MEASUREMENTS AND THERMODYNAMIC MODELING OF VAPOR-LIQUID EQUILIBRIA FOR BINARY SYSTEMS OF ISOPROPYL CHLOROACETATE WITH CYCLOHEXANE, ISOPROPANOL AND BENZENE AT 101.3 kPa

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Abstract - In this work, the vapor-liquid equilibrium experimental data for the systems of isopropyl chloroacetate + isopropanol, isopropyl chloroacetate + cyclohexane and isopropyl chloroacetate + benzene were measured by a modified Rose-type recirculating still under the pressure of 101.3 kPa. The thermodynamic consistency of the measured data was verified by the Herington and van Ness methods, respectively. The experimental data were correlated by the NRTL, Wilson, and UNIQUAC activity coefficient models, and the corresponding interaction parameters of the three models were obtained. The root-mean-square deviations between the experimental data and calculated results for the temperature and the mole fraction of the vapor phase were less than 0.58 K and 0.0066, respectively. In addition, the excess Gibbs energy was calculated for the three systems.

Keywords: Vapor-liquid equilibrium; Isopropyl chloroacetate; Correlation; Thermodynamic model.

INTRODUCTION

Isopropyl chloroacetate is a raw material and intermediate, which is widely used in the synthesis of nonsteroidal anti-inflammatory drugs, such as naproxen, ketoprofen and ibuprofen. Generally, isopropyl chloroacetate can be synthesized by esterification of chloroacetic acid and isopropanol with a catalyst, such as cation exchange resin (Patwardhan and Sharma, 1990), inorganic salts (Liu and You, 2013), and ionic liquids (Liu et al., 2007). During the esterification process, the water-carrying agent is required to remove water continuously to increase the esterification yield. Ma et al. (2006) reported the synthesis of isopropyl chloroacetate using cyclohexane as a water-carrying agent in their work. Wang et al. (2003) used benzene as a water-carrying agent to separate water from the esterification process. After the reaction, a mixture of isopropyl chloroacetate, unreacted isopropanol and water-carrying agent is obtained. To separate isopropyl chloroacetate from the mixture by distillation, vapor-liquid equilibrium (VLE) data are required.

Until now, some works have reported the preparation of isopropyl chloroacetate (Xu et al., 2011; Liu and You, 2012). However, for separation of isopropyl chloroacetate from the reacted solution, the VLE data for the systems of isopropyl chloroacetate + isopropanol, isopropyl chloroacetate + cyclohexane and isopropyl chloroacetate + benzene have not been reported in the NIST database. Therefore, it is necessary to generate the VLE data for these systems, which can be useful for the separation and purification
of isopropyl chloroacetate from the mixture by distillation.

In this work, the VLE data for the systems isopropyl chloroacetate + isopropanol, isopropyl chloroacetate + cyclohexane and isopropyl chloroacetate + benzene were measured under the pressure of 101.3 kPa. To ensure the reliability of the measured VLE data, the thermodynamic consistency test was performed by the Herington and van Ness method. The non-random two-liquid (NRTL) (Renon and Prausnitz, 1968; Liu et al., 2019), Wilson (Wilson, 1964; Li, 2014), and the universal quasi-chemical (UNIQUAC) (Abrams and Prausnitz, 1975) activity coefficient models were used to correlate the experimental VLE data and the binary interaction parameters for the three models were regressed. In addition, the calculation of the excess Gibbs energy for the three systems from the VLE data was listed.

**EXPERIMENTAL**

**Chemicals**

Isopropyl chloroacetate, cyclohexane, isopropanol and benzene were commercial grade chemicals in this work. The mass purities of isopropyl chloroacetate, cyclohexane, isopropanol and benzene were 0.980, 0.995, 0.997 and 0.995, respectively, which were confirmed by gas chromatography (GC) and all the reagents were used directly. The boiling point temperatures for the chemicals were determined by a modified Rose-type recirculating still. The relevant information of the chemicals, such as CAS number, supplier, boiling temperature and so on, is given in Table 1.

