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# Separation of Azeotropic Mixtures of Ethyl Acetate + Methylcyclohexane: Vapor−Liquid Equilibrium Measurements

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**ABSTRACT:** It is a challenge to separate ethyl acetate from methylcyclohexane because of the azeotropic phenomenon. To provide a basis for the design of the separation process, the isobaric vapor−liquid equilibria for an ethyl acetate + methylcyclohexane binary system were measured at 101.3 and 20.0 kPa using a modified Othmer-type still. The results show that ethyl acetate and methylcyclohexane form a miscible azeotropic mixture with minimum boiling temperature (349.99 K at 101.3 kPa), of which the composition varies slightly with decreasing pressure ($\leq$101.3 kPa). It implies that ethyl acetate cannot be separated from methylcyclohexane by pressure-swing distillation. The azeotropy of ethyl acetate and methylcyclohexane disappears in the presence of decane ($\sim$0.5 mole fraction), which means that ethyl acetate can be separated from methylcyclohexane by extractive distillation with decane as an entrainer.
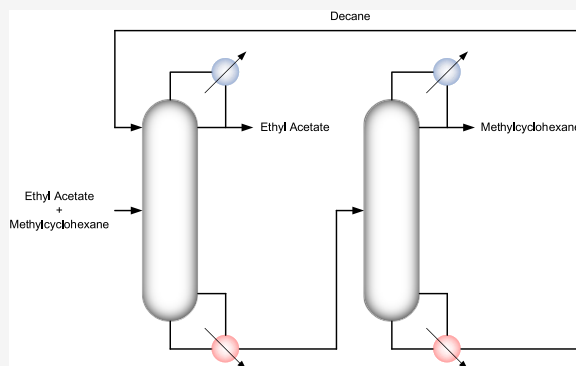
## 1. INTRODUCTION

As the ester of ethanol and acetic acid, ethyl acetate is a colorless liquid with a characteristic sweet smell. It is manufactured on a large scale for use as a solvent, being favored because of its low cost, low toxicity, low viscosity, and agreeable odor. In the flexible packaging industry, ethyl acetate is used as a solvent in inks designed for flexographic and rotogravure printing processes, where its main function is to dissolve the resin, control the viscosity, and modify the drying rate.[1]

Methylcyclohexane is a colorless liquid with a faint benzene-like odor. It is used as a green organic solvent, with properties similar to those of saturated hydrocarbons such as heptane. As a lowly toxic toluene substitute, methylcyclohexane is used more and more in the flexible packaging industry nowadays.[2]

During the drying of printed material, solvent-laden air from the dryer is passed through a solvent recovery system. A typical recovery system, i.e., rotary bed absorber, uses activated carbon to absorb the solvent. A saturated bed is regenerated by steam and sometimes $N_2$. The solvent-laden steam is then condensed to a multicomponent mixture, including ethyl acetate and methylcyclohexane. More than 95% of the ink solvents can be recovered using this process. Discharge of the mixed organic solvents results in serious environmental pollution and is also a waste of raw materials. Therefore, the resultant mixture needs to be separated and reused in terms of environment and economy.[3]

Distillation is the process to separate components of a homogeneous liquid mixture by using selective boiling and condensation. In the chemical industry, distillation is used

abundantly to separate mixed organic solvents. The design and optimization of a distillation process require a reliable knowledge of the vapor−liquid equilibrium (VLE) behavior of the system concerned. However, to the best of the author's knowledge, the VLE data for the ethyl acetate + methylcyclohexane binary system are not reported in the literature. Worse still, the binary interaction parameters for activity coefficient models, i.e., the Wilson, NRTL, and UNIQUAC equations, are not available in commercial chemical process simulators for such binary systems. It is a major bottleneck in process design and technoeconomic evaluation of the recovery of aforementioned organic solvents. Measurement and subsequent analyses of the VLE data presented in this article will help in tackling the bottleneck.

## 2. MATERIALS AND METHODS

**2.1. Materials.** Decane, ethanol, ethyl acetate, and methylcyclohexane were analytical reagents, the purities of which were checked by a gas chromatography (GC) equipped with a flame ionization detector (FID). All the chemicals were used without further purification since the impurities did not exceed 0.5% (Table 1).

