Measurement and Prediction of Isothermal Vapor–Liquid Equilibrium and Thermodynamic Properties of a Turpentine + Rosin System Using the COSMO-RS Model

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ABSTRACT: The vapor–liquid equilibrium (VLE) of components of a turpentine + rosin system were measured at 313.2 and 333.2 K using headspace gas chromatography. The thermodynamic properties of the turpentine + rosin system such as activity coefficients, total pressure, partial pressure, excess Gibbs energies, and excess enthalpies were calculated using the COSMO-RS model. The results showed that the activity coefficients were greater than 1 for all components of turpentine except for longifolene, indicating a positive deviation from Raoult’s law for all components of turpentine except for longifolene. The total pressures were about 1 kPa at 313.2 K and about 3 kPa at 333.2 K. Meanwhile, the excess Gibbs energies $G^E$ and excess enthalpies $H^E$ of the system were positive, indicating that the mixing of the components of turpentine and rosin was endothermic. Moreover, the hydrogen bonding interaction energy $H_{(hydrogen bonding)}$ contributed the most for the excess enthalpies $H^E$.

1. INTRODUCTION

Pine oleoresin, a highly viscous resin secreted from the resinous tract of pine trees, is composed of turpentine (monoterpenes and sesquiterpenes) and rosin (diterpenes). Rosin is a nonvolatile solid mixture with a higher boiling point. The main components of rosin are resin acids. Rosin is widely used in materials, chemicals, and chemical engineering because of its excellent properties such as anticorrosion, moisture resistance, insulation, adhesion, and emulsification. Turpentine mainly consists of monoterpenes and sesquiterpenes. The main components of monoterpenes are $\alpha$-pinene, camphene, $\beta$-pinene, limonene, and $p$-cymene, which are easily volatile; the main component of sesquiterpenes is longifolene. Turpentine is applied widely in the synthesis of various fine chemicals, such as spices, medicine, and additives. Since these pine oleoresin derivatives have various applications in chemical industries, higher oleoresin yields are economically desirable.

Currently, pine oleoresin is often extracted by tapping living trees with the “debarking” (bark-peeling) method, in which bark removal is performed periodically, allowing pine oleoresin to be secreted and collected. However, pine oleoresin tapping is open-ended. As the easily volatile components of turpentine, such as $\alpha$-pinene, camphene, $\beta$-pinene, limonene, and $p$-cymene, are constantly evaporating into the atmosphere, about half of the turpentine yield is lost. Would the components of rosin (such as abietic acid, palustric acid, neoabietic acid, pimaric acid, sandopimaric acid, dehydroabietic acid, and isopimaric acid) have any effect on the interaction between the components of turpentine (such as $\alpha$-pinene, camphene, $\beta$-pinene, limonene, $p$-cymene, and longifolene) and thus affect their volatilization? Therefore, vapor–liquid equilibrium (VLE) data of components of turpentine and rosin is worth investigating.

To date, some VLE data of the aforementioned components of turpentine have already been reported. The isobaric VLE data of an $\alpha$-pinene + $\beta$-pinene system was obtained by Wang et al. Sun et al. reported the vacuum VLE data of an $\alpha$-pinene + $\beta$-pinene + $p$-cymene system at 53.5 and 80 kPa. Ruan et al. provided the isobaric VLE data for a pinane + $\alpha$-pinene + longifolene system. In their work, the activity coefficients of each component in each binary system were derived, and the excess Gibbs energy and excess enthalpy were obtained. Wu et al. reported the isobaric VLE data of binary systems with camphene, (+)-3-carene, (−)-$\beta$-caryophyllene, $p$-...
cyrene, and α-pinene at 101.33 kPa. They found calculated values by NRTL, Wilson, and UNIQUAC models that were in good agreement with the experimental VLE data. However, fewer reports providing VLE data of systems containing components of rosin were found. Since both turpentine and rosin contain many components which are not easily separated, VLE data for the turpentine + rosin system measured by the usual method of Ellis and Rose using a double-cycle equilibrium kettle seemed difficult. Therefore, the headspace gas chromatography (HSGC) method is used for the determination of VLE because this method has several advantages such as short VLE time, low dosage of reagents, and accurate temperature control.18–21

In this work, the isothermal VLE of components of the turpentine + rosin system were measured using the HSGC method at 313.2 and 333.2 K. The thermodynamic properties such as activity coefficients, total pressure, partial pressure, excess Gibbs energies, and excess enthalpies of the system were calculated by the COSMOtherm software based on the COSMO-RS model to provide more basic data for the turpentine + rosin system.

