Ternary Phase Equilibria for Mixtures of Supercritical Methanol + C18 Fatty Acid, Methyl Esters + 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (α-Tocopherol)

Tao Fang,[†,‡] Yusuke Shimoyama,[§] Yoshio Iwai,[§] Mitsuru Sasaki,[‡] and Motonobu Goto*[,‡]

Department of Chemical Engineering, Xi'an Jiaotong University, Xi'an 710049, China, Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan, and Department of Chemical Engineering, Kyushu University, 744 Motooka Nishi-ku, Fukuoka 819-0395, Japan

Ternary phase equilibrium data for methanol + C18 fatty acid, methyl esters + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (α-tocopherol) were measured at (523 and 548) K and (6 and 8) MPa. The experimental results indicated that the two-phase region shrinks with increasing pressure. Additionally, temperature has the opposite influence to that of pressure; i.e., the two-phase area expands with temperature. The experimental data were correlated using the Peng−Robinson equation of state (PR EOS). An exponent-type mixing rule was adopted for the energy parameter of the PR EOS. The binary parameters for methanol + C18 fatty acid, methyl esters and methanol + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol pairs in the mixing rules were determined from the phase equilibrium data for the binary systems. For the C18 fatty acid, methyl esters + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol pair, the data for the ternary system were used for the determination of the binary parameters. The correlated results with the exponent-type mixing rule are more accurate than those in the case of the conventional mixing rule. The experimental data can be used for designing the supercritical methanol process for producing biofuel and tocopherols from soybean oil byproducts. Notably, this work is the first to report the ternary phase equilibrium data of methanol + C18 fatty acid, methyl esters + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol at high temperatures and pressures.

Introduction

Biodiesel fuel, which consists of fatty acid methyl esters (FAMEs) produced by transesterification of vegetable oils with methanol, is a possible solution to our fossil fuel limitations. Supercritical methanol has been used for the transesterification of vegetable oils without catalysts.[1−4] In a previous study,[5] supercritical methanol was used to treat deodorizer distillate (DOD), a byproduct from the soybean oil refining process. The experimental results showed that supercritical methanol could potentially be utilized as a process for modifying DOD to produce FAMEs and tocopherols.

FAMEs are the main products of the modification process. However, tocopherols are also produced, and as high-value compounds, it is necessary to prevent them from being damaged. For process design, it is essential to understand the phase behavior for methanol + FAMEs + tocopherols at high temperatures and pressures. In a previous study,[6] phase equilibria for supercritical methanol + C18 FAMEs and supercritical methanol + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)-chroman-6-ol (α-tocopherol) binary systems were measured. C18 FAMEs, including methyl octadecanoate (C18:0), methyl (*Z*)-octadec-9-enoate (C18:1), methyl (*Z*)-octadec-7-enoate (C18:1), and methyl (9*E*,13*E*)-octadeca-9,13-dienoate (C18:2), contribute to more than 0.8 (mole fraction) of the FAMEs produced from the reaction of soybean oil or oil byproducts with methanol.[7] In the temperature range from (523 to 573) K, when the pressure is lower than the critical pressure of methanol (8.097 MPa), the mole fractions of methanol in the vapor phase are very close to unity for both systems. The distribution of C18 FAMEs and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)-chroman-6-ol in vapor greatly increases in the pressure region over the critical pressure of methanol.

In this study, a flow-type apparatus was employed to measure the vapor−liquid equilibria for the mixtures of methanol + C18 FAMEs + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)-chroman-6-ol at high temperatures and pressures. The phase equilibria were correlated using the Peng−Robinson equation of state (PR EOS).[8] An exponent-type mixing rule[9] was applied to the energy parameter of the PR EOS.

Experimental Section

Materials. 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyltetradecyl)-chroman-6-ol (CAS number: 1406-18-4), methanol (CAS number: 67-56-1), and C18 FAMEs mixture were obtained from Wako Pure Chemical Industries, Inc. (Tokyo, Japan). Among them, the purities of 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol and methanol were 0.98 (mass fraction) by GC.

In the C18 FAMEs used in this work, there were some impurities besides C18 FAMEs. Before measurement, the composition in the material was determined by gas chromatography−mass spectrometry (GC−MS) and gas chromatography−thermal conductivity detector (GC−TCD) with the conditions for the GC−MS analysis reported in a previous work.[6]

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* Corresponding author. Tel.: +81-96-342-3664. Fax: +81-96-342-3679. E-mail: mgoto@kumamoto-u.ac.jp.
[†] Xi'an Jiaotong University.
[‡] Kumamoto University.
[§] Kyushu University.