## Table 1. Details of the Chemicals Used

| chemical name | CAS No. | supplier | mass fraction purity | analysis method |
|---|---|---|---|---|
| decane | 124-18-5 | Shanghai Macklin Biochemical Co., Ltd. | 0.995 | GC |
| ethanol | 64-17-5 | Sinopharm Chemical Reagent Co., Ltd. | 0.999 | GC |
| ethyl acetate | 141-78-6 | Sinopharm Chemical Reagent Co., Ltd. | 0.999 | GC |
| methylcyclohexane | 108-87-2 | Saan Chemical Technology (Shanghai) Co., Ltd. | 0.999 | GC |
| water | 7732-18-5 | from a Milli-Q® pure & ultrapure water purification system | ≥18.2 MΩ·cm | |

**2.2. Apparatus and Procedure.** Isobaric VLE data were generated using a modified Othmer-type still (CE-2, Beiyang Chemical Engineering Experimental Equipment Co., Ltd. of Tianjin University, Tianjin, China) as illustrated schematically in Figure 1. The pressure within the still was regulated by a
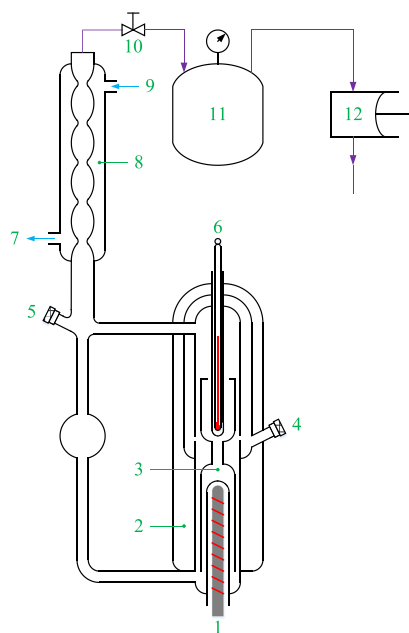


**Figure 1.** Schematic diagram of the apparatus: (1) electrical coil heater; (2) vacuum jacket; (3) boiling chamber; (4) outlet valve for the liquid sample; (5) outlet valve for the vapor sample; (6) thermometer; (7) cooling water outlet; (8) condenser; (9) cooling water inlet; (10) ball valve; (11) reservoir; and (12) vacuum pump.

vacuum pump (V-100, Buchi Operations India Private Limited, Mumbai, India) equipped with an absolute pressure gauge-sensor made from aluminum oxide-ceramic. The fluctuation of pressure was reduced by a reservoir (6 L) to be ±0.1 kPa. The equilibrium temperature is measured by a high-precision mercury-in-glass thermometer with a resolution of 0.1 K.

For each run, a liquid mixture (∼60 mL) was introduced into the still and then heated slowly using an electrical coil heater (∼50 W). Normally, it took about 60 min to achieve the equilibrium temperature of the mixture. Once the equilibrium was ensured (fluctuation of temperature ± 0.1 K), both the

condensed vapor and the returning liquid in equilibrium with the vapor were withdrawn and analyzed.

**2.3. Analysis.** Sample analysis was performed in a GC (GC9160, Shanghai Ouhua Anlysis Instrument Co., Shanghai, China) equipped with an FID. The HP-5MS capillary column (60 m × 0.25 mm × 0.25 μm) was operated at an oven temperature of 80 °C. The injector/detector temperatures were fixed at 130 °C throughout the determination. Nitrogen (99.999% of purity) was used as carrier gas at 25 mL/min.

A calibration curve established using gravimetrically prepared standard solutions was used to convert the peak area ratio to mass fraction and then mole fraction of the sample. The calibration curve covered a broad range of compositions to avoid extrapolation and ensure an accurate analysis of equilibrium compositions. Each sample was analyzed at least three times and the mean value was reported.

## 3. RESULTS AND DISCUSSION

**3.1. Validation of the Apparatus.** To validate the reliability of the apparatus employed, the isobaric VLE data for the well-known ethanol + water binary system were measured at 101.3 kPa. The data are presented in Table 2 and

**Table 2. Experimental VLE Data for the Ethanol (1) + Water (2) Binary System at 101.3 kPa**[a]

| $T$ (K) | $x_1$ | $y_1$ | $\alpha_{12}$ |
|---|---|---|---|
| 370.15 | 0.0163 | 0.1323 | 9.204 |
| 367.15 | 0.0292 | 0.2281 | 9.825 |
| 364.65 | 0.0452 | 0.2791 | 8.177 |
| 362.55 | 0.0620 | 0.3597 | 8.505 |
| 361.05 | 0.0809 | 0.3861 | 7.145 |
| 359.85 | 0.0972 | 0.4359 | 7.180 |
| 358.95 | 0.1154 | 0.4495 | 6.262 |
| 357.75 | 0.1311 | 0.4802 | 6.123 |

[a]Standard uncertainties are $u(p) = 0.5$ kPa, $u(T) = 0.2$ K, and $u(x) = u(y) = 0.002$, respectively.