**Apparatus and procedure**

The apparatus used in this work was a modified Rose-type recirculating still which is presented in detail in Figure 1. The equilibrium temperature was determined by a mercury thermometer with the accuracy of ± 0.1 K. The pressure was measured by a mercury U-shaped manometer and the accuracy of the manometer was ± 0.1333 kPa. In each experiment, a liquid mixture of 50 ml was charged into the equilibrium still and heated. The vapor condensate was recirculated and mixed with the liquid in the still, which could make enough contact for the two phases. To reach the equilibrium state, the recirculation time for the two phases was maintained for at least 50 min at a constant temperature, then the equilibrium temperature was recorded. At the same time, 0.3 ml of the vapor and the liquid phases were withdrawn by syringe for analysis, respectively. All the samples were analyzed by GC.

Gas chromatography (GC7900, Shanghai Tianmei Scientific Instrument Co., Ltd.) was used to analyze the samples, which was equipped with a flame ionization detector (FID) and a capillary column. The carrier gas was high-purity nitrogen with the purity of 99.999 wt%. The boiling temperature was measured at 101.3 kPa. The standard uncertainties \( u_P \) and \( u_T \) are \( u(P) = 0.35 \text{kPa}, u(T) = 0.35 \text{K} \). Suppliers: (1) TCI (Shanghai) Development Co., Ltd.; (2) Tianjin Kemio Chemical Co., Ltd., (3) Tianjin Fuyu Chemical Co., Ltd.

**Table 1. Information of the chemicals.**

| Name            | CAS     | Supplier | Mass fraction | \( T_b/\text{K} \) | Analysis method |
|-----------------|---------|----------|---------------|------------------|----------------|
| Isopropyl chloroacetate | 105-48-6 | (1)      | ≥0.980        | 422.85          | GC             |
| Isopropanol     | 67-63-0 | (2)      | ≥0.997        | 355.11          | GC             |
| Cyclohexane     | 110-82-7| (2)      | ≥0.995        | 353.83          | GC             |
| Benzene         | 71-43-2 | (3)      | ≥0.995        | 353.23          | GC             |

*a* Gas chromatography. *b* The boiling temperature was measured at 101.3 kPa. The standard uncertainties \( u_P \) and \( u_T \) are \( u(P) = 0.35 \text{kPa}, u(T) = 0.35 \text{K} \). *c* Suppliers: (1) TCI (Shanghai) Development Co., Ltd.; (2) Tianjin Kemio Chemical Co., Ltd., (3) Tianjin Fuyu Chemical Co., Ltd.
Analysis

Before analyzing the compositions of the samples, the area correction normalization method (Dai et al., 2014; Wu et al., 2018) was applied to calibrate the GC in this work. First, five different standard samples were prepared gravimetrically with an AR1140 electronic balance (Ohaus Corporation) with an accuracy of ±0.0001 g. The five different standard samples with known compositions were analyzed by GC and the peak area of GC was calibrated. The samples of the vapor and liquid phases were analyzed at least three times, and the average values were recorded.

RESULTS AND DISCUSSIONS

Experimental VLE results

The experimental VLE data of isopropyl chloroacetate + isopropanol, isopropyl chloroacetate + cyclohexane and isopropyl chloroacetate + benzene were measured at the pressure of 101.3kPa and are listed in Table 3. The T-x-y profiles for the three systems are plotted in Figures 2-4.

The equilibrium relationship of the system is represented by the following equation (Smith et al., 2001):

$$\phi_i, y, p = x, y, \phi_i^e, p^e \exp \left[ \frac{V_i^L (p - p_i^s)}{RT} \right]$$

(1)