2. RESULTS AND DISCUSSION

2.1. Applicability of the COSMO-RS Model. In order to investigate the applicability of the COSMO-RS model to the system in this work, the isothermal VLE data of a β-pinene (1) + p-cymene (2) system in the literature25 were selected and compared with the values calculated using the COSMO-RS model in this work, as shown in Figure 1. The average absolute percentage deviation (AAPD) was calculated by eq 1.

\[ \text{AAPD}(T) = \sum_{i=1}^{n} \frac{|T_{\text{calc}} - T_{\text{ref}}|}{T_{\text{calc}}} \times 100\% \]  

where \( T_{\text{calc}} \) is the temperature calculated by COSMO-RS and \( T_{\text{ref}} \) is the temperature from the literature.22

The obtained AAPD was 0.04%, indicating that the calculated data with the COSMO-RS model were in good agreement with the literature data. Thus, the COSMO-RS model can be applied to predict the VLE data for the turpentine + rosin system in this study.

2.2. Vapor–Liquid Equilibrium Results. The isothermal VLE data were experimentally determined via the HSGC method. In order to verify the reliability of the HSGC method used in this work, the isothermal VLE data of the citral (1) + linalool (2) system at 333.2 K were measured and the experimental data were compared with the literature data.23 In Figure 2, the calculated AAPD was 0.85%, indicating that the HSGC method is reliable.

![Figure 2. Comparison of experimental and literature data for P−x−y of the citral (1) + linalool (2) system at 333.2 K.](https://doi.org/10.1021/acsomega.1c05167)
As can be seen, system were calculated using COSMO-RS as shown in Table 4. The excess Gibbs energies and excess enthalpies of the system were positive, indicating that the mixing process of the components of turpentine and rosin was endothermic. Moreover, both the $G^E$ and $H^E$ values increased with the decreasing mole fraction of turpentine components and increasing temperature. This may be attributed to the spatial effect. Since the components of rosin with a tricyclic phenanthrene skeleton are larger than the components of turpentine, with the mole fraction of the components of rosin increasing, the spatial effect makes the mixing of more rosin and the components of turpentine take more heat. Similar spatial effects are observed for mixtures of p-cymene + β-caryophyllene + 3-carene reported by Yao et al.\textsuperscript{26}

As shown in Table 4, $H^E_{\text{VDW}}$ is negative, indicating that the interactions between homogeneous molecules are smaller than that between heterogeneous molecules. This is because of the heterogeneity between the components of turpentine and rosin, which is confirmed by the σ-profiles analysis. According to the distribution of σ-profiles in Figure 3, the surface shielding charges of the components of turpentine were distributed in the weak polar region of $[-0.01, +0.01]$ e/Å$^2$, indicating that the components of turpentine were weak polar molecules. Obviously, two broad peaks were observed in the $[-0.02, −0.01]$ e/Å$^2$ hydrogen bond donor region, which were attributed to hydroxyl oxygen for the components of rosin, while one broad peak in the hydrogen bond acceptor region of $[+0.005, +0.015]$ e/Å$^2$ was attributed to carbonyl, reflecting the fact that the components of rosin were the polar compounds with both hydrogen bond donors and hydrogen bond acceptors.

Moreover, as can be seen from Table 4, $H^E_{\text{HB}}$ contributes most to the excess enthalpies $H^E$, which is probably due to the

| $x_1$ | $x_1'$ | $x_2$ | $x_2'$ | $x_3$ | $x_3'$ | $x_4$ | $x_4'$ | $x_5$ | $x_5'$ | $x_6$ | $y_1$ | $y_2$ | $y_3$ | $y_4$ | $y_5$ | $y_6$ |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |
| 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 |
| 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |
| 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |

*Standard uncertainties $u$ are $u(T) = 0.1$ K, $u(x_1) = 0.0021$, and $u(y_1) = 0.0023$.\textsuperscript{27}*

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The components of rosin increased, the activity coefficients of α-pinene, camphene, β-pinene, p-cymene, and limonene showed a gradually increasing trend but that of longifolene gradually decreased. It can also be seen from Table 2 that the activity coefficients were greater than 1 for all components of turpentine except for longifolene (6), indicating a positive deviation from Raoult’s law for all components of turpentine except for longifolene, which is attributed to strong attractive forces in the liquid phase between the components of turpentine. It means that, under the conditions of a mixture of volatile components, for α-pinene, camphene, β-pinene, p-cymene, and limonene, the intermolecular forces of their mixture are less than those of the pure one, as described by Prausnitz et al.\textsuperscript{25}