compared with the ones reported in the past few years in Figure 2. The comparison shows that the VLE data obtained experimentally agree well with the ones reported in the
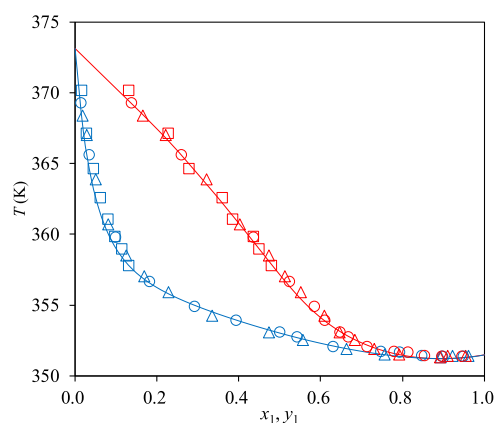


**Figure 2.** $T$-$x$-$y$ diagram for the ethanol (1) + water (2) binary system at 101.3 kPa. The symbols in red and blue represent vapor and liquid compositions determined, respectively. □ represents the data determined in this work, ○ represents the ones determined by Lai et al.,[4] △ represents the ones determined by Peng et al.,[5] while the smooth line is the value predicted using the UNIFAC model.

literature,[4,5] indicating that the apparatus, procedure, and analysis method employed are reliable. The relative volatility of ethanol (1) to water (2) is calculated by the method elucidated in the latter part of this work.

**3.2. Isobaric VLE of the Azeotropic Mixture of Ethyl Acetate + Methylcyclohexane.** The isobaric VLE data for the ethyl acetate + methylcyclohexane binary system were determined at 101.3 and 20.0 kPa in the present work, the vapor was therefore regarded as ideal gas and thus the activity coefficient is expressed as the modified Raoult's law

$$\gamma_i = \frac{y_i p}{x_i p_i^s} \tag{1}$$

where $\gamma_i$ is the activity coefficient of component $i$ in the liquid phase; $x_i$ and $y_i$ are the mole fractions of component $i$ in vapor and liquid phases, respectively; $p$ is the pressure of the system; $p_i^s$ is the saturated vapor pressure of component $i$ at temperature $T$, which is correlated using the following Antoine equation

$$\ln(p_i^s/\text{kPa}) = A_i - \frac{B_i}{T/\text{K} + C_i} \tag{2}$$

where $A_i$, $B_i$, and $C_i$ are parameters of the Antoine equation for component $i$.[6,7] The parameters for ethyl acetate and methylcyclohexane are listed in Table 3.

**Table 3. Parameters of the Antoine Equation**

| component | $A_i$ | $B_i$ | $C_i$ | reference |
|---|---|---|---|---|
| ethyl acetate | 14.228 | 2799.54 | −58.92 | Li et al.[8] |
| methylcyclohexane | 14.584 | 3490.08 | −23.41 | Loras et al.[9] |

The relative volatility of ethyl acetate (1) to methylcyclohexane (2) is calculated by the following equation

$$\alpha_{12} = \frac{x_2 y_1}{x_1 y_2} \tag{3}$$

The isobaric VLE data obtained for the ethyl acetate + methylcyclohexane binary system are presented in Table 4. The boiling points of ethyl acetate and methylcyclohexane determined at atmospheric pressure are 349.79 and 373.25 K, respectively. The values are in line with the ones reported in the literature,[10−12] further validating the reliability of the apparatus and procedure employed to determine the VLE. The activity coefficient $\gamma$ is plotted against liquid composition ($x_1$) in Figures S1 and S2. The ethyl acetate + methylcyclohexane binary system shows positive deviation ($\gamma > 1$) from ideal behavior at 101.3 and 20.0 kPa.

**3.3. Thermodynamic Consistency Test.** The thermodynamic consistency of experimental VLE data was checked thoroughly using Fredenslund's test,[13] Wisniak's L-W test,[14] and Van Ness's point-to-point test[15] in the present work.

