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# Isobaric vapor–liquid equilibria of the binary mixtures propylene glycol methyl ether + propylene glycol methyl ether acetate, methyl acetate + propylene glycol methyl ether and methanol + propylene glycol methyl ether acetate at 101.3 kPa

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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) data for three binary systems (PM + PMA, MeAc + PM and MeOH + PMA) at 101.3 kPa were measured in a double circulating still of modified Othmer type. The thermodynamic consistency of the experimental data was checked by Herington method. The experimental data were correlated with NRTL and Wilson models. The binary interaction parameters of both models have been obtained by simplex method. The root mean square deviations (RMSD) for the vapor phase fraction and the boiling temperature are less than 0.01 and 0.5 K, respectively. The results indicate that the calculated values by NRTL and Wilson models are in good agreement with the experimental data and no azeotropic behavior has been found in the three binary systems. The research findings would provide basic data for the design and analysis of distillation process.



## 1. Introduction

Propylene glycol methyl ether acetate (PMA) is an important industrial solvent and extensively employed in ink, coatings, printing, dyeing, pesticides and other fields, due to its kindly environmental performance, excellent thermostability and small change of viscosity versus temperature. As a low toxicity solvent, PMA is gradually replacing ethylene glycol ether and ester solvents. Therefore, the demand for PMA is gradually increasing and the production of PMA grows greatly. A new synthesis process for PMA, the transesterification of propylene glycol methyl ether (PM) and methyl acetate (MeAc) to form PMA and by-product methanol (MeOH) is investigated in this work. Transesterification reactions are equilibrium limited reactions and usually could not react completely. In order to obtain PMA with desired purity, the separation and purification process (distillation was preferred) should be included in the whole production process. The vapor–liquid equilibrium data at atmospheric pressure are necessary for the design of distillation process and separation the mixture of PMA, PM, MeAc and MeOH. Many studies on experimental measures and correlations of VLE data were reported in the literatures [1–5]. But only the VLE data of two binary systems MeAc + MeOH [6,7] and MeOH + PM [8] are available in the literatures. The VLE data of the binary systems PM + PMA, MeAc + PM, MeOH + PMA and MeAc + PMA have not been available so far.

First, the isobaric VLE data for the binary PM (1) + PMA (2), MeAc (1) + PM (2) and MeOH (1) + PMA (2) were investigated at 101.3 kPa in a double circulating still of modified Othmer type. Meanwhile, the VLE data of the binary systems were both tested for thermodynamic consistency by the Herington method. Additionally, the binary VLE data were correlated by NRTL [9] and Wilson [10] models, which can provide the basic data for the design and simulation of reaction distillation.

## 2. Experimental

### 2.1. Materials

The main materials used in the VLE experiments are propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (PMA), methanol (MeOH), methyl acetate (MeAc) and Isopropanol (IPA). All the materials are high-purity grade (mass% ≥ 99.5%), PM and PMA were purchased from Aladdin, the other three chemicals were from Sinopharm. The purity of these materials was determined by gas chromatograph (GC) and no detectable impurity was observed, the purity of each pure component was listed in Table 1.

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**Nomenclature**

*List of symbols*

| | |
|---|---|
| $A, B, C$ | Antoine constants |
| $F_{ob}$ | objective function |
| $p_i^s$ | saturated vapor pressure (kPa) of component $i$ |
| $p$ | total pressure (kPa) |
| $N$ | the number of experimental points |
| $T$ | Temperature (K) |
| $x$ | mole fraction in the liquid phase |
| $y$ | mole fraction in the vapor phase |
| $g_{ij}$ | NRTL binary interaction parameter (J mol$^{-1}$) |

*Greek letters*

| | |
|---|---|
| $\rho$ | density |
| $\phi_i^s$ | fugacity coefficients of component $i$ in the pure phase |
| $\hat{\phi}_i^v$ | fugacity coefficients of component $i$ in the mixture vapor phase |
| $\alpha_{ij}$ | NRTL non-randomness parameter |
| $\Lambda ij$ | Wilson binary interaction parameter |
| $\gamma_i$ | activity coefficient |

*Subscripts*

| | |
|---|---|
| cal | calculated value |
| exp | experimental data |
| $i, j$ | component $i, j$ |
| 1, 2 | components 1, 2 |

*Superscripts*

| | |
|---|---|
| $s$ | saturation state |

The density ($\rho$), refractive index ($n_D$) and normal boiling point are measured and compared with the literature values in order to determine the purity of materials further. The results are shown in Table 2. The densities of pure compounds were measured at 298.15 K using the Anton Paar DMA-58 density meter with an accuracy of ±0.0001 g/cm$^3$. The refractive index of each pure compound was measured at 298.15 K using an Abbe refractometer Atago 3T with an accuracy of $\pm 10^{-4}$. The boiling points were measured at 101.3 kPa using a double circulating still of modified Othmer type with an error of ±0.1 K. The density, refractive index and normal boiling point showed a good agreement with the literature values. Therefore, no further purification was performed for these materials.