### 2.4. Total Pressure and Partial Pressure

The total pressure and partial pressure of α-pinene (1), camphene (2), β-pinene (3), p-cymene (4), limonene (5), and longifolene (6) of the turpentine + rosin system calculated using COSMO-RS are shown in Table 3. As shown in Table 3, the total and partial pressure were increased as the mole fraction of the rosin components and the temperature increased. The total pressure was about 1 kPa at 313.2 K and 3 kPa at 333.2 K. Moreover, α-pinene and β-pinene have the highest contribution to the total pressure since their molar fractions in the initial prepared samples were greater than those in the other components of turpentine.

### 2.5. Excess Gibbs Energies and Excess Enthalpies

The excess Gibbs energies $G^E$ and excess enthalpies $H^E$ of the system were calculated using COSMO-RS as shown in Table 4. As can be seen, $G^E$ and $H^E$ of the system were positive, gradually decreasing. It can also be seen from Table 2 that the activity coefficients were greater than those in the other components of turpentine, while one broad peak in the hydrogen bond acceptor region of $[-0.01, +0.01]$ e/Å$^2$, indicating that the mixing process of the components of turpentine and rosin was endothermic. Moreover, both the $G^E$ and $H^E$ values increased with the decreasing mole fraction of turpentine components and increasing temperature. This may be attributed to the spatial effect. Since the components of rosin with a tricyclic phenanthrene skeleton are larger than the components of turpentine, with the mole fraction of the components of rosin increasing, the spatial effect makes the mixing of more rosin and the components of turpentine take more heat. Similar spatial effects are observed for mixtures of p-cymene + β-caryophyllene + 3-carene reported by Yao et al.\textsuperscript{26}

As shown in Table 4, $H^E_{\text{VDW}}$ is negative, indicating that the interactions between homogeneous molecules are smaller than that between heterogeneous molecules. This is because of the heterogeneity between the components of turpentine and rosin, which is confirmed by the σ-profiles analysis. According to the distribution of σ-profiles in Figure 3, the surface shielding charges of the components of turpentine were distributed in the weak polar region of $[-0.01, +0.01]$ e/Å$^2$, indicating that the components of turpentine were weak polar molecules. Obviously, two broad peaks were observed in the $[-0.02, −0.01]$ e/Å$^2$ hydrogen bond donor region, which were attributed to hydroxyl oxygen for the components of rosin, while one broad peak in the hydrogen bond acceptor region of $[+0.005, +0.015]$ e/Å$^2$ was attributed to carbonyl, reflecting the fact that the components of rosin were the polar compounds with both hydrogen bond donors and hydrogen bond acceptors.

Moreover, as can be seen from Table 4, $H^E_{\text{HB}}$ contributes most to the excess enthalpies $H^E$, which is probably due to the
Table 2. Activity Coefficients of α-Pinene (1), Camphene (2), β-Pinene (3), p-Cymene (4), Limonene (5), and Longifolene (6) of the Turpentine + Rosin System at 313.2 and 333.2 K**

| x₀₁ | x₀₂ | x₀₃ | x₀₄ | x₀₅ | x₀₆ |
|-----|-----|-----|-----|-----|-----|
|     |     |     |     |     |     |

\[
x_0 = 1.002 \begin{array}{c}
0.844 \\
0.835 \\
0.825 \\
0.816 \\
0.805 \\
0.797 \\
0.786 \\
0.775 \\
0.765 \\
0.755 \\
0.745 \\
0.734
\end{array}
\]

\[
T/K = 313.2
\]  

\[
0.844 \quad 0.835 \quad 0.825 \quad 0.816 \quad 0.805 \quad 0.797 \quad 0.786 \quad 0.775 \quad 0.765 \quad 0.755 \quad 0.745 \quad 0.734
\]

\[
x_0 = 1.001 \begin{array}{c}
0.843 \\
0.834 \\
0.824 \\
0.815 \\
0.805 \\
0.793 \\
0.783 \\
0.773 \\
0.764 \\
0.754 \\
0.745 \\
0.734
\end{array}
\]

\[
T/K = 333.2
\]  

\[
0.843 \quad 0.834 \quad 0.824 \quad 0.815 \quad 0.805 \quad 0.793 \quad 0.783 \quad 0.773 \quad 0.764 \quad 0.754 \quad 0.745 \quad 0.734
\]

**Standard uncertainties u, u(γᵢ) = 0.0051.

fact that the oxygen atom of the carboxyl group in the components of rosin can be considered as a hydrogen bond acceptor and can readily form hydrogen bonds with the methyl and methylene groups in the components of turpentine. This is consistent with the σ-profiles analysis results from Figure 3, where the peaks of +0.007 and +0.012 e/Å² are attributed to the oxygen atom of the carboxyl group in the components of rosin.