Generally, the exponential term \(\exp[\frac{V_i^L (p - p_i^s)}{RT}]\) is approximately equal to 1 under atmospheric pressure. In addition, the vapor phase could be regarded as an ideal gas, thus \(\phi_i\) and \(\phi_i^e\) are equal to 1. Thus, Eq. 1 can be simplified as follows:

$$y, p = x, y, p_i^e \tag{2}$$

Table 3. Experimental VLE data for temperature \(T\), liquid phase mole fraction \(x_i\), vapor phase mole fraction \(y_i\), activity coefficient \(\gamma_i\), excess Gibbs energy \(G^E\), the results for cyclohexane (1) + isopropyl chloroacetate (2), isopropanol (1) + isopropyl chloroacetate (2) and benzene (1) + isopropyl chloroacetate (2) at 101.3kPa.*

| \(T\) (K) | \(x_1\) | \(y_1\) | \(\gamma_1\) | \(\gamma_2\) | \(G^E\) (J·mol⁻¹) |
|-----------|--------|--------|-------------|-------------|----------------|
| 353.83    | 1.0000 | 0.0000 | -           | -           | 0.00           |
| 355.65    | 0.9333 | 0.9894 | 1.0046      | 1.6575      | 112.32         |
| 357.64    | 0.8000 | 0.9685 | 1.0818      | 1.5909      | 431.71         |
| 360.60    | 0.7001 | 0.9519 | 1.1149      | 1.3574      | 503.03         |
| 366.02    | 0.5667 | 0.9239 | 1.1470      | 1.1921      | 468.21         |
| 370.33    | 0.4870 | 0.8961 | 1.1503      | 1.1599      | 444.25         |
| 376.60    | 0.3932 | 0.8549 | 1.1510      | 1.0789      | 317.49         |
| 381.35    | 0.3297 | 0.8162 | 1.1603      | 1.0393      | 237.34         |
| 385.20    | 0.2835 | 0.7755 | 1.1645      | 1.0352      | 217.65         |
| 389.60    | 0.2366 | 0.7215 | 1.1662      | 1.0344      | 201.46         |
| 394.96    | 0.1837 | 0.6508 | 1.1932      | 1.0125      | 139.85         |
| 400.25    | 0.1403 | 0.5634 | 1.1976      | 1.0116      | 117.18         |
| 405.30    | 0.1035 | 0.4668 | 1.2017      | 1.0100      | 94.14          |
| 410.45    | 0.0700 | 0.3560 | 1.2117      | 1.0043      | 59.49          |
| 416.85    | 0.0323 | 0.1903 | 1.2270      | 1.0041      | 36.62          |
| 418.96    | 0.0215 | 0.1325 | 1.2288      | 1.0011      | 19.18          |
| 422.85    | 0.0000 | 0.0000 | -           | -           | 0.00           |

* Standard uncertainties \(u(T), u(P), u(x)\) and \(u(y)\) are \(u(T)=0.35\ K, u(P)=0.35\ kPa, u(x)=0.0116, u(y)=0.0122\.

Figure 2. T-x-y phase equilibrium for the system cyclohexane (1) + isopropyl chloroacetate (2) at 101.3 kPa: ●, experimental data; —, calculated by the NRTL model.
The Wagner 25 parameters $C_{ij}$ to $C_{xx}$, as well as the $T_{rij}$ and $T_{ric}$ for each pure component $i$, were taken from the Aspen Plus physical properties databank and listed in Table 4. In the meantime, the activity coefficient was calculated by Eq. 2, and the results are listed in Table 3.

To evaluate the non-ideality of the three binary systems, the excess Gibbs energy $G^E$ (Acevedo et al., 1988; Shi et al., 2017) was calculated as follows:

$$G^E = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right)$$

The calculated results of $G^E$ are presented in Table 3 and Figure 5. As shown in Figure 5, the three binary systems exhibit positive deviations from Raoult’s law, which indicates the non-ideality of the solutions for three binary systems. Furthermore, the values of the excess Gibbs free energy for three binary systems follow the order of isopropyl chloroacetate + cyclohexane > isopropyl chloroacetate + isopropanol > isopropyl chloroacetate + benzene.

