# Three Binary Azeotropic Systems for 1-(Methoxymethoxy)-propane, 1-(Ethoxymethoxy)-propane, and Methoxy(methoxymethoxy)methane with Three Alcohols at 101.33 kPa: Experimental Data, Correlation, and Purification

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ABSTRACT: The isobaric vapor−liquid equilibrium (VLE) data for three binary systems of 1-(methoxymethoxy)-propane and ethanol, 1-(ethoxymethoxy)-propane and 1-butanol, methoxy(methoxymethoxy)methane and 1-propanol at 101.33 kPa were measured using an improved Rose still. Three minimum boiling azeotropes were found for three binary systems containing ethanol, 1-butanol, and 1-propanol for which the azeotropic temperature and composition are 349.35 K and 70.95 mol % (ethanol), 384.02 K and 36.02 mol % (1-butanol), 368.68 K and 69.26 mol % (1-propanol), at 101.33 kPa, respectively. The VLE measurements were correlated by the Van Laar, Wilson, and nonrandom two-liquid models, and the results showed that the measurements had a good correlation by using the three models for the three binary systems, respectively. The measurements of these three binary systems were thermodynamic as checked by the Herington semiempirical method.
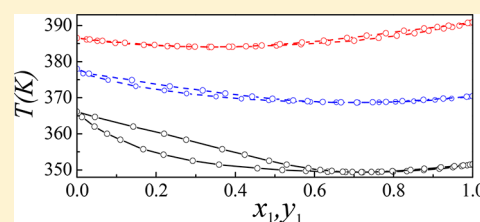
1. INTRODUCTION

Oxygenated compounds can reduce soot formation and increase the combustion efficiency during combustion which can be used as additives of gasoline or diesel. These compounds such as methoxy(methoxymethoxy)methane (DMM$_2$), 1-(methoxymethoxy)-propane (MMP), and 1-(ethoxymethoxy)-propane (EMP) can be synthesized from methylal, formaldehyde, methanol, ethanol, and 1-propanol.[1−5] However, before their separation technology can be devoped, the vapor−liquid equilibrium (VLE) measurements and their azeotropic state with alcohols mixture must be determined. The VLE and azeotropic state data are always required for engineering use, such as in the design of a distillation process. Here, we have measured the isobaric VLE measurements at 101.33 kPa for binary mixtures composed of three systems in this study to provide a reference for the development of distillation technology in the process of purifying these oxygenated compounds.

In addition, the thermodynamics consistency of these VLE measurements about three binary systems was checked with the help of the traditional area test and direct test methods. These VLE data have been compared with the result correlated by the Van Laar,[6] Wilson,[7] and the NRTL[8] models.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Methanol, ethanol, 1-propanol, 1-butanol, methylal, and formaldehyde were supplied from the Sinopharm Chemical Reagent. The DMM$_2$, MMP, and EMP (molecular structure in Figures 1, 2, and 3) were synthesized by using methanol, ethanol, 1-propanol, methylal, and formaldehyde[9,10]
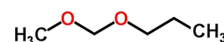

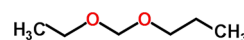**Figure 1.** Molecular structure of MMP.
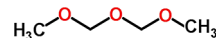

Figure 2. Molecular structure of EMP.

Figure 3. Molecular structure of DMM$_2$.

with the help of an acid catalyst under some different situations. The DMM$_2$ was synthesized by the mixture containing methylal and formaldehyde under the situation of 383.15 K and 1.0 MPa using H$_2$SO$_4$ as catalyst, and the yield is about 26%. The MMP was synthesized by the mixture containing methylal and 1-propanol under the situation of 373.15 K and 0.8 MPa using AlCl$_3$ as catalyst, and the yield is about 42%. The main byproducts are 1-(methoxymethoxymethoxy)-propane (MMMP) and 1-(propoxymethoxy)-propane (PMP). The EMP was synthesized by the mixture containing ethanol, 1-propanol, and methylal under the situation of 363.15 K and 0.6 MPa using the FeCl$_3$ as catalyst, and the yield is about 38%. The byproducts in the synthetic product are 1-(ethoxymethoxy)-ethane (EME), 1-(ethoxymethoxymethoxy)-ethane
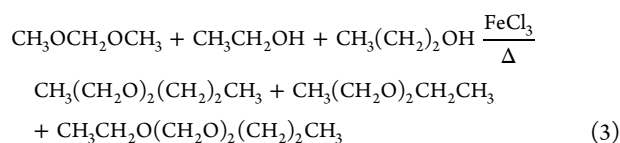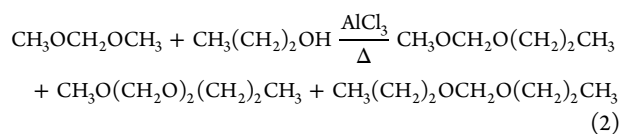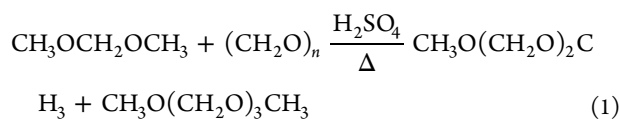
Table 1. Comparison of Density (ρ) at 293.15 K, Refractive Index (n_D) at 298.15 K and the Boiling Points (T_b) at 101.33 kPa of the Pure Components with Literature Data

component	T_b (K)[a]		ρ (293.15 K)(kg/m³)[b]		n_D (298.15 K)[b]	
	this work	lit.	this work	lit.	this work	lit.
ethanol	351.51	351.46[c]	789.2	789.3[d]	1.3595	1.3594[c]
		351.55[c]		789.1[c]		1.3593[c]
1-propanol	370.42	370.34[d]	803.6	803.6[d]	1.3835	1.3837[c]
		370.35[c]		803.4[e]		1.3833[e]
1-butanol	390.92	390.81[c]	809.5	809.7[d]	1.3971	1.3971[c]
		390.90[d]		809.5[c]		1.3974[c]
MMP	366.13	366.12[f]	841.2	841.4[f]	1.3757	1.3757[f]
EMP	386.53	386.53[g]	831.1	831.4[g]	1.3818	
DMM₂	378.00	377.95[h]	958.0	960.0[i,k]	1.3790	1.3789[h]
		378.15[i]		959.7[j,k]		

[a]Standard uncertainties u are $u(T) = 0.1K$, $u(P) = 0.05$ kPa. [b]Standard uncertainties u are $u(T) = 0.2K$, $u(P) = 0.3$ kPa, $u(\rho) = 0.2$ kg/m³, $u(n_D) = 0.0002$. [c]Standard literature.[12] [d]Standard literature.[13] [e]Standard literature.[14] [f]Standard literature.[3] [g]Standard literature.[4] [h]Standard literature.[1] [i]Standard literature.[15] [j]Standard literature.[16] [k]The data of refractive index for DMM₂ was the measurement at the temperature of 298.15 K.