3. CONCLUSIONS

The isothermal VLE of the components of the turpentine + rosin system at 313.2 and 333.2 K were measured by headspace gas chromatography. The thermodynamic properties of the system such as activity coefficients, total pressure, partial pressure, excess Gibbs energies, and excess enthalpies were calculated using COSMO-RS model. The results showed that the activity coefficients were greater than 1 for all components of turpentine except for longifolene, indicating a positive deviation from Raoult’s law. The total pressures were about 1 kPa at 313.2 K and 3 kPa at 333.2 K. Meanwhile, G² and H² of the system were positive, indicating that the mixing process for the components of turpentine and rosin was endothermic. The interactions between homogeneous molecules were smaller than those of heterogeneous molecules and resulted in negative H² (VDW). Moreover, H² (HB), which was caused by the hydrogen bonding interaction, contributed the most for the excess enthalpies H².

4. COMPUTATIONAL METHODOLOGY

4.1. COSMO-RS Model. The COSMO-RS (Conductor-like Screening Model for Realistic Solvation) model allows prediction of thermodynamic properties of mixtures without relying on experimental data. The basis of the COSMO-RS model calculation is the surface shielding charge distribution σ. The intermolecular interaction can be described by the shielding charge interaction between the small pieces of molecules in contact with each other on the molecular surface. The energy of intermolecular interactions is given by eqs 2–4.

\[
E_{\text{MF}}(\sigma, \sigma') = \frac{a_{\text{eff}}}{2} (\sigma, \sigma')^2
\]

\[
E_{\text{HB}}(\sigma, \sigma') = \varepsilon_{\text{HB}} \min(0, \sigma \sigma' + \sigma_{\text{HB}}^2)
\]

\[
E_{\text{VDW}}(\sigma, \sigma') = \varepsilon_{\text{VDW}} (\tau_{\text{VDW}} + \tau_{\text{VDW}}')
\]

where E_{\text{MF}} is the asymmetric energy of the shielding charge, E_{\text{HB}} is the energy of the intermolecular hydrogen bond, E_{\text{VDW}} is the energy of the reference state in solution, σ and σ' are the surface shielding charge density of the two interacting blobs, a_{\text{eff}} is the effective contact area, α is an interaction parameter, ε_{\text{HB}} is the hydrogen bond strength, σ_{\text{HB}} is the threshold for hydrogen bonding, and τ_{\text{VDW}} and τ_{\text{VDW}}' are element specific adjustable parameters.

The calculations using the COSMO-RS model occur over two steps. The first step is the quantum chemical calculations for the various substances involved in the system. These

Table 3. Total Pressure and Partial Pressure of α-Pinene (1), Camphene (2), β-Pinene (3), p-Cymene (4), Limonene (5), and Longifolene (6) of the Turpentine + Rosin System at 313.2 and 333.2 K

| x₀₁ | x₀₂ | x₀₃ | x₀₄ | x₀₅ | x₀₆ |
|-----|-----|-----|-----|-----|-----|
|     |     |     |     |     |     |

\[
x_0 = 1.176 \begin{array}{c}
0.844 \\
0.835 \\
0.825 \\
0.816 \\
0.805 \\
0.797 \\
0.786 \\
0.775 \\
0.765 \\
0.755 \\
0.745 \\
0.734
\end{array}
\]

\[
T/K = 313.2
\]  

\[
0.844 \quad 0.835 \quad 0.825 \quad 0.816 \quad 0.805 \quad 0.797 \quad 0.786 \quad 0.775 \quad 0.765 \quad 0.755 \quad 0.745 \quad 0.734
\]

\[
x_0 = 1.106 \begin{array}{c}
0.843 \\
0.834 \\
0.824 \\
0.815 \\
0.805 \\
0.793 \\
0.783 \\
0.773 \\
0.764 \\
0.754 \\
0.745 \\
0.734
\end{array}
\]

\[
T/K = 333.2
\]  

\[
0.843 \quad 0.834 \quad 0.824 \quad 0.815 \quad 0.805 \quad 0.793 \quad 0.783 \quad 0.773 \quad 0.764 \quad 0.754 \quad 0.745 \quad 0.734
\]

**Standard uncertainties u, u(P)= 0.0089 kPa.
quantum chemical calculations for the COSMO-RS model are performed by the Turbomole software based on density generalization theory, which can generate cosmo files to describe the molecular surface shielding charge $\sigma$ in a short time. The next step is the calculations of the microscopic intermolecular forces or the chemical potential to obtain thermodynamic properties by inputting the liquid phase composition and temperature using the COSMOtherm software.

