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# Isobaric vapor–liquid equilibrium for the binary systems of 1-propanol + 1-(methoxymethoxy)-butane and 1-butanol + 1-(methoxymethoxy)-butane at 101.3 kPa

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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) data for 1-propanol + 1-(methoxymethoxy)-butane and 1-butanol + 1-(methoxymethoxy)-butane systems were measured at 101.3 kPa with a modified Rose still. The results indicated that two minimum temperature binary azeotropes were formed in two systems above. Thermodynamic consistency of the experimental data was confirmed by the Herington semi-empirical method. Saturated vapor pressure data for the pure component of 1-(methoxymethoxy)-butane used in the VLE calculations were measured. The experimental binary system equilibrium data were correlated by Van Laar, Wilson, and Non-Random Two Liquids (NRTL) activity coefficient models. The corresponding binary interaction parameters of the Van Laar, Wilson, and NRTL models were also obtained. By comparing the experimental value with the calculation values of the three models, the results showed that the Wilson and NRTL models used satisfactorily correlate the experimental results of two binary systems above.



## 1. Introduction

As is well known, the oxygenated compounds (molecules that contain oxygen in their structures) can reduce soot formation during combustion when added into diesel fuels. Polyoxymethylene methyl butyl ether is oxygenated compound, and it can increase the cetane number when added to diesel fuels [1]. 1-(Methoxymethoxy)-butane belongs to a kind of polyoxymethylene methyl butyl ether. They can be produced on a large scale from methanol and 1-butanol, but no isobaric vapor–liquid equilibrium (VLE) data are available for alcohols + 1-(methoxymethoxy)-butane mixture in the purification process. In this paper, we present isobaric VLE measurements for the mixture of 1-propanol + 1-(methoxymethoxy)-butane and 1-butanol + 1-(methoxymethoxy)-butane at 101.3 kPa and a series of saturated vapor pressure data for the pure component of 1-(methoxymethoxy)-butane to provide a reference for the purification of polyoxymethylene methyl butyl ether.

In addition, the experimental VLE data of two binary systems we investigated were thermodynamically consistent, and the activity coefficients were calculated and correlated with the Van Laar [2], Wilson [3], and Non-Random Two Liquids (NRTL) [4] equations.

## 2. Experimental

### 2.1. Chemicals

The chemicals used were 1-propanol, 1-butanol, and 1-(methoxymethoxy)-butane (molecular structure is shown in Fig. 1). The purity levels and sources of the chemicals used in this study are presented in Table 1. Analytical purity-grade 1-propanol and 1-butanol were purchased from Sinopharm Chemical Reagent. The 1-(methoxymethoxy)-butane was synthesized using formaldehyde, methanol and 1-butanol with acid catalyzing [5] and purified by distillation. The nominal purity of 1-propanol and 1-butanol were ≥99.7 wt%, with water content of 0.03 wt%. We checked these compounds with gas chromatography (GC6820, Agilent) and detected no appreciable peaks of impurities. The results show that the purity of 1-propanol and 1-butanol was ≥99.9 wt% and the purity of 1-(methoxymethoxy)-butane was ≥99.9 wt%.

We determined the purity of the chemicals by comparing their densities ($\rho$), and refractive indices ($n_D$) at 298.15 K and normal

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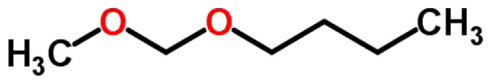

**Fig. 1.** The molecular structure of 1-(methoxymethoxy)-butane.

boiling points at 101.3 kPa with the corresponding literature values [6–10] as shown in Table 2. We measured the density of each pure chemical at 298.15 K by the pycnometer method. We measured the refractive index of each pure chemical at 298.15 K with an Abbe refractometer, with an accuracy of ±0.0001. We measured the normal boiling points at 101.3 kPa using a modified Rose still, with uncertainty of ±0.1 K. The results show that the measured densities, refractive indices, and normal boiling points were essentially consistent with literature values.

### 2.2. Sample analysis

The compositions of the equilibrium vapor and liquid samples were analyzed using the Agilent GC6820 with TCD. The type of chromatographic column was Porapak N (0.3 mm × 2 m; Hangzhou Kexiao Chemical Instrument Company, China). Splitless injection was used and the carrier gas was hydrogen at a flow rate of 60 mL/min. The temperature of the injector and detector was 433.15 K. The oven was operated at a programmed temperature that ranged from 423.15 to 513.15 K. We used the area normalization method to obtain quantitative results in the analysis. Analysis was performed at least three times for each liquid and vapor sample.