![Figure 3. T-x-y phase equilibrium for the system isopropanol (1) + isopropyl chloroacetate (2) at 101.3 kPa: ●, experimental data; —, calculated by the NRTL model.](image3)

![Figure 4. T-x-y phase equilibrium for the system benzene (1) + isopropyl chloroacetate (2) at 101.3 kPa: ●, experimental data; —, calculated by the NRTL model.](image4)

![Figure 5. Excess Gibbs energy for the three systems at 101.3 kPa: ▲, cyclohexane (1) + isopropyl chloroacetate (2); ●, isopropanol (1) + isopropyl chloroacetate (2); ■, benzene (1) + isopropyl chloroacetate (2), --, calculated by the NRTL model.](image5)

### Table 4. Parameters of the Wagner 25 equation.

| Component             | $C_{ij}$ | $C_{ii}$ | $C_{xx}$ | $p_x$/kPa | $T_x$/K | $T_{meas}$/K | $T_{upper}$/K |
|-----------------------|----------|----------|----------|-----------|---------|--------------|---------------|
| Isopropanol           | -3.7705  | -3.9060  | -3.7705  | 3420.33   | 614.00  | 190.00       | 614.00        |
| Cyclohexane           | -3.1898  | -2.1203  | -3.1898  | 4070.44   | 553.40  | 279.82       | 553.40        |
| Isopropyl chloroacetate | -2.3246  | -7.6671  | -2.3246  | 4751.67   | 508.27  | 185.24       | 508.27        |
| Benzene               | -2.2948  | -2.2948  | -2.2948  | 4894.12   | 562.02  | 278.47       | 562.02        |

* Taken from the Aspen Plus Physical Properties Databank.
Thermodynamic consistency tests

For the binary mixtures, the Herington and van Ness method were used to check the consistency of the experimental data.

The Herington method (Herington and Inst, 1951; Alinejhad et al., 2018) based on the Gibbs–Duhem theory was adopted which can be described as follows:

\[
D = 100 \times \frac{S_1 - S_2}{S_1 + S_2} = 100 \times \frac{\int_0^1 \ln(\gamma_1 / \gamma_2) \, dx}{\int_0^1 \ln(\gamma_1 / \gamma_2) \, dx}
\]  

(6)

\[
J = 150 \times \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}}
\]  

(7)

The \(\ln(\gamma_1 / \gamma_2)\) vs \(x\) diagram is shown in Figure 6 and \(T_{\text{max}}\) and \(T_{\text{min}}\) are the maximum and minimum boiling points, respectively. The criterion of the Herington test is that the absolute value of \(|D - J|\) should be less than 10. As shown in Table 5, the results of thermodynamic consistency for all three systems are all less than 10, which indicates that the experimental data of the three systems passed the thermodynamic consistency test.

The van Ness test method (Van Ness et al., 1973; Gao et al., 2016a) is expressed by the following equations:

\[
\Delta y = \frac{1}{N} \sum_{i=1}^{N} \Delta y_i = \frac{1}{N} \sum_{i=1}^{N} 100\left|\gamma_i^\text{ex} - \gamma_i^\text{cal}\right|
\]  

(8)

\[
\Delta P = \frac{1}{N} \sum_{i=1}^{N} \Delta P_i = \frac{1}{N} \sum_{i=1}^{N} 100\left|\frac{P^\text{exp} - P_i^\text{cal}}{P_i^\text{cal}}\right|
\]  

(9)

The obtained VLE data can pass the thermodynamic consistency test if the values of \(\Delta y\) and \(\Delta P\) are both less than 1. The test results are presented in Table 6. As seen from Table 6, the results of \(\Delta y\) and \(\Delta P\) are all less than unity, which indicates that the measured VLE data are thermodynamically consistent.

VLE data correlation

The measured experimental VLE data were correlated by the NRTL, Wilson and UNIQUAC activity coefficient models. For the UNIQUAC model, the structural parameters \(r\) and \(q\) are presented in Table 7. The expressions of the activity coefficient models are as follows:

NRTL:

\[
\ln y_i = \frac{\sum_j x_j \tau_{ij} G_{ij}}{\sum_j x_j G_{ij}} + \sum_j \frac{x_j G_{ij}}{\sum_i x_i G_{ij}} \left(\frac{\sum_k x_k \tau_{im} G_{mk}}{\sum_k x_k G_{mk}} - \tau_{ij}\right)
\]  

(10)

Wilson:

\[
\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}
\]  

(11)

\[
\alpha = 0.3
\]

(12)

\[
\ln y_i = 1 - \ln \left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ij} x_j}{\sum_k A_{ik} x_k}
\]  