### 4.2. Activity Coefficients

The activity coefficients for a given finite concentration can be calculated using the COSMO-RS model, in which the molar or mass fraction of the target compound is set as the desired value in the solvent composition. The activity coefficient of component $i$ of the mixture at molar fraction $x_i$ is calculated by eq 5.\(^3\)

$$\ln(\gamma_i) = \frac{\mu_i^s(x) - \mu_i^{(p)}}{RT}$$

where $\mu_i^s(x)$ is the chemical potential of component $i$ in the mixture, $\mu_i^{(p)}$ is the chemical potential of the pure component $i$, and $R$ is the gas constant.

### 4.3. Pressure

The total pressure of the VLE is calculated by eq 6.

$$P = \sum_{i=1}^{n} P_i = \sum_{i=1}^{n} P_i^0 x_i$$

where $P_i$ is the partial pressure of component $i$, $P_i^0$ is the vapor pressure of component $i$, $x_i$ is the molar fraction of component $i$ in the liquid phase, and $\gamma_i$ is the activity coefficient of component $i$ in the liquid phase. $P_i^0$ and $\gamma_i$ are both calculated by the COSMOtherm software.

### 4.4. Excess Gibbs Energies

The excess Gibbs energies at a given temperature and mixing conditions are calculated by eq 7.

$$G^e = RT \sum_{i=1}^{n} x_i \ln(\gamma_i)$$

where $x_i$ is the molar fraction of component $i$ in the liquid phase, $\gamma_i$ is the activity coefficient of component $i$ in the liquid phase calculated by the COSMO-RS, and $R$ is the gas constant.

### 4.5. Excess Enthalpies

To further investigate the nature of intermolecular interactions in solution, another important thermodynamic property, excess enthalpies $H_i^e$, is calculated by the COSMO-RS model based on eqs 8–11.

$$H_i^e = H_i^e(MF) + H_i^e(HB) + H_i^e(VDW)$$

$$H_i^e(MF) = x_i H_i^e(MF) + x_{i-1} H_{i-1}^e(MF) + \ldots + x_1 H_1^e(MF)$$

$$H_i^e(HB) = x_i H_i^e(HB) + x_{i-1} H_{i-1}^e(HB) + \ldots + x_1 H_1^e(HB)$$
Table 5. Mole Fraction and CAS Numbers of the Main Components of Turpentine and Rosin Used in This Study

| Components of turpentine | α-pinene | camphene | β-pinene | limonene | p-cymene | longifolene |
|-------------------------|----------|----------|----------|----------|----------|-------------|
| Mole fraction           | 0.851    | 0.017    | 0.078    | 0.018    | 0.022    | 0.014       |
| CAS                     | 80-56-8  | 79-92-5  | 127-91-3 | 138-86-3 | 99-87-6  | 475-20-7    |

| Components of rosin    | abietic acid | palustic acid | neoabietic acid | pimaric acid | dehydroabietic acid | sandopimaric acid | isopimaric acid |
|------------------------|--------------|---------------|-----------------|--------------|---------------------|-------------------|----------------|
| Mole fraction          | 0.440        | 0.247         | 0.156           | 0.088        | 0.047               | 0.015             | 0.007          |
| CAS                    | 514-10-3     | 1945-53-5     | 471-77-2        | 127-27-5     | 471-74-9            | 1740-19-8         | 5835-26-7      |

H^E(VDW) = x_i H^E_i(VDW) + x_2 H^E_2(VDW) + ... + x_n H^E_n(VDW)

Figure 4. Molecular structures of the main components of turpentine and rosin used in this study.