### 2.2. Analysis

To determine the concentration of the liquid and vapor samples, gas chromatograph (GC2014, Shimadzu Corporation) was used. Flame ionization detector (FID) was used together with a RTX-5 capillary column (30 m × 0.25 mm × 0.25 μm). The capillary column was used with a temperature programmed analysis. The temperature of capillary column firstly kept at 313.15 K for 3 min, then increased to 443.15 K at the rate of 40 K/min and maintained at 443.15 K for 1 min. The temperature of the injection port and detector were controlled at 523.15 K and 553.15 K, respectively. Nitrogen gas with a purity of 99.99% was used as the carrier gas at a flow rate of 1 mL/min, the injected volume was 1 μL. The compositions were determined by the internal standard method with the calibration curve. The final value of each sample was analyzed at least three times. With these repeated procedures, the accuracy of the equilibrium composition measurements was within ±0.0005 mole fraction.

### 2.3. Apparatus and procedures

The double circulating still, a modified Othmer type [11] was used to measure the VLE data. The equilibrium temperature was measured by a mercury thermometer with an accuracy of ±0.1 K. Additionally, the double circulating still was equipped with a digital manometer and a vacuum pump to keep the pressure of system at 101.3 kPa with the accuracy of ±0.1 kPa. Since the atmospheric pressure changed slightly during the experiments, so the temperature were corrected to 101.3 kPa with the following equation [12]:

$$T = T_{\mathrm{exp}} + \frac{1}{\sum_{i=1}^{2} B_i x_i / (T_{\mathrm{exp}} + C_i)^2} \times \frac{101.3 - P_{\mathrm{exp}}}{P_{\mathrm{exp}}} \quad (1)$$

where $T_{\mathrm{exp}}$ (K) is the experimental temperature at the real pressure; $B_i$ and $C_i$ are the Antoine constants of component $i$, shown in

**Table 1**
Materials description.

| Chemical name | Source | Initial mass fraction purity (mass%) | Purification method | Analysis method |
|---|---|---|---|---|
| Methyl acetate (MeAc) | Sinopharm | 99.86 | None | GC[a] |
| Methanol (MeOH) | Sinopharm | 99.80 | None | GC |
| Isopropanol (IPA) | Sinopharm | 99.68 | None | GC |
| Propylene glycol methyl ether (PM) | Aladdin | 99.90 | None | GC |
| Propylene glycol methyl ether acetate (PMA) | Aladdin | 99.85 | None | GC |

[a] Gas chromatograph.

**Table 2**
Comparison of density ($\rho$) and refractive index ($n_D$) at 298.15 K and boiling points ($T_b$) at 101.3 kPa of pure components with the literature data.

| Compound | $T_b$ (K) | | $\rho$ (g/cm$^3$) | | $n_D$ | |
|---|---|---|---|---|---|---|
| | This work | Literature | This work | Literature | This work | Literature |
| Methyl acetate | 330.4 | 330.05 [6]<br>330.018 [17] | 0.9275 | 0.9273 [6]<br>0.92790 [17] | 1.3596 | 1.3590 [6]<br>1.3589 [15] |
| Methanol | 337.7 | 337.85 [6]<br>337.696 [17] | 0.7869 | 0.7868 [6]<br>0.78664 [17] | 1.3269 | 1.3271 [6]<br>1.32652 [17] |
| Isopropanol | 355.6 | 355.392 [17] | 0.7814 | 0.78126 [17] | 1.3750 | 1.3752 [17] |
| PM | 393.3 | 393.25 [18]<br>393.04 [19] | 0.9165<br>– | 0.9164 [8]<br>0.9165 [20] | 1.4024<br>– | 1.4017 [18]<br>– |
| PMA | 419.0 | 419.13 [19] | 0.9630 | 0.9614 [21] | 1.4000 | 1.3991 [22] |

$u(T_b) = \pm 0.1$ K; $u(\rho) = \pm 0.0001$ g/cm$^3$; $u(n_D) = \pm 0.0001$.