(EMME), PMP, and a minor other compound. After that, we carried out a complex separation and purification process in order to obtain high purity chemicals.

$$CH_3OCH_2OCH_3 + (CH_2O)_n \xrightarrow[\Delta]{H_2SO_4} CH_3O(CH_2O)_2CH_3 + CH_3O(CH_2O)_3CH_3 \tag{1}$$

$$CH_3OCH_2OCH_3 + CH_3(CH_2)_2OH \xrightarrow[\Delta]{AlCl_3} CH_3OCH_2O(CH_2)_2CH_3 + CH_3O(CH_2O)_2(CH_2)_2CH_3 + CH_3(CH_2)_2OCH_2O(CH_2)_2CH_3 \tag{2}$$

$$CH_3OCH_2OCH_3 + CH_3CH_2OH + CH_3(CH_2)_2OH \xrightarrow[\Delta]{FeCl_3} CH_3(CH_2O)_2(CH_2)_2CH_3 + CH_3(CH_2O)_2CH_2CH_3 + CH_3CH_2O(CH_2O)_2(CH_2)_2CH_3 \tag{3}$$

2.2. Purification. Ethanol, 1-propanol, and 1-butanol with purities of 99.8 wt % used in the VLE experiment were supplied from the Sinopharm Chemical Reagent. These compounds were further purified by a separation process of the secondary rectification using a rectifying tower with 25 theoretical plates and a reflux ratio at 3:1. After the separation process, the purity of the three alcohols reached over 99.9 wt %, and the water content was less than 0.03 wt % in the three alcohols.

There is no azeotropic state between DMM₂ with methylal or methanol as proven in our early studies, so the purification method of DMM₂ is simply direct atmospheric rectification with the help of the rectifying tower as mentioned above under similar operating conditions. However, there are some azeotropic states between MMP (or EMP) with some alcohols, therefore MMP and EMP were purified by a complicated separation technology in which the separation process is similar to the purification method of 1-(methoxymethoxy)-2-methyl-propane that was described in our previous paper.[11] Considering that there are two binary azeotropes between 1-propanol with MMP or EMP, the mass content of alcohol for the lower boiling point is higher than that of the other compound in the synthetic materials of MMP and EMP. Therefore, the 1-propanol was consumed during the reaction. In the mixture after reaction, the content of 1-propanol was very small, being about 3−8 wt %.

First, most of the methanol or ethanol (unreacted) was removed by flash distillation in the reaction products of MMP and EMP. Afterward, a small quantity of formaldehyde decomposed from methylal in the reaction product was removed by washing using an alkaline hydrogen peroxide solution. Following, atmospheric distillation was used to achieve the separation of methanol, ethanol, and methylal, and concentrates were obtained which mainly consist of MMP, MMMP, PMP, and 1-propanol or EMP, EME, EMME, PMP, and 1-propanol.

Thereafter, the technology of reduced pressure distillation was used to achieve the separation of MMP (containing the 1-propanol of approximately 8.5 wt %) and MMMP at 101.3 ± 1 kPa and 362.5 ± 1 K. Similarly, the technology of reduced pressure distillation was used to achieve the separation of EMP (containing the 1-propanol of approximately 4.8 wt %) and EME and PMP at 101.3 ± 1 kPa and 369.5 ± 1 K. In the course of the experiment, we found that the boiling points of EME and PMP are about 361 ± 1 K and 410 ± 1 K, respectively, and there is no azeotropic state between EMP with EME or PMP. Consequently, this separation process was easy to implement.

Afterward, the technology of reduced pressure distillation was operated at 22 ± 1 kPa and 324 ± 1 K for MMP or at 26 ± 1 kPa and 323 ± 1 K for EMP before removing water; conveying the boiling portion of 362.5 ± 1 K or 369.5 ± 1 K which separated at 101.3 ± 1 kPa to rectification under vacuum; collecting the distillate of 366.1 or 386.5 K at 101.33 kPa upon secondary rectification as the experimental chemical of MMP and EMP. The theoretical plate number and the reflux ratio of the rectifying tower used in the purification process above were 25 and 3:1.

2.3. Analysis. An Agilent gas chromatograph (GC) 7890B with a thermal conductivity detector (TCD) and a flame ionization detector (FID, equipped with one chromatographic column of porapak N (Hangzhou Kexiao Chemical Instrument Company, China) and another capillary column of KB-5 (Kromat corporation, America) was used to measure the content of these chemicals. We did not find any significant impurities in the six chemicals after purification. The results showed that the purities of ethanol, 1-propanol, 1-butanol, DMM₂, MMP, and EMP were ≥ 99.9 wt %. We set the temperatures of detector, injector, and column box at 483.15 K, 473.15 K, and 373.15 to 453.15 K (programmed temperature, heating rate of 10 K/min), respectively. The quantitative results

Table 2. Materials Description

chemical name	ethanol	1-propanol	1-butanol	DMM₂	MMP	EMP
source	Sinopharm, China	Sinopharm, China	Sinopharm, China	Homemade	Homemade	Homemade
molecular formula	C_2H_6O	C_3H_8O	$C_4H_{10}O$	$C_4H_{10}O_3$	$C_5H_{12}O_2$	$C_6H_{14}O_2$
CASRN	64-17-5	71-23-8	71-36-3	628-90-0	71739-38-3	139157-75-8
suppliers' purity (wt %)	99.8	99.8	99.8			
purification method	distillation	distillation	distillation	distillation and dehydration	distillation and dehydration	distillation and dehydration
final purity (wt %)	99.9	99.9	99.9	99.9	99.9	99.9
water content (wt %)	0.03	0.03	0.02	0.02	0.02	0.02
analysis method	GC	GC	GC	GC	GC	GC

Table 3. Correlated Experiment Data and Deviations of Ethanol (1) + MMP (2) System by Van Laar, Wilson, and NRTL at 101.33 kPa