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Table 1. Composition of the C18 FAME Mixture Used in the Phase Equilibrium Measurement

compound	trivial name of FAME	area fraction	mole fraction
methyl tetradecanoate	methyl myristate (C14:0)	0.0246	0.0335
methyl hexadecanoate	methyl palmate (C16:0)	0.0502	0.0558
methyl (*Z*)-hexadec-9-enoate	methyl palmitioleate (C16:1)	0.0593	0.0669
methyl heptadecanoate	methyl acyclopropaneate (C17:0)	0.0160	0.0187
methyl octadecanoate	methyl stearate (C18:0)	0.0142	0.0137
methyl (*Z*)-octadec-9-enoate	methyl oleate (C18:1)	0.7288	0.7617
methyl (*Z*)-octadec-7-enoate	methyl oleate (C18:1)	0.0560	
methyl (9*E*,13*E*)-octadeca-9,13-dienoate	methyl linoleate (C18:2)	0.0509	0.0497

The analysis results are shown in Table 1, and more details of the mixture composition can be found in the previous work.[6] In the material used for phase equilibrium measurement, methyl (*Z*)-octadec-9-enoate (C18:1, CAS number: 112-62-9) is the main FAME with the area fraction of 0.7288, and other compounds are also FAMEs with different carbon chains, including methyl tetradecanoate (CAS number: 124-10-7), methyl hexadecanoate (CAS number: 112-39-0), methyl (*Z*)-hexadec-9-enoate (CAS number: 1120-25-8), methyl heptadecanoate (CAS number: 1731-92-6), methyl octadecanoate (CAS number: 112-61-8), and methyl (9*E*,13*E*)-octadeca-9,13-dienoate (CAS number: 112-63-0). Totally, the area fraction of C18 FAMEs is 0.8499. Additionally, the GC−TCD analysis with external standards was performed, and the results show that the content of C18 FAMEs is 0.8251 (mole fraction). The experimental measurements were conducted with a flow-type method for which a large amount of material is necessary for the phase equilibrium measurements. There is a practical difficulty for obtaining large amounts of C18 FAMEs with high purity (> 0.9 mol fraction). Consequently, the mixture with total C18 FAME purity of 0.8251 mol fraction was employed in this work due to their availability. Taking into account the impurities, the system of methanol + C18 methyl esters + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol is, to be exact, a pseudoternary system. Additionally, for GC−TCD analysis used for measurement, the analysis data for C18 FAMEs were applied for calculating the composition in liquid and vapor samples.

Apparatus and Procedure. A flow-type apparatus (AKICO Inc., Tokyo, Japan)[6] was adopted to avoid thermal decomposition and pressure fluctuation caused by sampling. The apparatus consisted of a feed system, an equilibrium cell, and a sampling effluent system. The phase behavior inside the cell could be observed through the sapphire windows of the equilibrium cell. The inner diameter and volume of the cell were 20 mm and 31 mL, respectively. An additional line with the equilibrium cell was used to maintain the position of the phase interface.

The system was heated to the desired temperature by electric heaters. A mixture composed of methanol, C18 FAMEs, and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol was supplied by a feed pump. The measurements were performed in the range of the feed rates from (7.49 to 9.34) $\mathrm{mL \cdot min^{-1}}$ because the experimental results were independent of the flow rate in this range. The pressurized mixture was sufficiently mixed through a line mixer before the mixture was loaded into the equilibrium cell. The residence time in the equilibrium cell was about (3.79 to 4.18) min. The temperatures at the entrance, top, and bottom of the cell were controlled within ± 1 K, and the pressure fluctuation was held to ± 0.02 MPa. The effluents from vapor and liquid phases were depressurized through expansion valves. Samples from the vapor and liquid phases were trapped into sampling bottles after the position of the phase interface was well stabilized. The sampling bottles were cooled in water baths to prevent volatilization of methanol. For each sample, the volume trapped in the bottle was about 10 mL. To obtain more accurate results, parallel measurements at each pressure and temperature condition were conducted four times, and each sample was analyzed twice. It was verified that C18 FAMEs and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol did not decompose during measurement, because no additional components were detected by gas chromatograph−mass spectrum analysis.

In this study, the influences of three factors on phase behavior were investigated: pressure [(6 and 8) MPa], temperature [(523 and 548) K], and initial feed compositions. Four initial feed compositions of (0.9, 0.7, 0.5, and 0.3) of the mole fraction of C18 FAMEs in the binary mixture of C18 FAMEs and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol were investigated. The mole fractions of methanol in the feed mixtures were about (0.95 to 0.98).