5. EXPERIMENTAL SECTION

5.1. Materials. Turpentine, provided by Guangxi Chaoyan Guoyou Forestry, mainly contains the following six components analyzed by gas chromatography: α-pinene, camphene, β-pinene, p-cymene, limonene, and longifolene. Rosin, provided by Guangxi Wuzhou Richeng Forestry Chemical Company, mainly contains the following seven components analyzed by gas chromatography: abietic acid, palustic acid, neoabietic acid, pimaric acid, dehydroabietic acid, sandopimaric acid, and isopimaric acid. The results of gas chromatography of turpentine and rosin are listed in Table 5. The molecular structures of the main components of turpentine and rosin are shown in Figure 4. Methanol (mass fraction, 99.9%, CAS, 67-56-1) and tetramethylammonium hydroxide solution (mass fraction, 25% aqueous solution, CAS, 75-59-2) were purchased from Shanghai Macklin Biochemical Company.

5.2. Apparatus and Procedure. The isothermal VLE data of components of the turpentine + rosin system at 313.2 and 333.2 K were measured by HSGC, which consists of a gas chromatography (GC) system (Agilent 7890B) and a headspace sampler (HS) (Agilent 7697A). GC included a HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column and a flame ionization detector (FID), while HS included an electro-pneumatic sampling system and a precision thermostat with an accuracy of 0.1 K. The carrier gas of GC was N₂ (99.999%) with a constant flow rate of 25 mL/min. The column temperature was 323.2 K at the beginning, and ramped to 343.2 at 5 K/min, ramped to 403.2 at 10 K/min, then ramped to 483.2 at 5 K/min and finally 523.2 at 20 K/min. The injector and detector temperature were 523.2 K.

5.3. Sample Preparation. Samples were prepared in appropriate mass ratios using an analytical balance (Mettler Toledo) with a precision of 1 × 10⁻⁴ g. The rosin was first poured into the headspace vial (equilibrium cell, 20 mL), and the others were injected with a pipet gun. Then, the headspace vial was sealed with an aluminum cap and placed on a sample tray, followed by heating for 60 min in the thermostat. Since the sample mixture (approximately 5 mL) and equilibrium cell were too small, 60 min was sufficient for the vapor and liquid phase to equilibrate with each other. Finally, the vapor phase in the headspace vial was automatically sampled and transported.
to the GC by the electro-pneumatic sampling system to obtain vapor phase composition. The liquid phase sample after vapor-liquid equilibrium was analyzed using GC following methyl esterification to obtain the liquid phase composition.

According to the properties and components of turpentine and rosins, six main components such as α-pinene (1), camphene (2), β-pinene (3), p-cymene (4), limonene (5), and longifolene (6) were selected for the VLE data measurements. The vapor-liquid phase components are all calculated by using eq 12.

$$x_i' = \frac{\sum_{i=1}^{n} A_i / M_i}{\sum_{i=1}^{n} A_i / M_i}$$

(12)