no.	T_{exp} (K)[a]	x_{1exp}[b]	y_{1exp}[b]	γ_1	γ_2	α_{12}[c]	Van Laar $\triangle T$[d]	Van Laar $\triangle y_1$[d]	Wilson $\triangle T$[d]	Wilson $\triangle y_1$[d]	NRTL $\triangle T$[d]	NRTL $\triangle y_1$[d]
1	366.13	0.0000	0.0000				0.44	0.0000	−0.42	0.0000	−0.42	0.0000
2	364.66	0.0124	0.0456	2.2317	1.0096	3.7972	0.62	0.0043	−0.16	0.0027	−0.14	0.0022
3	361.99	0.0446	0.1425	2.1424	1.0164	3.5619	0.52	0.0128	−0.07	0.0081	−0.03	0.0070
4	360.00	0.0762	0.2203	2.0847	1.0165	3.4235	0.35	0.0148	−0.10	0.0081	−0.05	0.0072
5	358.34	0.1099	0.2762	1.9281	1.0314	3.0898	0.16	0.0257	−0.17	0.0177	−0.14	0.0175
6	355.74	0.1677	0.3670	1.8539	1.0483	2.8774	0.32	0.0213	0.13	0.0125	0.13	0.0134
7	354.22	0.2188	0.4240	1.7397	1.0678	2.6272	0.27	0.0213	0.16	0.0127	0.13	0.0143
8	352.51	0.2927	0.4857	1.5924	1.1140	2.2821	0.34	0.0219	0.28	0.0148	0.23	0.0169
9	351.46	0.3592	0.5302	1.4758	1.1636	2.0125	0.36	0.0209	0.31	0.0158	0.25	0.0179
10	350.48	0.4560	0.5851	1.3341	1.2509	1.6826	0.34	0.0170	0.26	0.0153	0.20	0.0168
11	349.98	0.5192	0.6148	1.2555	1.3365	1.4779	0.38	0.0165	0.29	0.0171	0.23	0.0178
12	349.69	0.5788	0.6442	1.1939	1.4232	1.3175	0.37	0.0136	0.26	0.0162	0.21	0.0162
13	349.49	0.6336	0.6718	1.1462	1.5191	1.1837	0.37	0.0109	0.23	0.0150	0.19	0.0143
14	349.41	0.6792	0.6961	1.1116	1.6108	1.0821	0.35	0.0084	0.20	0.0136	0.16	0.0124
15	349.38	0.7219	0.7190	1.0815	1.7201	0.9858	0.34	0.0077	0.17	0.0135	0.14	0.0120
16	349.41	0.7617	0.7441	1.0595	1.8261	0.9098	0.32	0.0055	0.13	0.0115	0.11	0.0099
17	349.50	0.7993	0.7704	1.0416	1.9391	0.8428	0.30	0.0035	0.09	0.0094	0.07	0.0078
18	349.65	0.8340	0.7972	1.0268	2.0598	0.7828	0.27	0.0022	0.04	0.0077	0.03	0.0063
19	349.97	0.8766	0.8431	1.0202	2.1214	0.7566	0.21	−0.0068	−0.05	−0.0024	−0.06	−0.0034
20	350.32	0.9158	0.8778	1.0025	2.3942	0.6600	0.21	−0.0007	−0.10	0.0024	−0.10	0.0019
21	350.74	0.9504	0.9201	0.9961	2.6182	0.6012	0.23	0.0004	−0.12	0.0021	−0.11	0.0021
22	351.04	0.9722	0.9538	0.9974	2.6741	0.5904	0.27	−0.0012	−0.10	−0.0004	−0.09	−0.0002
23	351.27	0.9862	0.9762	0.9971	2.7474	0.5753	0.30	−0.0008	−0.08	−0.0005	−0.08	−0.0003
24	351.45	0.9961	0.9933	0.9976	2.7506	0.5755	0.33	−0.0004	−0.06	−0.0003	−0.06	−0.0003
25	351.51	1.0000	1.0000				0.35	0.0000	−0.05	0.0000	−0.05	0.0000
maximum deviation							0.62	0.0257	−0.42	0.0177	−0.42	0.0179
average absolute deviation							0.33	0.0095	0.16	0.0088	0.14	0.0087

[a]Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.05$ kPa. [b]Expanded uncertainties U are $U(x_1) = U(y_1) = 0.0046$, $P = 0.95$. [c]Relative volatility. The antoine equation used is $\alpha_{ij} = \frac{y_i}{y_j} / \frac{x_i}{x_j}$. [d]Calculation: $\Delta T = (T_{cal} - T_{exp})$, $\Delta y_1 = (y_{1cal} - y_{1exp})$.

were acquired by the area normalization method in the process of analysis. The water contents were analyzed by the GC7890B with porapak N and TCD for which the detection limit for water content in an organic compound is 0.001 wt %. The water content was ≤ 0.03 wt % in ethanol and 1-propanol and ≤ 0.02 wt % in 1-butanol, MMP, EMP, DMM₂. The sources, purity, and water content of the reagents are listed in Table 1.

As additional purity checks, we tested the normal boiling points, densities (ρ), and refractive indices (n_D) of six pure chemicals and compared these measurements with the literature values[12−16] presented in Table 2. The methods of measurement and calculation for three physical property parameters have been described in our previous paper.[4]

The normal boiling point of each pure chemical at 101.33 kPa was measured by a modified Rose still whose uncertainty is 0.05 K and 0.02 kPa. The density of each pure chemical was measured at 293.15 ± 0.1 K and 101.33 ± 0.25 kPa by the pycnometer (Tianjin Glass Company LTD, Tianjin, China) method for which the uncertainty of its capacity was 0.03%. The pycnometer was verified by calculating on the basis of weight the filling quality when absolutely packed with the distilled water at 25 °C. The electronic analytical balance (Mettler Toledo Instrument Company, Switzerland) for which the accuracy is 0.0001 was used to weigh the relative quality. The refractive index of each pure chemical was measured at 298.15 ± 0.1 K and 101.33 ± 0.15 kPa by an Abbe refractometer (Shanghai INESA Instrument Company, China).

Table 4. Experiment Data and Deviations Correlated of 1-Butanol(1) + EMP (2) System by Van Laar, Wilson and NRTL at 101.33 kPa