Analysis Methods. The contents of methanol and C18 FAMEs in the vapor and liquid samples were analyzed by GC−TCD (GL Sciences Inc., Tokyo, Japan). The temperatures for oven temperature, injector, and detector were kept at 453 K, and the injection volume was 1 μL.

The 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol analysis was performed with a Shimadzu CLASS - LC10/M10A, SPD-10A detector (Shimadzu Inc., Tokyo, Japan) equipped with a silica gel column (150 × 4.6 mm, packing: Inertsil SIL 150 A 5 μm, GL Sciences Inc., Tokyo, Japan). The mobile phase was methanol at 1 $\mathrm{mL \cdot min^{-1}}$; the injection volume was 3 μL; the UV wavelength was 295 nm; and the temperature of the column was 298 K. The result was calculated from an external standard of 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol.

For all liquid phase samples, the contents of 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol were generally high. Consequently, these samples were diluted with methanol before chromatographic analysis, and the final concentrations of the sample solutions were in the range of (0.01 to 0.06) $\mathrm{g \cdot g^{-1}}$ (sample/solution).

Correlation

The Peng−Robinson equation of state (PR EOS)[8] was used for the correlations of the phase equilibria for supercritical methanol + C18 FAMEs + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol systems. An exponent-type mixing rule[9] was adopted for the energy parameter. PR EOS is given by the following equations.

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \tag{1}$$

$$a = 0.457235 \frac{R^2 T_c^2}{p_c} \alpha \tag{2}$$

$$\alpha = \left[1 + \kappa\left\{1 - \left(\frac{T}{T_c}\right)^{0.5}\right\}\right]^2, \ \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{3}$$

$$b = 0.07780\frac{RT_c}{p_c} \tag{4}$$

where p, v, R, and T are the pressure (Pa), molar volume ($m^3 \cdot mol^{-1}$), gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), and temperature (K), respectively. The parameters a and b are the energy ($Pa \cdot m^6 \cdot mol^{-2}$) and size ($m^3 \cdot mol^{-1}$) parameters, respectively. ω is the acentric factor, and the subscript c denotes the critical properties. The critical properties and acentric factors of C18 FAMEs were estimated with the group contribution method proposed by Gani's group,[10,11] while simultaneously the average molecular weight of C18 FAMEs was calculated according to the mole fractions of four C18 FAMEs (methyl octadecanoate (C18:0), methyl (*Z*)-octadec-9-enoate (C18:1), methyl (*Z*)-octadec-7-enoate (C18:1), and methyl (9*E*,13*E*)-octadeca-9,13-dienoate (C18:2)). For 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol, the values from the literature[12] were used as their critical properties and acentric factor. For methanol, the experimental data of the critical properties and acentric factor are available.[13] The critical properties and acentric factors of methanol, C18 FAMEs, and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol in this study are listed in Table 2.

For the energy parameter in the PR EOS, an exponent-type mixing rule[9] was adopted. This mixing rule applies to the systems in which the polarities and molecular sizes for the compounds in the mixture are largely different. The exponent-type mixing rule is given as follows

$$a = \sum_i \sum_j x_i^{\beta_{ij}} x_j^{\beta_{ji}} a_{ij} \tag{5}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{6}$$

where x is the mole fraction. The subscripts i and j denote the components i and j. The introduction of the exponential parameter β_{ij} expresses the contact probability of molecule i around molecule j. This means that nonrandomness in the mixture can be evaluated empirically. The value of β_{ii} should be unity, because the parameter is for pure compound i. When β_{ij} is unity, the mixing rule is the conventional mixing rule. For the energy and size parameters, the combining rules are given by the following equations

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{7}$$

$$b_{ij} = (1 - l_{ij})\frac{b_i + b_j}{2} \tag{8}$$

where k_{ij} ($k_{ij} = k_{ji}$ and $k_{ii} = 0$) and l_{ij} ($l_{ij} = l_{ji}$ and $l_{ii} = 0$) are the binary parameters. The binary parameters k_{ij}, l_{ij}, and β_{ij} were determined from the phase equilibrium data for the binary and ternary systems. The parameter k_{ij} was optimized at each temperature.

Results and Discussion

The isotherms at (523 and 548) K for the ternary system of methanol (1) + C18 FAMEs (2) + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) were measured at pressures of (6 and 8) MPa. The experimental data are listed in Table 3.