Fredenslund et al.[13] represented the reduced excess Gibbs free energy $g^E$ by highly flexible Legendre polynomials

$$g^E = \frac{G^E}{RT} = \sum x_i \ln \gamma_i = x_1(1 - x_1) \sum_{j=0}^{K} a_j L_j(x_1) \tag{4}$$

where $G^E$ is the excess Gibbs free energy; $R$ is the universal gas constant; $K$ is the order of Legendre polynomial used, normally 3−5; $a_j$ is the coefficient of Legendre polynomial $L_j(x)$, which is expressed as

**Table 4. Experimental VLE Data for the Ethyl Acetate (1) + Methylcyclohexane (2) Binary System[a]**

| $p$ (kPa) | $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|---|---|---|---|---|---|---|
| 101.3 | 373.25 | 0.0000 | 0.0000 | | 1.000 | |
| | 363.93 | 0.1019 | 0.2940 | 1.874 | 1.044 | 3.668 |
| | 359.43 | 0.1879 | 0.4272 | 1.694 | 1.074 | 3.222 |
| | 356.15 | 0.2869 | 0.5224 | 1.505 | 1.130 | 2.719 |
| | 354.24 | 0.3562 | 0.5979 | 1.474 | 1.120 | 2.687 |
| | 352.80 | 0.4514 | 0.6411 | 1.306 | 1.228 | 2.171 |
| | 351.63 | 0.5739 | 0.6989 | 1.164 | 1.378 | 1.723 |
| | 350.70 | 0.6434 | 0.7348 | 1.125 | 1.494 | 1.536 |
| | 350.15 | 0.7074 | 0.7800 | 1.106 | 1.538 | 1.466 |
| | 349.71 | 0.7871 | 0.8274 | 1.070 | 1.682 | 1.297 |
| | 349.48 | 0.8599 | 0.8779 | 1.047 | 1.821 | 1.172 |
| | 349.45 | 0.9278 | 0.9249 | 1.023 | 2.177 | 0.9584 |
| | 349.79 | 1.000 | 1.000 | 1.000 | | |
| 20.0 | 325.75 | 0.0000 | 0.0000 | | 1.000 | |
| | 316.67 | 0.0772 | 0.3296 | 2.947 | 0.9929 | 5.878 |
| | 312.65 | 0.1748 | 0.4775 | 2.239 | 1.021 | 4.313 |
| | 311.05 | 0.2373 | 0.5397 | 2.000 | 1.041 | 3.770 |
| | 309.45 | 0.3353 | 0.6057 | 1.705 | 1.095 | 3.045 |
| | 308.15 | 0.4594 | 0.6502 | 1.416 | 1.263 | 2.188 |
| | 307.70 | 0.5148 | 0.6823 | 1.353 | 1.303 | 2.024 |
| | 307.35 | 0.6143 | 0.7090 | 1.197 | 1.524 | 1.530 |
| | 307.03 | 0.7291 | 0.7569 | 1.093 | 1.838 | 1.157 |
| | 306.93 | 0.7765 | 0.7869 | 1.071 | 1.962 | 1.063 |
| | 306.86 | 0.8572 | 0.8537 | 1.057 | 2.113 | 0.9726 |
| | 307.27 | 0.9308 | 0.9172 | 1.026 | 2.426 | 0.8233 |
| | 307.90 | 1.000 | 1.000 | 1.000 | | |

[a]Standard uncertainties are $u(p) = 0.5$ kPa, $u(T) = 0.2$ K, and $u(x) = u(y) = 0.0033$, respectively.

$$L_j(x) = \frac{(2j - 1)x L_{j-1}(x) - (j - 1)L_{j-2}(x)}{j} \tag{5}$$

with

$$L_0(x) = 1 \tag{6}$$

$$L_1(x) = x \tag{7}$$

as the first two Legendre polynomials. The Legendre polynomials are orthogonal so that their coefficients are independent of the number of terms used to represent a particular continuous function, i.e., the reduced excess Gibbs free energy in this case.[16] To find the coefficient $a_j$ ($j = 0, 1, ..., K$) which represents the reduced excess Gibbs free energy under consideration best, one route is to implement a least squares regression.[13]

As recommended by Wisniak et al.,[16] the reduced excess Gibbs free energy ($g^E$) is plotted against the mole fraction of ethyl acetate in the liquid phase ($x_1$) in Figure 3, which demonstrates that the excess Gibbs free energies for the ethyl acetate + methylcyclohexane binary system are positive within the entire composition range under the pressures concerned. The experimental data are correlated using Legendre polynomials with 5 terms ($K = 4$) in the present work, as shown in Figure 3 with solid lines. The analytical expression given by eq 4 allows the calculation of pertinent activity coefficient and from there, the predicted value of vapor composition. According to Fredenslund et al.,[13] a set of VLE data is declared thermodynamically consistent if
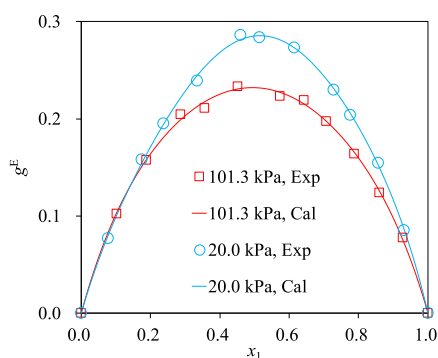
**Figure 3.** Reduced excess Gibbs free energy for ethyl acetate (1) + methylcyclohexane (2) binary system plotted against liquid composition. The experimental data are correlated using Legendre polynomials with 5 terms ($K = 4$). The subscripts "Exp" and "Cal" denote the experimental and calculated values, respectively.