no.	T_{exp} (K)[a]	x_{1exp}[b]	y_{1exp}[b]	γ_1	γ_2	α_{12}[c]	Van Laar		Wilson		NRTL	
							ΔT[d]	Δy_1[d]	ΔT[d]	Δy_1[d]	ΔT[d]	Δy_1[d]
1	386.53	0.0000	0.0000				1.12	0.0000	−0.07	0.0000	−0.07	0.0000
2	386.13	0.0245	0.0325	1.5713	1.0006	1.3345	1.03	0.0047	−0.03	0.0013	−0.02	0.0013
3	385.78	0.0516	0.0643	1.4995	1.0053	1.2640	0.93	0.0104	−0.01	0.0041	0.00	0.0040
4	385.21	0.0972	0.1212	1.5312	1.0085	1.2808	0.89	0.0099	0.11	0.0005	0.11	0.0004
5	384.61	0.1692	0.1962	1.4561	1.0200	1.1983	0.80	0.0108	0.21	−0.0009	0.21	−0.0008
6	384.27	0.2289	0.2534	1.4082	1.0311	1.1433	0.78	0.0078	0.30	−0.0040	0.30	−0.0038
7	384.13	0.2830	0.2983	1.3481	1.0464	1.0772	0.72	0.0072	0.31	−0.0037	0.31	−0.0034
8	384.05	0.3342	0.3395	1.3030	1.0633	1.0240	0.71	0.0052	0.35	−0.0045	0.35	−0.0042
9	384.11	0.3930	0.3840	1.2502	1.0858	0.9626	0.64	0.0034	0.33	−0.0044	0.33	−0.0042
10	384.26	0.4517	0.4274	1.2040	1.1124	0.9060	0.57	0.0012	0.30	−0.0045	0.29	−0.0043
11	384.48	0.5042	0.4672	1.1693	1.1372	0.8623	0.50	−0.0019	0.25	−0.0056	0.25	−0.0055
12	384.82	0.5662	0.5130	1.1291	1.1763	0.8072	0.44	−0.0035	0.21	−0.0049	0.20	−0.0050
13	385.31	0.6343	0.5688	1.0974	1.2181	0.7605	0.37	−0.0082	0.15	−0.0072	0.14	−0.0074
14	385.82	0.7006	0.6237	1.0689	1.2791	0.7085	0.40	−0.0090	0.17	−0.0060	0.16	−0.0063
15	386.57	0.7624	0.6824	1.0456	1.3318	0.6695	0.32	−0.0111	0.07	−0.0068	0.06	−0.0071
16	387.20	0.8083	0.7320	1.0335	1.3678	0.6476	0.30	−0.0135	0.01	−0.0087	0.01	−0.0089
17	387.88	0.8533	0.7807	1.0188	1.4342	0.6121	0.32	−0.0104	−0.01	−0.0056	−0.01	−0.0057
18	388.52	0.8891	0.8261	1.0108	1.4776	0.5924	0.33	−0.0095	−0.05	−0.0051	−0.05	−0.0051
19	389.20	0.9270	0.8774	1.0044	1.5523	0.5634	0.42	−0.0058	−0.01	−0.0024	−0.01	−0.0023
20	389.60	0.9483	0.9107	1.0048	1.5781	0.5561	0.51	−0.0051	0.04	−0.0024	0.04	−0.0024
21	389.98	0.9664	0.9392	1.0028	1.6344	0.5375	0.57	−0.0027	0.07	−0.0007	0.07	−0.0007
22	390.72	0.9936	0.9877	0.9991	1.7012	0.5174	0.58	−0.0004	0.01	0.0000	0.01	0.0000
23	390.92	1.0000	1.0000				0.56	0.0000	−0.02	0.0000	−0.02	0.0000
maximum deviation							1.12	−0.0135	0.35	−0.0087	0.35	−0.0089
average absolute deviation							0.60	0.0062	0.13	0.0036	0.13	0.0036

[a]Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.05$ kPa. [b]Expanded uncertainties U are $U(x_1) = U(y_1) = 0.0030$, $P = 0.95$. [c]Relative volatility. The antoine equation used is $\alpha_{ij} = \frac{y_i}{y_j} / \frac{x_i}{x_j}$. [d]$\Delta T = (T_{cal} - T_{exp})$, $\Delta y_1 = (y_{1cal} - y_{1exp})$

Table 5. Experiment Data and Deviations Correlated of 1-Propanol (1) + DMM₂ (2) System by Van Laar, Wilson, and NRTL at 101.33 kPa

no	T_{exp} (K)[a]	x_{1exp}[b]	y_{1exp}[b]	γ_1	γ_2	α_{12}[c]	Van Laar		Wilson		NRTL	
							ΔT[d]	Δy_1[d]	ΔT[d]	Δy_1[d]	ΔT[d]	Δy_1[d]
1	378.00	0.0000	0.0000				0.50	0.0000	−0.47	0.0000	−0.47	0.0000
2	376.67	0.0154	0.0305	1.5779	1.0175	2.0175	1.11	0.0027	0.23	0.0007	0.24	0.0006
3	374.85	0.0791	0.1390	1.4914	1.0191	1.8790	0.74	0.0118	0.13	0.0044	0.15	0.0042
4	373.16	0.1488	0.2349	1.4258	1.0299	1.7560	0.59	0.0168	0.17	0.0073	0.18	0.0073
5	372.02	0.2209	0.3178	1.3560	1.0380	1.6433	0.31	0.0179	0.01	0.0086	0.02	0.0090
6	371.17	0.2771	0.3749	1.3165	1.0518	1.5644	0.29	0.0165	0.05	0.0082	0.05	0.0088
7	370.30	0.3515	0.4428	1.2664	1.0729	1.4660	0.26	0.0128	0.06	0.0066	0.06	0.0073
8	369.72	0.4157	0.4944	1.2221	1.0998	1.3741	0.25	0.0105	0.08	0.0064	0.07	0.0071
9	369.26	0.4851	0.5467	1.1785	1.1346	1.2800	0.24	0.0073	0.07	0.0055	0.06	0.0060
10	369.03	0.5354	0.5828	1.1483	1.1657	1.2119	0.22	0.0051	0.05	0.0051	0.04	0.0053
11	368.84	0.5901	0.6212	1.1189	1.2066	1.1393	0.22	0.0028	0.05	0.0045	0.03	0.0045
12	368.71	0.6557	0.6675	1.0875	1.2661	1.0541	0.23	0.0004	0.04	0.0037	0.02	0.0035
13	368.70	0.7107	0.7073	1.0634	1.3264	0.9839	0.22	−0.0013	0.00	0.0031	0.00	0.0027
14	368.74	0.7634	0.7474	1.0443	1.3981	0.9170	0.24	−0.0023	0.00	0.0026	0.00	0.0021
15	368.85	0.8052	0.7812	1.0308	1.4664	0.8637	0.25	−0.0026	−0.01	0.0025	−0.01	0.0020
16	369.05	0.8513	0.8224	1.0183	1.5495	0.8087	0.26	−0.0029	−0.04	0.0018	−0.04	0.0015
17	369.40	0.9053	0.8760	1.0065	1.6802	0.7390	0.28	−0.0017	−0.07	0.0020	−0.06	0.0019
18	369.78	0.9469	0.9258	1.0025	1.7751	0.6987	0.32	−0.0019	−0.08	0.0005	−0.07	0.0005
19	370.26	0.9900	0.9850	1.0019	1.8843	0.6601	0.41	−0.0006	−0.05	−0.0001	−0.05	−0.0001
20	370.42	1.0000	1.0000				0.41	0.0000	−0.07	0.0000	−0.07	0.0000
maximum deviation							1.11	0.0179	−0.47	0.0086	−0.47	0.0090
average absolute deviation							0.37	0.0059	0.09	0.0037	0.09	0.0037

[a]Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.05$ kPa. [b]Expanded uncertainties U are $U(x_1) = U(y_1) = 0.0028$, $P = 0.95$. [c]Relative volatility. The antoine equation used is $\alpha_{ij} = \frac{y_i}{y_j} / \frac{x_i}{x_j}$. [d]$\Delta T = (T_{cal} - T_{exp})$, $\Delta y_1 = (y_{1cal} - y_{1exp})$.