where $x_i'$ is the mole fraction of the six main components of turpentine in liquid phase without rosin, $y_i$ is the mole fraction of the six main components of turpentine, $A_i$ is peak area of component $i$ in the vapor-liquid phase in gas chromatography, $M_i$ is the molar mass of component $i$, and $n$ is the six main components of turpentine.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Garcia-Navas, D. F.; Bustamante, F.; Villa, A. L.; Alarcón, E. Esteriﬁcation of rosin with methyl alcohol for fuel applications. Rev. Fac. Ing. Univ. Antioquia 2020, 100, 10–20.
(2) Liu, P.; Liu, X. M.; Saburi, T.; Kubota, S.; Huang, P. X.; Wada, Y. Thermal Stability Evaluation of Rosin Acids and Rosin Modiﬁed Resins. ACS omega. 2020, 5 (4), 29102–29109.
(3) Han, C. R.; Zhou, R. N.; Han, B.; Tian, C.; Xu, P. F.; Song, X. L. The research progress in molecular self-assembly of rosin resin acids and their derivatives. Chem. Ind. For. Prod. 2019, 39 (5), 1–10.
(4) Yu, C.; Chen, C. W.; Gong, Q. H.; Zhang, F. A. Preparation of polymer microspheres with a rosin moiety from rosin ester, styrene and divinylbenzene. Polym. Int. 2012, 61 (11), 1619–1626.
(5) Tao, P.; Li, J. J.; Li, J.; Shang, S. B.; Song, Z. Q. Enhanced performance of rosin-based epoxy composites mixed with carbon nanotubes and cork powders from oriental oak bark. Ind. Crops. Prod. 2020, 158, 110351.
(6) Li, Q. G.; Liu, H.; Shang, S. B.; Song, Z. Research progress of rosin and its derivatives in polymer synthesis. Chem. Ind. For. Prod. 2017, 37 (4), 23–29.
(7) Vevere, L; Fridrihsone, A; Kirlukus, M; Cabulis, U. A Review of Wood Biomass-Based Fatty Acids and Rosin Acids Use in Polymeric Materials. Polymers. 2020, 12 (11), 2706.
(8) Kugler, S.; Ossowicz, P.; Malarczyk-Matusiak, K.; Wierzbička, E. Advances in rosin-based chemicals: the latest recipes, applications and future trends. Molecules. 2019, 24 (9), 1651.
(9) Jeevanantham, A. K.; Reddy, D. M.; Goyal, N.; Bansal, D.; Kumar, G.; Kumar, A.; Nanthagopal, K.; Ashok, B. Experimental study on the effect of cetane improver with turpentine oil on CI engine characteristics. Fuel 2020, 262, 116551.
(10) Farcas, A. D.; Mot, A. C.; Zagrean-Tuza, C.; Ticolea, M.; Sevastre, B.; Kulak, M.; Silagh-Dumitrescu, R.; Parvu, A. Remarkable rutin-rich Hypericum capitatum extract exhibits anti-inﬂammatory effects on turpentine oil-induced inﬂammation in rats. BMC Complementary Altern. Med. 2019, 19 (1), 1–13.
(11) Kaplan, C.; Alma, M. H.; Tutus, A.; Çetinkaya, M.; Karaosmanoğlu, F. Engine performance and exhaust emission tests of sulfate turpentine and No: 2 diesel fuel blend. Pet. Sci. Technol. 2005, 23 (11–12), 1333–1339.
(12) Zhang, Q. G.; Bi, L. W.; Zhao, Z. D.; Chen, Y. P.; Li, D. M.; Gu, Y.; Wang, J.; Chen, Y. X.; Bo, C. Y.; Liu, X. Z. Application of ultrasonic spraying in preparation of p-cymene by industrial dipentene dehydrogenation. Chem. Eng. J. 2010, 159, 190–194.
(13) Cătinescu, G. M.; Socolci, S. A.; Rotar, I.; Vidican, R.; Bunghez, F.; Tofană, M.; Plesa, A.; Muntean, M. Volatile proﬁle of minimally processed herbs during cold storage. Rom. Biotechnol. Lett. 2016, 21 (5), 1923.
(14) Wang, L. L.; Chen, X. P.; Wei, X. J.; Ma, J. Study on the vapor–liquid equilibrium of α-pinene and β-pinene system. Nat. Gas. Ind. 2002, 3, 57–60 (in Chinese).
(15) Sun, L. X.; Liao, D. Q.; Wang, K.; Sun, J. H.; Tong, Z. F. Vapor–liquid equilibrium data for α-pinene + β-pinene + p-cymene at reduced pressure. J. Chem. Ind. Eng. 2018, 69 (7), 2822–2828 (in Chinese).
(16) Ruan, F. X.; Che, J. J.; Hu, J.; Wang, Y.; Yuan, Bo.; Zhou, L. C. Vapor–liquid equilibrium of pinnae–α-pinene–longifolene system and its excess Gibbs free energy and excess enthalpy. J. Chem. Eng. Chin. Univ. 2015, 29 (6), 1306–1312 (in Chinese).
(17) Wu, J. Z.; Wang, L. L.; Chen, X. P.; Wei, X. J.; Liang, J. Z.; Yao, G. Y.; Zheng, P. Measurement and correlation of vapor–liquid equilibrium data for binary systems composed of camphene, (+)-3-carene, (−)-β-caryophyllene, p-cymene, and α-pinene at 101.33 kPa. Thermochim. Acta 2019, 769, 178318.

(18) Kolb, B.; Ettre, L. S. Static headspace-gas chromatography: theory and practice; John Wiley & Sons, 2006.

(19) Dai, Y.; Yu, Z. H.; Zhan, J. B.; Yue, B. S.; Xie, J.; Wang, H.; Chai, X. S. Determination of starch gelatinization temperatures by an automated headspace gas chromatography. J. Chromatogr. A 2019, 1602, 419–424.

(20) Yan, N.; Wan, X. F.; Chai, X. S.; Chen, R. Q. Determination of Chlorinated Volatile Organic Compounds in Polyamine Epichlorhydrin Solution by Headspace Gas Chromatography. J. Chromatogr. A 2017, 1496, 163–166.