$$\sum_{j=1}^{N} \frac{|y_{ij,\text{Exp}} - y_{ij,\text{Cal}}|}{N} \leq 0.01 \tag{8}$$

where $N$ is the number of experimental points, Exp denotes the experimental value, and Cal denotes the estimated value. The average absolute deviations of $y_{ij,\text{Exp}}$ from $y_{ij,\text{Cal}}$ determined are 0.009 and 0.010 at 101.3 and 20.0 kPa, respectively.

Wisniak[14] developed an additional test for thermodynamic consistency based on eq 4, which is described by the following equations

$$L = \frac{\sum T_i^{\text{o}} x_i \Delta S_i}{\sum x_i \Delta S_i} - T \tag{9}$$

$$W = \frac{RT}{\sum x_i \Delta S_i} \left( \sum x_i \ln \gamma_i - \sum x_i \ln \frac{y_i}{x_i} \right) \tag{10}$$

$$D = 100 \times \frac{\left| \int_0^1 L \, dx_1 - \int_0^1 W \, dx_1 \right|}{\int_0^1 L \, dx_1 + \int_0^1 W \, dx_1} \tag{11}$$

where $T_i^{\text{o}}$ is the boiling point of component $i$ at the equilibrium pressure $p$; $\Delta S_i$ is the entropy of vaporization of the same under identical conditions. According to Wisniak,[14] a set of VLE data is considered to be thermodynamically consistent if $D < 5$. The entropy of vaporization for ethyl acetate and methylcyclohexane is taken from Aspen Plus V12 (Aspen Technology, Inc., Bedford, Massachusetts, USA) physical property databank and listed in Table 5, as well as the values of $D$ calculated.

The aforementioned Fredenslund's test and Wisniak's L-W test are necessary but not sufficient thermodynamic consistency test since they are based on global statistics and as such do not take the possibility of local inconsistency into

**Table 5. Result of Wisniak's L-W Test for the Ethyl Acetate (1) + Methylcyclohexane (2) Binary System**

| | $\Delta S^a$ ($J \cdot mol^{-1} \cdot K^{-1}$) | | | | |
|---|---|---|---|---|---|
| $p$ (kPa) | ethyl acetate | methylcyclohexane | $\int_0^1 L dx_1$ | $\int_0^1 W dx_1$ | $D$ |
| 101.3 | 91.77 | 87.18 | 6.67 | 7.16 | 3.48 |
| 20.0 | 113.68 | 104.72 | 6.73 | 6.31 | 3.26 |

$^a$Taken from the Aspen Plus V12 physical property databank.

consideration.[16] For this reason, Van Ness's point-to-point test[15] is used to access the local thermodynamic consistency of the experimental VLE data for the ethyl acetate + methylcyclohexane binary system. According to Van Ness,[15] the residuals identified by the following equation will distribute randomly along the full concentration range if the VLE data are thermodynamically consistent

$$\Delta \ln \frac{\gamma_1}{\gamma_2} = \ln \frac{\gamma_{1,\text{Cal}}}{\gamma_{2,\text{Cal}}} - \ln \frac{\gamma_{1,\text{Exp}}}{\gamma_{2,\text{Exp}}} \tag{12}$$

To implement the Van Ness' point-to-point test to the isobaric VLE data for the ethyl acetate + methylcyclohexane binary system, the value of $\ln(\gamma_1/\gamma_2)$ for every point was calculated and then fitted using the NRTL model. The distribution of residuals given by eq 12 is shown in Figure 4. A
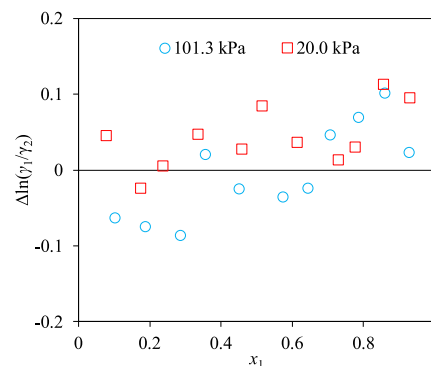


**Figure 4.** Results of Van Ness's point-to-point test for isobaric VLE data for the ethyl acetate (1) + methylcyclohexane (2) binary system at 101.3 and 20.0 kPa.

statistical test of Durbin-Watson[17] was carried out to check whether or not the distribution of residuals is random. The statistic values (DW) are 2.08 and 1.79 for the isobaric VLE data at 101.3 and 20.0 kPa, respectively. The result signifies that the distribution of residuals is random.