Table 6. Parameters in the Extended Antoine Equation[a]

component	A	B	C	E	F	G	T range (K)
ethanol[b]	67.56720	−7164.30000	−7.32700	0.000	3.1340×10^{-06}	2	273.0−405.0
1-propanol[b]	88.13400	−8498.60000	0.00000	−9.077	8.3303×10^{-18}	6	273.0−423.0
1-butanol[c]	22.10877	−3137.02000	−94.43000	0.000	0.0000	0	288.0−404.0
DMM_2[d]	74.72410	−7223.44000	−8.25216	0.000	0.0000	0	295.0−395.0
MMP[e]	18.77778	−1773.91012	−121.50099	0.000	0.0000	0	290.0−380.0
EMP[f]	20.92615	−3068.23568	−60.03471	0.000	0.0000	0	314.0−394.0

[a]The extended antoine equation used is eq 14. [b]Standard literature.[12] [c]Standard literature.[17] [d]Standard literature.[16] The antoine equation used is

$$\ln p_i^s (\text{mm Hg}) = A + \frac{B}{T(K)} + C \ln T(K)$$

[e]Standard literature.[3] [f]Standard literature.[4]

These results showed that these measurements were basically consistent with literature data. We analyzed the compositions of vapor and liquid samples at the equilibrium state by the same GC and operating condition above.

2.4. Apparatus and Procedure. Similar to our previous work, the VLE data of three binary mixtures above at 101.33 kPa were measured by a dynamic modified Rose still[1] which is a typical experiment apparatus: its total capacity is 150 mL, and the reflux rate of the condensate is about 10−15 mL/min. A detailed description about the operation and veracity of the apparatus in measuring the VLE value has been reported.[4,11]

First, compound no. 1 was injected into the kettle, and the content of another compound in the kettle was increased from 0% to 100% at intervals. There are 20−25 sets of samples measured for which the concentrations are different in one binary system experiment. In the experiment, we measured the temperature by using a precise standard mercury thermometer (Beijing Glass Research Institute Co., second-class) with an error range of less than 0.1 K. Meanwhile, the experimental apparatus must remain sealed under the pressure demand which was kept at 101.33 ± 0.03 kPa by the pressure control system in the measuring process. We usually measure the pressure of the apparatus by a digital display vacuum measuring instrument (Taizhou Aide Mechanical and Electrical Technology Co., VR-208C-510A) with an error range of less than 0.02 kPa, which was controlled and adjusted by two buffer bottles (the volume is 5 L) and a sealed rubber tube (its length and inner diameter are 1 m and 0.8 cm, respectively) with a moving clip.

In the process of experiment, sufficient equilibrium could be established by continuously circulating the liquid and vapor phase when the temperature remained constant for 60 min. Two condensed samples of vapor and liquid (the volume is 2 mL, respectively) were withdrawn rapidly and simultaneously when sufficient equilibrium was set up to analyze their content.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. The isobaric VLE experiment data, activity coefficients, relative volatility, and their deviations comparing measurements with calculation values which were correlated by using Van Laar, Wilson, and NRTL models for three binary mixtures composed of MMP + ethanol, EMP + 1-butanol, and DMM_2 + 1-propanol at 101.33 kPa are listed in Tables 3, 4, and 5.

3.2. Expanded Uncertainty. The calculation method of the uncertainty is similar to the methods which are described in a previous reference.[11−18] The expanded uncertainty (U) of

experimental data for chromatographic analysis includes five aforementioned elements which can be described by eq 4.

$$U = K_c \sqrt{(u_{r(sample)})^2 + (u_{r(true)})^2 + (u_{r(cal)})^2 + (u_{r(rep)})^2 + (u_{r(LOD)})^2}$$

(4)

where in this equation, $u_{r(sample)}$ means for the relative standard uncertainty of sediment sample mass determination, $u_{r(true)}$ represents the relative standard uncertainty of recovery determination, $u_{r(cal)}$ stands the relative standard uncertainty of calibration step, $u_{r(rep)}$ stands the relative standard uncertainty of repeatability, $u_{r(LOD)}$ stands the relative standard uncertainty of LOD determination. These relative standard uncertainties can be calculated by eqs 5, 6, 7, and 8:

$$u_{r(true)} = \frac{RSD_R}{\sqrt{n}}$$

(5)

$$u_{r(cal)} = \frac{RSD_f}{\sqrt{n}}$$

(6)

$$u_{r(rep)} = \frac{RSD_x}{\sqrt{n}}$$

(7)

$$u_{r(LOD)} = \frac{LOD}{c_m}$$

(8)

RSD is the relative standard deviation calculated by using the following eq 9:

$$RSD = \frac{SD}{\bar{x}} = \sqrt{\frac{\sum_i^n (x_i - \bar{x})}{(n-1)\bar{x}^2}}$$

(9)

The expanded uncertainty of the VLE measurement of three binary systems, MMP + ethanol, EMP + 1-butanol, and DMM_2 + 1-propanol, were calculated by these equations, using a coverage factor of 2 (for P = 95%). The highest values of the U of the three binary systems were 0.0046, 0.0030, and 0.0028, respectively.

3.3. Thermodynamic Consistency. The thermodynamic consistency of the VLE experimental data for the three binary systems was checked by the traditional area test and the direct test methods. Under normal conditions the value of D−J must be less than 10; D and J are calculated by eqs 10 and 11:[19,20]

$$D = \frac{|I|}{\sum} \times 100$$

(10)

$$J = 150 \times \frac{\theta}{T_{min}}$$

(11)

$I = \int_0^1 \ln(\gamma_1/\gamma_2) \, dx_1$, $\sum = \int_0^1 |\ln(\gamma_1/\gamma_2)| \, dx_1$, $\theta = T_{max} - T_{min}$. The T_{min} and T_{max} are the lowest and the highest boiling point (K) in three binary systems VLE data, respectively.

The equilibrium relationship about the VLE system is expressed by eq 12:

$$y_i \varphi_i^V P = x_i \gamma_i \varphi_i^s p_i^s \exp\left(\frac{V_i^l(p - p_i^s)}{RT}\right) \tag{12}$$

where, in this equation, φ_i^V means for the fugacity coefficient of component i in the vapor mixture. φ_i^s stands for the fugacity coefficient of pure vapor i at the state of equilibrium. P and T are the system total pressure and equilibrium temperature. Considering the experimental operation at low pressure (101.33 kPa), and assuming the vapor phase as an ideal gas, we neglect the pressure effect of the liquid phase fugacity in eq 13.

$$y_i p = x_i \gamma_i p_i^s \tag{13}$$

where p_i^s stands for the saturated vapor pressure of pure component i under the corresponding equilibrium temperature, which is calculated by the extended Antoine eq 14. The parameters of the six studied chemicals are listed in Table 6.

$$\ln p_i^s (\text{Pa}) = A + \frac{B}{T(\text{K}) + C} + DT(\text{K})$$
$$+ E \ln T(\text{K}) + FT(\text{K})^G \tag{14}$$

The results of thermodynamic consistency for three binary systems measurements are illustrated in Table 7 and Figures 4, 5, and 6, which indicate that they have passed the consistency test of thermodynamics.

