 | 0.81 | 440.3 | 0.131 | 0.949 | 0.54 |
| 522.6 | 0.000 | 0.000 | 1.00 | 1.00 | 505.4 | 0.000 | 0.000 | 1.00 |
| 760      | 339.9 | 0.902 | 0.980 | 1.08 | 340.8 | 0.760 | 0.979 | 1.24 |
| 342.9 | 0.623 | 0.979 | 1.38 | 43.37 | 349.0 | 0.474 | 0.979 | 1.41 |
| 359.8 | 0.321 | 0.978 | 1.37 | 5.66 | 359.8 | 0.321 | 0.978 | 1.37 |
| 377.1 | 0.217 | 0.977 | 1.10 | 2.27 | 377.1 | 0.217 | 0.977 | 1.10 |
| 420.8 | 0.157 | 0.975 | 0.41 | 0.37 | 420.8 | 0.157 | 0.975 | 0.41 |
| 434.3 | 0.129 | 0.973 | 0.36 | 0.24 | 434.3 | 0.129 | 0.973 | 0.36 |
| 459.8 | 0.101 | 0.970 | 0.23 | 0.13 | 459.8 | 0.101 | 0.970 | 0.23 |

B. Experimental Data and Thermodynamic Consistency.

The experimental vapor liquid equilibrium data for the binary system ethanol(1) + eugenol(2) at pressures 400 and 760 mmHg are shown in Table 2. The activity coefficients γ_i in Table 2 were calculated by Eq. 3 [13]:

\[ \gamma_i = \frac{P y_i}{P_i s_i} \]

Since the experiments were conducted at such low pressure, the vapor phase was assumed as the ideal gas. In order to ensure the reliability of the VLE experimental data, the thermodynamic consistency was tested by a semiempirical method suggested by Herington [14]. The values of D and J were calculated as

\[ D = 100 \left( \frac{1}{x_2} \int x_2 \ln \frac{y_2}{y_1} dx_2 \right) \]

\[ J = 150 \left( T_{max} - T_{min} \right) \frac{T_{max}}{T_{min}} \]

where T_max and T_min were the maximum and minimum boiling temperatures in the studied systems, respectively. Herington suggested that the experimental points were considered to be thermodynamically consistent if the value of D < J or (D - J) < 1 [15]. The D value was obtained from a Ridich-Kister equation regressed from the ln(γ_1/γ_2) and x_1 data. The test results were presented in Table 3 which indicated that the experimental data satisfied the testing criterion.

C. Correlation of VLE Data

The experimental data were correlated with the Wilson, NRTL and UNIQUAC models to obtain the binary parameters by minimizing the objective function as

\[ OF = \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \gamma_i^{\exp} - \gamma_i^{cal} \right) \]

where i represent the number of data from 1 to N and j denote the number of component in the system. In order to evaluate the reliability of the interaction parameters, the Root Mean Square Deviations (RMSD) of the vapor mole fraction and bubble-point temperature between the experimental and the calculated values are indicated. The correlation results and the RMSD are shown in Table 4 and illustrated graphically in Figs. 3–4. It can be seen that the Wilson, NRTL, and UNIQUAC models describe well the vapor phase mole fraction and bubble-point temperature. Comparatively, the Wilson model represents the best calculation results where the RMSD values of T and γ_1 for the binary system of ethanol (1) + eugenol (2) using the Wilson models are 4.962, 0.017, and 9.271, 0.020 at 400 and 760 mmHg, respectively. From the view of industrial applications, the Wilson, NRTL, and UNIQUAC models can be used to calculate the VLE data of the binary systems.

TABLE 4. BINARY INTERACTION PARAMETERS AND RMSD FOR THE SYSTEM ETHANOL (1) + EUGENOL (2)

| Model        | Parameters | RMSD  |
|--------------|------------|-------|
| Wilson       | A_a, A_b   |       |
| NRTL         |            |       |
| UNIQUAC      |            |       |

P = 400 mmHg

| Model        | Parameters | RMSD  |
|--------------|------------|-------|
| Wilson       | -1916.511, -1534.04 | 9.271, 0.02 |
| NRTL         | -1058.165, 816.279 | 9.675, 0.02 |
| UNIQUAC      | -604.059, 465.007 | 11.388, 0.296 |

P = 760 mmHg

| Model        | Parameters | RMSD  |
|--------------|------------|-------|
| Wilson       | 1898.662, -1454.904 | 4.962, 0.017 |
| NRTL         | -993.816, 728.3 | 5.969, 0.017 |
| UNIQUAC      | -480.548, 247.342 | 6.736, 0.967 |
IV. CONCLUSION

The isobaric vapor liquid equilibria of the system ethanol and eugenol were experimentally measured at pressures of 400 and 760 mmHg. These data are thermodynamically consistent based on the thermodynamics consistency using the Herington method. The activity coefficients evaluated with the Wilson, NRTL and UNIQUAC equations show a good correlation of the experimental data.
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