Based on the results of Fredenslund's test, Wisniak's L-W test, and Van Ness's point-to-point test, the isobaric VLE data for the ethyl acetate + methylcyclohexane binary system are confirmed to be thermodynamically consistent.

**3.4. Regression of VLE Data.** The isobaric VLE data for the ethyl acetate + methylcyclohexane binary system are also shown graphically in Figure 5 along with the UNIFAC model prediction. As shown in Figure 5, ethyl acetate and methylcyclohexane form a positive azeotrope or minimum-boiling azeotrope. However, the azeotropic point is hardly detectable as it falls within the region where the change in temperature is very small with respect to liquid composition. The approach proposed by Njenga[18] was therefore adopted to determine the azeotropic composition of the ethyl acetate + methylcyclohexane binary system in this work. The azeotropic points and compositions determined are listed in Table 6 along with the values reported by Gmehling and Bölts[19] for comparison.

One may note that the UNIFAC model provides a moderate quantitative prediction of isobaric VLE data for the ethyl acetate + methylcyclohexane binary system. To facilitate the design and optimization of the recovery process of such a system, experimental VLE data for the ethyl acetate + methylcyclohexane binary system were further correlated
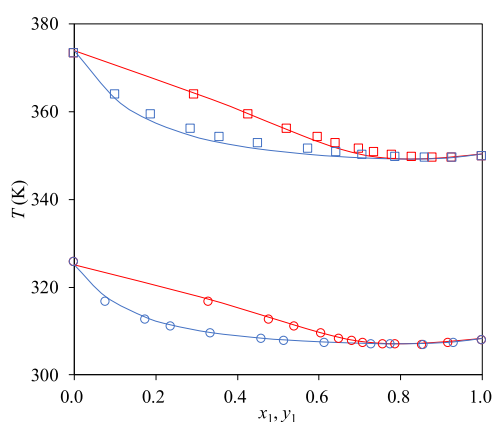
**Figure 5.** *T-x-y* diagram for ethyl acetate (1) + methylcyclohexane (2) binary system at 101.3 kPa (□) and 20.0 kPa (○). The symbols in red and blue represent vapor and liquid compositions determined, respectively. The smooth lines are the values predicted using the UNIFAC model.

**Table 6. Azeotropic Points and Compositions Determined for the Ethyl Acetate (1) + Methylcyclohexane (2) Binary System**

| $p$ (kPa) | $T$ (K) | liquid mole fraction (x) | | source |
|---|---|---|---|---|
| | | $x_1$ | $x_2$ | |
| 101.3 | 349.99 | 0.9259 | 0.0741 | this work |
| 20.0 | 307.31 | 0.8231 | 0.1769 | |
| 101.83 | 349.90 | 0.9000 | 0.1000 | Gmehling and Bölts[19] |
| 20.15 | 307.05 | 0.8215 | 0.1785 | |

with classical activity coefficient models of Wilson, NRTL, and UNIQUAC to generate the missing binary interaction parameters. The correlation of experimental VLE data was implemented in Aspen Plus V12. The maximum likelihood objective function, with the Britt-Luecke algorithm and the Deming initialization method, was used for model fitting. The maximum likelihood objective function is given as

$$\text{OF} = \sum_{j=1}^{N} \left[ \left( \frac{T_{j,\text{Cal}} - T_{j,\text{Exp}}}{\sigma^T} \right)^2 + \left( \frac{p_{j,\text{Cal}} - p_{j,\text{Exp}}}{\sigma^p} \right)^2 \right. $$
$$\left. + \left( \frac{x_{j,\text{Cal}} - x_{j,\text{Exp}}}{\sigma^x} \right)^2 + \left( \frac{y_{j,\text{Cal}} - y_{j,\text{Exp}}}{\sigma^y} \right)^2 \right] \tag{13}$$

where $\sigma$ denotes the standard deviation corresponding to a specific parameter. The VLE data predicted by Wilson, NRTL, and UNIQUAC models are listed in Tables S1−S3 in Supporting Information. As shown in Figures S3−S5, Wilson, NRTL, and UNIQUAC models result in practically the same

fit of experimental VLE data for the ethyl acetate + methylcyclohexane binary system and the performance is better than that of the UNIFIC model. The procedure proposed by Marcilla et al.[20,21] was used to ensure the consistency of correlation parameters listed in Tables 7 and 8.