Table 7. Thermodynamic Consistency Test of VLE Data

system	T_{max} (K)	T_{min} (K)	D	J	$D - J$
ethanol (1) + MMP	366.13	349.35	11.280	7.205	4.075
1-butanol(1) + EMP	390.92	380.02	7.109	2.695	4.414
1-propanol (1) + DMM$_2$	378.00	368.68	8.451	3.792	4.659

The relative volatilities between MMP, EMP, and DMM$_2$ with the relevant alcohol are illustrated in Tables 3, 4, and 5 which are calculated by the eq 15:

$$\alpha_{ij} = \frac{y_i}{y_j} \Big/ \frac{x_i}{x_j} \tag{15}$$

The evolution of relative volatility for three binary systems indicated that it is difficult to separate two compounds in binary system mixtures by ordinary distillation.

3.4. Correlations for Binary VLE. In this work, the experimental isobaric VLE data for three binary mixtures composed of MMP + ethanol, EMP + 1-butanol, and DMM$_2$ + 1-propanol at 101.33 kPa were correlated by the van Laar, Wilson, and NRTL models. The binary interaction parameters of all models were estimated using the minimization of the following objective function, OF. The results are shown in Table 8.

$$\text{OF} = \sum_{k=1}^n \left(\sum_{i=1}^2 (y_{i,k,\text{cal}} - y_{i,k,\text{exp}})^2 + (T_{k,\text{cal}} - T_{k,\text{exp}})^2 \right) \tag{16}$$
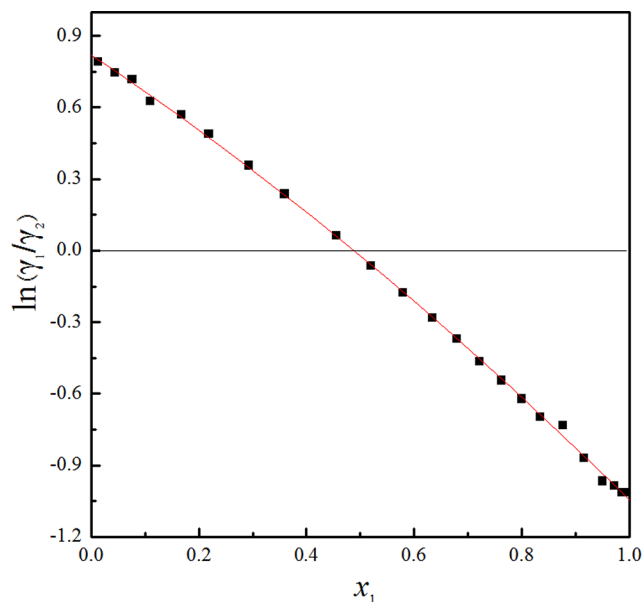

Figure 4. Diagram of $\ln(\gamma_1/\gamma_2)$ to $x1$ for the ethanol(1) and MMP(2) system.
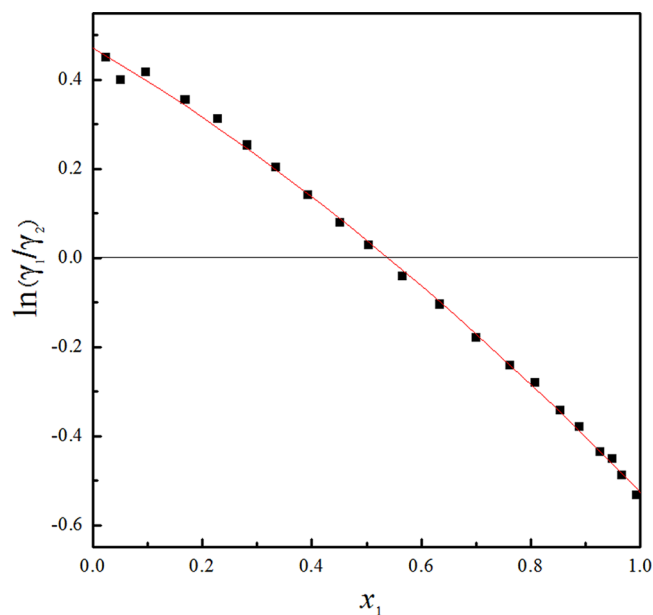

Figure 5. Diagram of $\ln(\gamma_1/\gamma_2)$ to $x1$ for the 1-butanol(1) and EMP(2) system.

The average absolute deviations for the equilibrium temperature and vapor phase mole fraction of three VLE systems above were also listed in Table 8. These binary energy interaction parameters can be obtained by these following equations:

Van Laar:

$$\Lambda_{ij} = (\lambda_{ij} - \lambda_{ii})/RT \tag{17}$$

$$z_i = \frac{|A_i|x_i}{|A_i|x_i + |B_i|(1 - x_i)} \tag{18}$$

$$A_i = \sum_j x_j \Lambda_{ij}/(1 - x_i) \tag{19}$$

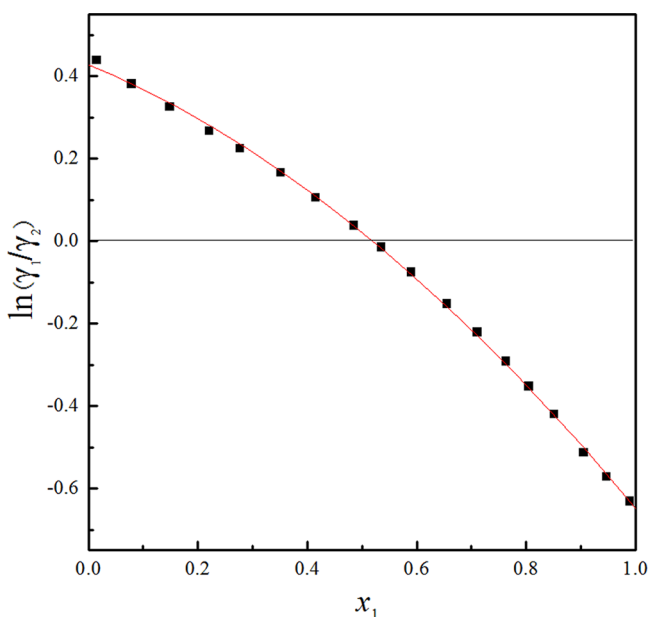**Figure 6.** Diagram of $\ln(\gamma_1/\gamma_2)$ to $x1$ for the 1-propanol(1) and DMM$_2$(2) system.

$$B_i = \sum_j x_j \Lambda_{ji}/(1 - x_i) \tag{20}$$

Wilson:

$$\Lambda_{ij} = \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{21}$$

NRTL:

$$\tau_{ij} = (\lambda_{ij} - \lambda_{ii})/RT, \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{22}$$

The γ_i can be calculated as follows:

Van Laaar:

$$\ln \gamma_i = A_i(1 - z_i)^2\left[1 + 2z_i\left(\frac{A_iB_i}{|A_iB_i|} - 1\right)\right] \tag{23}$$

Wilson:

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{n} \Lambda_{ij}x_j\right) - \sum_{k=1}^{n}\left(\frac{\Lambda_{ki}x_k}{\sum_{j=1}^{n}\Lambda_{kj}x_j}\right) \tag{24}$$