(21) Wichitnithad, W.; Sudtannon, O.; Sirisunak, P.; Cheewatanakornkool, K.; Nantaphol, S.; Rojsittthisak, P. Development of a Sensitive Headspace Gas Chromatography–Mass Spectrometry Method for the Simultaneous Determination of Nitrosamines in Losartan Active Pharmaceutical Ingredients. ACS omega. 2021, 6 (16), 11048–11058.

(22) Xu, X. Q.; Liao, D. Q.; Li, L. S.; Chen, X. P.; Tong, Z. F. Determination and correlation of atmospheric pressure vapor–liquid equilibrium of α-alkene + β-pinene + p-cymene hydrocarbons. J. Chem. Eng. 2007, 2970–2974 (in Chinese).

(23) Zheng, P.; Wang, L. L.; Chen, X. P.; Wei, X. Z.; Liang, J. Z.; Wu, J. Z. Excess Gibbs Energies and Isothermal Vapor–Liquid Equilibrium for Citral + Linalool, Citral + α-Pinene, and Linalool + α-Pinene Systems Using Headspace Gas Chromatography. J. Chem. Eng. Data 2020, 65 (7), 3593–3604.

(24) Chu, Y. H.; Zhang, X. P.; Hillestad, M.; He, X. Z. Computational prediction of cellulose solubilities in ionic liquids based on COSMO-RS. Fluid Phase Equilib. 2018, 475, 25–36.

(25) Prausnitz, J. M.; Lichtenthaler, R. N.; De Azevedo, E. G. Molecular thermodynamics of fluid-phase equilibria; Pearson Education. 1998.

(26) Yao, G. Y.; Wang, L. L.; Chen, X. P.; Liao, D. Q.; Tong, Z. F.; Lei, F. H.; Li, P. F. Excess enthalpies of binary systems of β-strophanthrene, p-cymene and 3-carene. J. Chem. Eng. Chin. Univ. 2018, 32 (4), 779–784 (in Chinese).

(27) Klamt, A. Conductor-like screening model for real solvent: a new approach to the quantitative calculation of solvation phenomena. J. Phys. Chem. 1995, 99 (7), 2224–2235.

(28) Klamt, A.; Eckert, F. COSMO-RS: a novel and efficient method for the priori prediction thermo-physical data of liquids. Fluid Phase Equilib. 2000, 172 (1), 43–72.

(29) Klamt, A.; Krooshof, G. J. P.; Taylor, R. COSMOSPACE: alternative to conventional activity coefficient models. AIChE J. 2002, 48 (10), 2332–2349.

(30) Klamt, A. The COSMO and COSMO-RS solvation models. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2011, 1 (5), 699–709.

(31) Sinnecker, S.; Rajendran, A.; Klamt, A.; Diedenhofen, M.; Neese, F. Calculation of solvent shifts on electronic g-tensors with the conductor-like screening model (COSMO) and its self-consistent generalization to real solvents (direct COSMO-RS). J. Phys. Chem. A 2006, 110 (6), 2235–2245.

(32) Klamt, A.; Eckert, F. Prediction of vapor liquid equilibria using COSMOtherm. Fluid Phase Equilib. 2004, 217 (1), 53–57.

(33) Gaudin, T. Exploring direct prediction of surface tension from COSMO-RS theory. Chem. Phys. Lett. 2018, 706, 308–31.

(34) Loschen, C.; Reinsch, J.; Klamt, A. COSMO-RS based predictions for the SAMPL6 logP challenge. J. Comput. Aided Mol. Des. 2020, 34 (4), 385–392.

(35) Balchandani, S.; Singh, R. COSMO-RS Analysis of CO2 Solubility in N-Methyl diethanolamine, Sulfolane, and 1-Butyl-3-methyl-imidazolium Acetate Activated by 2-Methylpiperazine for Postcombustion Carbon Capture. ACS omega. 2021, 6 (1), 747–761.

(36) Ruiz, E.; Ferro, V. R.; Palomar, J.; Ortega, J.; Rodriguez, J. J. Interactions of ionic liquids and acetone: thermodynamic properties, quantum-chemical calculations, and NMR analysis. J. Phys. Chem. B 2013, 117 (24), 7388–7398.

(37) Wang, Z. H.; Liu, S. L.; Jiang, Y. F.; Lei, Z. G.; Zhang, J.; Zhu, R. S.; Ren, J. W. Methyl chloride dehydration with ionic liquid based on COSMO-RS model. Green Energy Environ. 2021, 6 (3), 413–421.