**Table 8. UNIQUAC Structural Parameters for Ethyl Acetate and Methylcyclohexane**

| component | $r$ | $q$ |
|---|---|---|
| ethyl acetate | 3.44957 | 3.116 |
| methylcyclohexane | 4.64469 | 3.548 |

The reduced Gibbs energy of mixing ($g^M = \frac{G^M}{RT}$) for the ethyl acetate + methylcyclohexane binary system at 101.325 kPa was calculated with the binary interaction parameters. In Figures S6−S8, $g^M$ for liquid and vapor phases of the acetate + methylcyclohexane binary system is plotted against the conjugated liquid and vapor compositions, respectively. No common tangent line to the $g^M$ curves for liquid phase exists in these figures. It implies that the ethyl acetate + methylcyclohexane system is miscible, which is verified experimentally. The tie-lines connecting the conjugated liquid and vapor compositions are tangent to $g^M$ curves for liquid and vapor phases simultaneously. The common tangent line between the Gibbs energy of mixing functions for liquid and vapor phases meets the criterion of Gibbs stability, i.e., the global minimum of Gibbs energy. To further assess the binary interaction parameters, both isobaric and isothermal VLE data for the ethyl acetate + methylcyclohexane binary system are predicted and compared with experimental ones in Figures S9−S14. The comparison validates the reliability of binary interaction parameters obtained in this work.

**3.5. Separation of the Azeotropic Mixture of Ethyl Acetate + Methylcyclohexane by Extractive Distillation.** As mentioned above, ethyl acetate and methylcyclohexane form a positive azeotrope. Such an azeotropic mixture is pressure insensitive, i.e., the composition varies slightly with pressure (<101.3 kPa). It is thus infeasible to separate ethyl acetate from methylcyclohexane by pressure-swing distillation.

Extractive distillation is an effective separation technique for the pressure-insensitive azeotropic mixture.[3,22] Here, we determined the VLE data for the ethyl acetate + methylcyclohexane system in the presence of decane to evaluate the feasibility to separate them by the extractive distillation process. The isobaric VLE data are presented in Table 9 and shown graphically in Figures 6 and S15.

As shown in Figure 6, the azeotropy of ethyl acetate and methylcyclohexane disappears in the presence of decane. It means that ethyl acetate can be separated from methylcyclohexane by extractive distillation with decane as an additive.

**Table 7. Estimated Parameters and Root Mean Square Deviations (RMSD) for Thermodynamic Models for the Ethyl Acetate (1) + Methylcyclohexane (2) Binary System**

| model[a] | $a_{12}$ | $a_{21}$ | $b_{12}$ (K) | $b_{21}$ (K) | $c_{12}$ | RMSD | |
|---|---|---|---|---|---|---|---|
| | | | | | | $T$ (K) | $y_1$ |
| Wilson | 2.473 | −0.2633 | −1075 | −77.97 | | 0.36 | 0.0116 |
| NRTL | 0.9351 | −2.749 | −174.6 | 1165 | 0.3 | 0.37 | 0.0117 |
| UNIQUAC | −0.4727 | 1.235 | 201.9 | −562.4 | | 0.37 | 0.0117 |

[a]Model equations are given in Appendix A.2.

**Table 9. Experimental VLE Data for the Ethyl Acetate (1) + Methylcyclohexane (2) System in the Presence of Decane (3) at 101.3 kPa**[a]

| $T$ (K) | $x_1$ | $y_1$ | $x_2$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|---|---|---|---|---|---|---|---|
| 396.95 | 0.0000 | 0.0000 | 0.4288 | 0.8382 |  | 0.9928 |  |
| 390.45 | 0.0255 | 0.2126 | 0.3113 | 0.6813 | 1.808 | 0.9637 | 3.805 |
| 386.45 | 0.0594 | 0.3334 | 0.2889 | 0.5415 | 1.425 | 0.9667 | 2.994 |
| 379.55 | 0.0909 | 0.5088 | 0.2633 | 0.4075 | 1.653 | 0.9310 | 3.615 |
| 376.75 | 0.1152 | 0.6218 | 0.2175 | 0.3125 | 1.584 | 0.8594 | 3.756 |
| 372.55 | 0.1844 | 0.7043 | 0.2166 | 0.2351 | 1.508 | 0.8746 | 3.518 |
| 368.45 | 0.2284 | 0.7748 | 0.1647 | 0.1753 | 1.458 | 0.9340 | 3.189 |
| 366.05 | 0.2869 | 0.8304 | 0.1296 | 0.1241 | 1.406 | 0.9505 | 3.020 |
| 365.30 | 0.3088 | 0.8443 | 0.1169 | 0.1044 | 1.396 | 0.9313 | 3.063 |
| 364.65 | 0.3356 | 0.8580 | 0.0935 | 0.0836 | 1.351 | 0.9652 | 2.861 |
| 363.15 | 0.3556 | 0.9123 | 0.0456 | 0.0445 | 1.304 | 1.013 | 2.633 |
| 362.15 | 0.4241 | 0.9541 | 0.0000 | 0.0000 | 1.249 |  |  |