NRTL:

$$\ln \gamma_i = \frac{\sum_{i=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k} + \sum_{i=1}^{n}\frac{G_{ji}x_j}{\sum_{k=1}^{c}G_{ki}x_k}\left(\tau_{ij} - \frac{\sum_{i=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k}\right) \tag{25}$$

These binary interaction energy parameters obtained can be used to predict these equilibrium temperature and vapor phase composition of a binary system. The $t-x-y$ diagrams about binary mixtures composed of MMP + ethanol, EMP + 1-butanol, and DMM$_2$ + 1-propanol at 101.33 kPa are depicted in Figures 7, 8, and 9 correlated by Van Laar, Wilson, and the
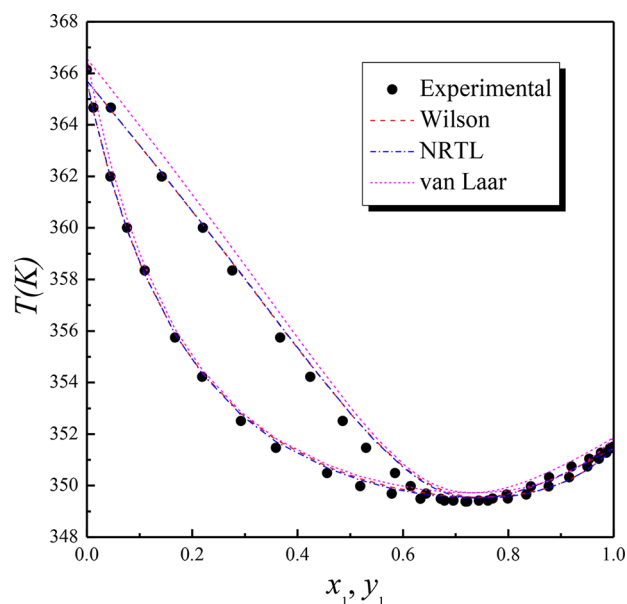

Figure 7. $T-x-y$ diagram for the ethanol (1) and MMP (2) system at 101.33 kPa.

Table 8. Van Laar, Wilson, and NRTL Equation Parameters and Mean Absolute Deviations of the Binary Systems

	model parameters			average absolute deviation	
model	$(\lambda_{12} - \lambda_{11})$/J·mol^{-1}	$(\lambda_{21} - \lambda_{22})$/J·mol^{-1}	α_{ij}[a]	$|\Delta T|$[b]	$|\Delta y_1|$[c]
		Ethanol (1) + MMP (2)			
Van Laar	2780.8918	3192.3886	0	0.33	0.0095
Wilson	−1119.7136	−2218.1119	0	0.16	0.0088
NRTL	2447.4308	726.0123	0.3	0.14	0.0087
		1-Butanol (1) + EMP (2)			
Van Laar	1914.6532	1944.2227	0	0.60	0.0062
Wilson	−734.2971	−1094.1274	0	0.13	0.0036
NRTL	1181.1145	597.2182	0.3	0.13	0.0036
		1-Propanol (1) + DMM$_2$ (2)			
Van Laar	1674.2004	2162.7502	0	0.37	0.0059
Wilson	−6.0401	−2024.5142	0	0.09	0.0037
NRTL	2582.2216	−537.0202	0.3	0.09	0.0037

[a]Parameter of NRTL is set to 0.3 when the mixture contains a polar component. [b]$|\Delta T| = \sum |T_{cal} - T_{exp}|/k$. [c]$|\Delta y_1| = \sum |y_{cal} - y_{exp}|/k$. k is the number of data points.
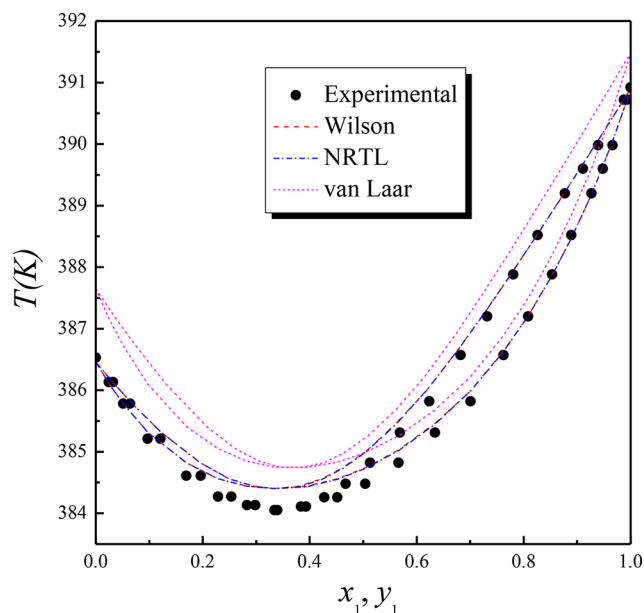
Figure 8. $T-x-y$ diagram for the 1-butanol (1) and EMP (2) system at 101.33 kPa.
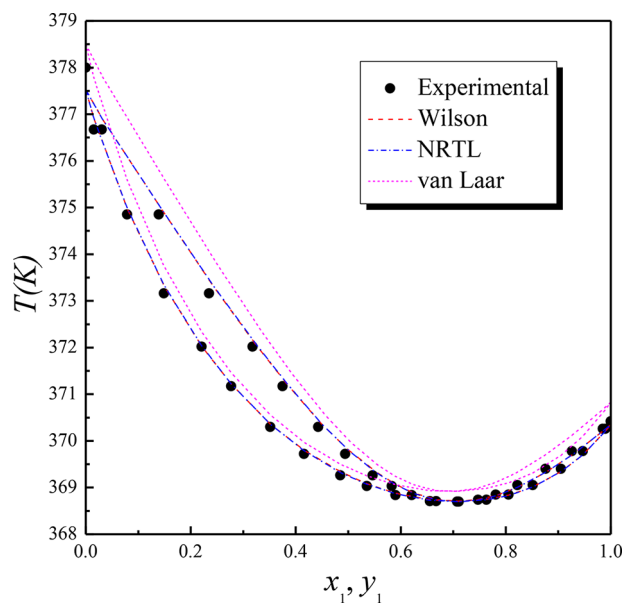

Figure 9. $T-x-y$ diagram for the 1-propanol (1) and DMM$_2$ (2) system at 101.33 kPa.

NRTL three models. By comparing, it is very significant that these calculated values can be correlated with a good degree of accuracy with these experimental data.

3.5. Calculation and Determination for Azeotropic Data. The azeotropic data of three binary systems for MMP + ethanol, EMP + 1-butanol, and DMM$_2$ + 1-propanol were estimated based on the $T-x-y$ diagram which was described by using these calculated data correlated by the NRTL model. The confirmed azeotropic states are 349.35 K and 70.95 mol % (ethanol), 384.02 K and 36.02 mol % (1-butanol), and 368.68 K and 69.26 mol % (1-propanol) for the three binary systems. In addition, we measured the azeotropic data of the three binary systems by a rectifying process using a rectifying column whose theoretical plate number is 25 under the condition of total reflux. The composition of the binary system mixtures are

50 mol % (MMP) + 50 mol % (ethanol), 50 mol % (EMP) + 50 mol % (1-butanol), and 50 mol % (DMM$_2$) + 50 mol % (1-propanol) in the kettle. The azeotropic data for these systems are 349.52 K and 70.84 mol % (ethanol), 384.20 K and 36.10 mol % (1-butanol), and 368.79 K and 69.16 mol % (1-propanol) measured by the rectifying process.