### 2.3. Apparatus and procedure

In this work, a modified Rose still was used to carry out the experiment. A detailed description of the apparatus has been reported and the reliability of its use in VLE study has been tested in our previous paper [1]. In this equilibrium process, both the vapor and the liquid phase were continuously circulating to ensure that equilibrium could be established. In each experiment, equilibrium between the vapor and the liquid phases was assumed when the temperature remained constant for 60 min or longer. The pressure control system with two bottles of buffer kept the system pressure at 101.30 ± 0.03 kPa, which was measured by a digital display vacuum measuring instrument (Chengdu Zhenghua Electronic Instrument Co., ZDY-II) with error range of less than 0.025 kPa.

**Table 3**
Comparison of experimental saturated vapor pressure data for 1-butanol at different temperatures with literature data.[a]

| No. | $p$(kPa) | $T_b$ (K) | | |
|---|---|---|---|---|
| | | This work | Literature [11][b] | Literature [12][b] |
| 1 | 101.33 | 390.88 | 390.98 | 390.75 |
| 2 | 80.00 | 384.38 | 384.40 | 384.37 |
| 3 | 53.33 | 373.90 | 373.75 | 374.00 |
| 4 | 40.47 | 367.34 | 367.00 | 367.34 |
| 5 | 26.67 | 357.79 | 357.19 | 357.81 |
| 6 | 20.00 | 351.41 | 350.90 | 351.59 |
| 7 | 13.33 | 343.02 | 342.53 | 343.28 |
| 8 | 8.00 | 333.27 | 332.76 | 333.51 |

[a] Standard uncertainties $u$ are $u(T_b) = \pm 0.1$ K, and $u(p) = \pm 0.01$ *kPa*.
[b] Calculated using the Antoine equation and equation parameters in the literature [11,12].

In addition, we measured the saturated vapor pressure data of 1-butanol within the scope of 10–101.33 kPa and compared with data in the literature [11,12] as shown in Table 3. The results showed that the apparatus used in measuring the saturated vapor pressure data is reliable.

## 3. Results and discussion

### 3.1. Experimental results

A series of saturated vapor pressure data for the pure component of 1-(methoxymethoxy)-butane is shown in Table 4. The isobaric VLE experimental data for the binary systems of 1-propanol + 1-(methoxymethoxy)-butane and 1-butanol + 1-

**Table 4**
Experimental saturated vapor pressure data for 1-(methoxymethoxy)-butane at different temperatures.[a]

| No. | $T_b$ (K) | $p$ (kPa) | No. | $T_b$ (K) | $p$ (kPa) |
|---|---|---|---|---|---|
| 1 | 322.39 | 8.01 | 8 | 375.14 | 59.90 |
| 2 | 344.03 | 20.00 | 9 | 377.68 | 64.95 |
| 3 | 354.88 | 30.00 | 10 | 380.07 | 69.92 |
| 4 | 358.96 | 34.84 | 11 | 384.46 | 79.80 |
| 5 | 362.81 | 39.85 | 12 | 388.45 | 89.80 |
| 6 | 369.65 | 50.00 | 13 | 390.12 | 94.40 |
| 7 | 372.54 | 55.02 | 14 | 392.59 | 101.33 |

[a] Standard uncertainties $u$ are $u(T_b) = \pm 0.1$ K, and $u(p) = \pm 0.01$ *kPa*.

**Table 1**
Materials description.

| Component | CAS | Source | Purity (mass%) | | Purification method |
|---|---|---|---|---|---|
| | | | Suppliers' | GC | |
| 1-Propanol | 71-23-8 | Sinopharm, China | ≥99.7 | ≥99.9 | None |
| 1-Butanol | 71-36-3 | Sinopharm, China | ≥99.7 | ≥99.9 | None |
| 1-(Methoxymethoxy)-butane | 76050-97-0 | Homemade | – | ≥99.9 | Distillation and dehydration |

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

| Component | $T_b$ (K) | | $\rho$(298.15 K)(g/cm$^3$) | | $n_D$ (298.15 K) | |
|---|---|---|---|---|---|---|
| | This work | Literature | This work | Literature | This work | Literature |
| 1-Propanol | 370.31 | 370.34 [6]<br>370.35 [8] | 0.7993 | 0.7995 [7]<br>0.7997 [9] | 1.3833 | 1.3837 [7]<br>1.3833 [9] |
| 1-Butanol | 390.84 | 390.81 [8]<br>390.90 [6] | 0.8052 | 0.8058 [7]<br>0.8059 [10] | 1.3967 | 1.3971 [7]<br>1.3970 [10] |
| 1-(Methoxymethoxy)-butane | 392.59 | – | 0.8371 | – | 1.3870 | – |

[a] Standard uncertainties $u$ are $u(T_b) = \pm 0.1$ K, $u(\rho) = \pm 0.0001$ g/cm$^3$, $u(n_D) = \pm 0.0001$.