(13)

Table 6. van Ness test for thermodynamic consistency check.

| System                  | \(\Delta P < 1\) | \(\Delta y < 1\) |
|------------------------|------------------|------------------|
| Cyclohexane (1) + isopropyl chloroacetate (2) | 0.16             | 0.5082           |
| +                      | 0.15             | 0.4951           |
| Isopropyl chloroacetate (2) | 0.15             | 0.4901           |
| +                      | 0.06             | 0.2745           |
| Isopropyl chloroacetate (2) | 0.08             | 0.2745           |
| +                      | 0.06             | 0.4439           |
| Isopropyl chloroacetate (2) | 0.08             | 0.4974           |

Figure 6. \(\ln(\gamma_1 / \gamma_2)\) vs. \(x\) plot for the three systems: ■, cyclohexane (1) + isopropyl chloroacetate (2); ●, isopropanol (1) + isopropyl chloroacetate (2); ▲, benzene (1) + isopropyl chloroacetate (2), --, calculated by the NRTL model.
UNIQUAC:

\[ \ln \gamma_i = \ln \frac{\Phi_{i|}}{x_i} + \frac{z}{2} q_i \ln \frac{0_i}{q_i} - q_i \ln \frac{0|}{q|} \sum_{j \neq i} \frac{0_j}{q_j} \frac{\tau_{ij}}{1 + \frac{q|}{q_|} \sum_{j \neq i} \tau_{ij}} \]  

(14)

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

(15)

\[ l_i = \left( \frac{z}{2} \right) (r_i - q_i)(r_i - 1) \]  

(16)

\[ \Phi_i = \frac{\sum_{j \neq i} \gamma_{ij} x_j}{\sum_{j \neq i} \gamma_{ij} x_k} \]  

(17)

\[ \theta_i = \frac{q_i x_i}{\sum q_k x_k} \]  

(18)

The interaction parameters of the above three models were obtained based on the maximum likelihood method by minimizing the following objective equation:

\[ Q = \sum_{i=1}^{N} \left[ \left( \frac{\sigma_{y_i} \gamma_i^{exp} - \sigma_{y_i} \gamma_i^{cal}}{\sigma_{y_i}} \right)^2 + \left( \frac{\sigma_{T} \gamma_i^{exp} - \sigma_{T} \gamma_i^{cal}}{\sigma_{T}} \right)^2 + \left( \frac{\sigma_{T} \gamma_i^{exp} - \sigma_{T} \gamma_i^{cal}}{\sigma_{T}} \right)^2 \right] \]  

(19)

The obtained interaction parameters of the NRTL, Wilson and UNIQUAC models in Aspen plus simulator (2013) are listed in Table 8. The root-mean-square deviations (RMSD) were employed to evaluate the difference between the experimental and the calculated results. The RMSD \((y_i)\) and RMSD \((T)\) are as follows:

\[ \text{RMSD}_{y_i} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_i^{exp} - y_i^{cal})^2} \]  

(20)

### Table 7. Structural parameters for the UNIQUAC equation.\(^a\)

| Component                      | \(r\) | \(q\) |
|--------------------------------|-------|-------|
| Isopropyl chloroacetate        | 4.663 | 4.064 |
| Cyclohexane                    | 4.047 | 3.240 |
| Isopropanol                    | 2.914 | 2.528 |
| Benzenes                       | 3.191 | 2.400 |

\(^a\) The structural parameters were taken from the Aspen plus physical properties databank.

The calculated RMSD values with the correlated parameters are presented in Table 8, which are less than 0.58 K and 0.006 respectively. As is shown in Table 8, the NRTL, Wilson and UNIQUAC models could correlate the VLE data for the three binary systems. Since the calculated results by the three model were graphically similar, the results correlated by the NRTL model were plotted in Figures 2-4.

According to the residuals of temperature and vapor mole fraction, the reliability of VLE data measured for each system has been checked (Orchilles et al., 2017; Mathias, 2017; Ma et al., 2018). Since the values of RMSD by the NRTL model were relatively larger than those of the Wilson and UNIQUAC models, the residuals of temperature and vapor mole fraction were calculated based on the difference between experimental values and the calculated values in the NRTL model. The residuals for the vapor mole fraction and temperature are less than 0.016 and 0.010 respectively.