4. CONCLUSIONS

In this work, the VLE data for three binary mixtures composed of MMP + ethanol, EMP + 1-butanol, and DMM$_2$ + 1-propanol at 101.33 kPa were measured by using a dynamic modified Rose still. The $t-x-y$ diagram of three binary systems at 101.33 kPa shows three minimum boiling azeotropes. The azeotropic states are 349.35 K and 70.95 mol %(ethanol) for MMP + ethanol mixture, 384.02 K and 36.02 mol %(1-butanol) for EMP + 1-butanol mixture, and 368.68 K and 69.26 mol %(1-propanol) for DMM$_2$ + 1-propanol mixture, respectively. Our VLE measurements passed the thermodynamic consistency test with the help of the Herington semiempirical method. They were correlated by using the Van Laar, Wilson, and NRTL models for which the binary interaction energy parameters were obtained, and there is a good correlation for the three models. The average absolute deviations ($\Delta T/\Delta y$) correlated under the Wilson and NRTL models were less than 0.16 K and 0.0088, respectively. Therefore, there is reason to believe that the measurements can be applied to design separation technologies during purifying the MMP, EMP, and DMM$_2$.

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■ ABBREVIATIONS AND SYMBOL LIST

A, B, C, D, E, F, G = parameters of the extended Antoine equation
$z_i, A_i, B_i, \Lambda_{ij}$ and Λ_{ji} = binary energy interaction parameters of van Laar model
Λ_{ij} and Λ_{ji} = binary energy interaction parameters of Wlsion model
Gij, and τ_{ij} = binary energy interaction parameters of NRTL model
T = absolute temperature
T_b = boiling temperature
V_i^l = the molar volume of pure liquid
P = pressure
p^s = saturated pressure

a_{ij} and b_{ij} = binary interaction parameters
x = mole fraction in liquid
y = mole fraction in vapor
n_D = refractive index
c = average concentration of the analyte

■ GREEK LETTERS

α = NRTL nonrandomness parameter
γ = activity coefficient
ρ = density
Δ = standard deviation

■ SUBSCRIPTS

cal = calculated value
exp = experimental value
i, j = component
k and n = data number

■ REFERENCES

(1) Song, Y. H.; Li, J. Q.; Zhang, H. P. Isobaric Vapor-Liquid Equilibrium for the Binary Systems of 1-Butanol + Methoxy-(methoxymethoxy)methane, and 1-Butanol + 2,4,6,8-Tetraoxanonane at 101.3 kPa. *Fluid Phase Equilib.* **2014**, *377*, 33−37.

(2) Song, Y. H.; Li, J. Q.; Ding, J. F. Vapor-Liquid Equilibrium for Methanol-methylal-poly methoxy System. *Chem. Eng. (China)*. **2015**, *312*, 30−34.

(3) Song, Y. H.; Li, J. Q.; Zhang, H. P. Isobaric (Vapor-Liquid) Equilibria for Binary Systems of Methanol + 1-(Methoxymethoxy)-propane and 1-Propanol + 1-(Methoxymethoxy)-propane at 101.33 kPa. *Fluid Phase Equilib.* **2015**, *405*, 83−87.

(4) Song, Y. H.; Wei, P. H.; Song, J. Measurement and Correlation of (Vapour−Liquid) Equilibrium for Binary Mixtures Composed of 1-(Ethoxymethoxy)-propane with Ethanol and 1-Propanol at 101.33 kPa. *J. Chem. Thermodyn.* **2017**, *110*, 237−242.

(5) Song, Y. H.; Wang, S. E.; Hua, H.; Song, J.; Wei, P.-H.; Li, C.-F. Measurement and Correlation of Isobaric Vapor-Liquid Equilibrium for Binary Systems of 1-(Ethoxymethoxy)-2-methyl-propane with Isobutanol or 1-Butanol at 101.33 kPa. *J. Chem. Eng. Data* **2017**, *62*, 2443−2449.

(6) Van Laar, J. J. The Vapor Pressure of Binary Mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

(7) Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(8) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

(9) Lorette, N. B.; Howard, W. L. Preparation of Ketals from 2, 2-Dimethoxypropane. *J. Org. Chem.* **1960**, *25*, 521−525.

(10) Gazizova, L. B. Synthesis of Unsymmetrical 1,1-Di(alkoxy)-alkanes and Their Sulfur-Containing Analogs. *Zhurnal Organicheskoi Khimii.* **1981**, *17*, 275−281.

(11) Song, Y. H.; Li, C. F.; Song, J. Measurement and Correlation of Isobaric Vapour−Liquid Equilibria for Binary Systems of 1-(Methoxymethoxy)-2-methyl-propane with 1-Butanol and Iobutanol at 101.33 kPa. *J. Chem. Thermodyn.* **2017**, *115*, 202−208.

(12) *TRC Thermodynamic Tables. Non-Hydrocarbons*; NIST/TRC Table Database; Thermodynamics Research Center, 2004.

(13) Cheng, N. L. *Solvent Handbook*, 5th ed.; Chemical Industry Press: Beijing, 2015.

(14) Wilson, H. L.; Wilding, W. V.; Neiditch, D. Vapor-Liquid Equilibrium Measurements on the N,N-dimethylformamide/1-Butanol System at 65 and 125.Degree. *J. Chem. Eng. Data* **1991**, *36*, 346−349.

(15) Burger, J.; Siegert, M.; Strofer, E. Poly(oxymethylene) dimethyl ethers as Components of Tailored Diesel Fuel: Properties, Synthesis and Purification Concepts. *Fuel* **2010**, *89*, 3315−3319.

(16) Boyd, R. H. Some Physical Properties of Polyoxymethylene Dimethyl Ethers. *J. Polym. Sci.* **1961**, *153*, 133−141.

(17) Walas, S. M. *Phase Equilibria Chemical Engineering*, 1st ed.; EUA: Butterworth: Boston, 1985.

(18) Konieczka, P.; Namieśnik, J. Estimating Uncertainty in Analytical Procedures Based on Chromatographic Techniques. *J. Chromatogr. A* **2010**, *1217*, 882−891.

(19) Ma, P. S. *Chemical Engineering Thermodynamics*; Chemical Industry Press: Beijing, 2009.

(20) Wisniak, J.; Apelblat, A.; Segura, H. An Assessment of Thermodynamic Consistency Tests for Vapor-Liquid Equilibrium Data. *Phys. Chem. Liq.* **1997**, *35*, 1−58.