[a]Standard uncertainties are $u(p)$ = 0.5 kPa, $u(T)$ = 0.2 K, and $u(x)$ = $u(y)$ = 0.0033, respectively.
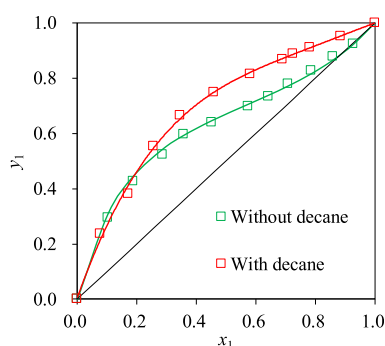


**Figure 6.** X-y diagram for the ethyl acetate (1) + methylcyclohexane (2) system at 101.3 kPa in the presence and absence of decane. For the ethyl acetate (1) + methylcyclohexane (2) + decane (3) ternary system, the composition of ethyl acetate is normalized by the mole fraction of decane. The smooth lines are the values predicted using the NRTL model.

## 4. CONCLUSIONS

Ethyl acetate and methylcyclohexane are organic solvents used widely in the flexible packaging industry. They are the main VOCs emitted from the plants, which need to be recovered due to environmental and economic concerns. To facilitate the design and optimization of the recovery process, the isobaric VLE data for the ethyl acetate + methylcyclohexane binary system were determined at 101.3 and 20.0 kPa in the present work. The VLE data were confirmed to be thermodynamically consistent by Fredenslund's test, Wisniak's L-W test, and Van Ness's point-to-point test and then fitted using Wilson, NRTL, and UNIQUAC models to obtain the binary interaction parameters. The results show that ethyl acetate and methylcyclohexane form a miscible azeotropic mixture with minimum boiling temperature, the composition of which varies very slightly with pressure. However, the azeotropy of ethyl acetate and methylcyclohexane vanishes in the presence of decane. It is suggested that the azeotropic mixture of ethyl acetate and methylcyclohexane cannot be separated by pressure swing distillation but by extractive distillation with decane as an entrainer.

## ■ APPENDIX A

### A.1. Uncertainty Quantification

The standard uncertainties of equilibrium compositions ($x_1$ and $y_1$) were estimated based on the standard deviation

derived from repeated measurements of the mixture with specified composition.

### A.2. Thermodynamic Models

Wilson model:[23]

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij}x_j\right) - \sum_j \frac{A_{ji}x_j}{\sum_k A_{jk}x_k}$$

(A.1)

where

$$\ln A_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

(A.2)

NRTL model:[24]

$$\ln \gamma_i = \frac{\sum_j G_{ji}\tau_{ji}x_j}{\sum_k G_{ki}x_k} + \sum_j \frac{G_{ij}x_j}{\sum_k G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_m G_{mj}\tau_{mj}x_m}{\sum_k G_{kj}x_k}\right)$$

(A.3)

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

(A.4)

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

(A.5)

The parameter for nonrandomness $c_{ij}$ is 0.3 for the binary system.

UNIQUAC model:[25]

$$\ln \gamma_i = \ln\frac{\varphi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\varphi_i} - q_i'\ln t_i' - q_i'\sum_j \frac{\theta_j'\tau_{ij}}{t_j'} + l_i + q_i'$$
$$- \frac{\varphi_i}{x_i}\sum_j l_j x_j$$

(A.6)

where

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right)$$

(A.7)

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.2c00682.

Plot of activity coefficient; validation of binary interaction parameters by comparing VLE data predicted with measured for ethyl acetate + methylcyclohexane binary system; thermodynamic consistency test of binary interaction parameters; comparison of experimental VLE data for ethyl acetate + decane binary system at 101.3 kPa; and the isobaric VLE data for ethyl acetate + methylcyclohexane binary system predicted by Wilson, NRTL, and UNIQUAC models (PDF)

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### Notes

The authors declare no competing financial interest.

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