The calculated RMSD values with the correlated parameters are presented in Table 8, which are less than 0.58 K and 0.006 respectively. As is shown in Table 8, the NRTL, Wilson and UNIQUAC models could correlate the VLE data for the three binary systems. Since the calculated results by the three model were graphically similar, the results correlated by the NRTL model were plotted in Figures 2-4.

### Table 8. The interaction parameters and root-mean-square deviations (RMSD) for binary systems.

| Model         | \(a_i\)  | \(a_2\)  | \(b_{ij}/K\) | \(b_{ij}/K\) | RMSD\((y_i)\) | RMSD\((T)\) |
|---------------|----------|----------|---------------|---------------|---------------|-------------|
| NRTL          | -2.7539  | 0.4169   | 1533.43       | -395.50       | 0.0606        | 0.58        |
| Wilson        | 0.2585   | 1.7588   | 53.88         | -1074.49      | 0.0057        | 0.54        |
| UNIQUAC       | 0.3081   | 0.1710   | -348.10       | 84.15         | 0.0058        | 0.54        |
| NRTL          | -10.0839 | 20.3022  | 3438.09       | -6918.72      | 0.0038        | 0.26        |
| Wilson        | -12.0894 | 5.4616   | 3991.10       | -3936.35      | 0.0035        | 0.26        |
| UNIQUAC       | 4.6921   | -10.2046 | -1827.72      | 3360.08       | 0.0037        | 0.23        |
| NRTL          | -10.2641 | 24.2028  | 3497.51       | -8392.13      | 0.0064        | 0.23        |
| Wilson        | -16.4172 | 5.1950   | 5562.50       | -1693.54      | 0.0043        | 0.17        |
| UNIQUAC       | 4.8828   | -12.9678 | -1552.45      | 4304.27       | 0.0066        | 0.21        |

\(^a\) NRTL, \(r_i = a_i + b_i/T\), the value of \(a_i\) was set at 0.3 for binary systems.

\(^b\) UNIQUAC, \(r_i = \exp(a_i + b_i/T)\).

\(^c\) Wilson, \(\ln A_i = a_i + b_i/T\).
The VLE data for the binary solutions of isopropyl chloroacetate + cyclohexane, isopropyl chloroacetate + isopropanol and isopropyl chloroacetate + benzene were generated at 101.3 kPa. The calculated excess Gibbs energy results indicate that the three systems show positive deviations from Raoult’s law. The thermodynamic consistency test for the experimental data was checked by the Herington and van Ness methods, and the measured VLE data passed the consistency tests. The thermodynamic models NRTL, Wilson, and UNIQUAC were adopted to fit the measured VLE data for the investigated systems and the binary interaction parameters of the models were regressed. The RMSD values for the mole fraction of vapor phase and the temperature were all less than 0.58 K and 0.0066, respectively.

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**NOMENCLATURE**

- **T**: Equilibrium temperature (K)
- **p**: Pressure (kPa)
- **N**: The point of the experimental data
- **α**: Non-randomness parameter in the NRTL model
- **r**: Area parameter of UNIQUAC
- **q**: Volume parameter of UNIQUAC
- **z**: Lattice coordination number in the UNIQUAC model
- **θ**: Area fraction in the UNIQUAC model
- **u**: Uncertainty
- **x**: Mole fraction in the liquid phase
- **y**: Mole fraction in the vapor phase
- **φ_i**: Fugacity coefficient of the vapor phase
- **φ_i^s**: Fugacity coefficient at the saturated pressure
- **γ**: Activity coefficient
- **V_i^L**: Liquid molar volume
- **R**: Universal gas constant (8.314 J.K⁻¹.mol⁻¹)
- **p_i^s**: Saturation vapor pressure
- **p_c**: Critical pressure of pure component
- **a, b**: Binary interaction parameters
- **σ**: Standard deviation
- **i,j**: Component i, j
- **cal**: Calculated property
- **exp**: Experimental property

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