Table 2. Critical Properties and Acentric Factors of Compounds Studied in This Study

compound	T_c/K	p_c/MPa	ω
methanol[13]	512.64	8.097	0.565
C18 FAMEs[10,11]	769.82	1.356	0.857
2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol[12]	1020	1.37	0.6165

Table 3. Experimental Results of Phase Equilibria for the Methanol (1) + C18 FAMEs (2) + 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) System[a]

p/MPa	x_2^0	y_1	y_2	y_3	δ^y ($\times 10^{-4}$)	x_1	x_2	x_3	δ^x
				$T = 523$ K					
6.0	0.9	0.9998	0.0001	0.0001	0.4	0.841	0.142	0.017	0.007
	0.7	0.9997	n.d.	0.0003	0.2	0.837	0.109	0.054	0.010
	0.5	0.9999	n.d.	0.0001	0.2	0.815	0.092	0.093	0.011
	0.3	0.9999	n.d.	0.0001	1.9	0.804	0.067	0.129	0.009
8.0	0.7	0.9990	0.0007	0.0003	0.2	0.942	0.036	0.022	0.004
	0.5	0.9991	0.0007	0.0002	1.1	0.939	0.031	0.030	0.004
	0.3	0.9995	0.0004	0.0001	0.3	0.932	0.024	0.044	0.003
				$T = 548$ K					
6.0	0.9	0.9996	0.0002	0.0002	0.3	0.756	0.218	0.026	0.006
	0.7	0.9998	0.0001	0.0001	0.03	0.716	0.187	0.097	0.005
	0.5	0.9998	0.0001	0.0001	0.5	0.707	0.148	0.145	0.011
8.0	0.9	0.9986	0.0012	0.0002	2.0	0.867	0.117	0.016	0.003
	0.7	0.9990	0.0007	0.0003	0.9	0.851	0.095	0.054	0.005
	0.5	0.9988	0.0011	0.0001	1.5	0.822	0.092	0.086	0.005
	0.3	0.9995	0.0004	0.0001	0.8	0.785	0.051	0.164	0.005

[a] $x_2^0 = (n_2^0)/(n_2^0 + n_3^0)$; n, amount of substance; superscript 0, feed mixture; n.d., not detected. Repeatability, $\delta^y = (1/3N)\sum_{i=1}^{3}\sum_{n=1}^{N}|y_i^n - y_i|$, $\delta^x = (1/3N)\sum_{i=1}^{3}\sum_{n=1}^{N}|x_i^n - x_i|$; N, number of samples.

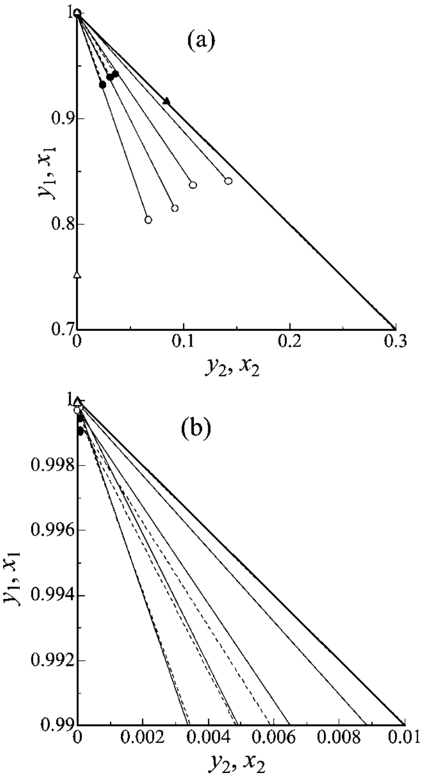

Figure 1. Phase equilibria for the methanol (1) + C18 FAMEs (2) + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) system at $T = 523$ K: (a) liquid−vapor equilibria; (b) equilibrium compositions in the vapor; ○−○, $p = 6.0$ MPa; ●- - -●, $p = 8.0$ MPa; ▲, binary data at $p = 6.0$ MPa; △, binary data at $p = 8.0$ MPa.

Figure 1 shows the phase equilibria at 523 K. As shown in Figure 1a, the methanol fractions in the liquid phase increase with pressure, while the methanol fractions in the vapor phase decrease as shown in Figure 1b. That means the solubilities of C18 FAMEs and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol in the vapor phase increase. It is revealed that the two-phase region shrinks with increasing pressure. At the lower pressure of 6 MPa, both C18 FAMEs and 2,5,7,8-

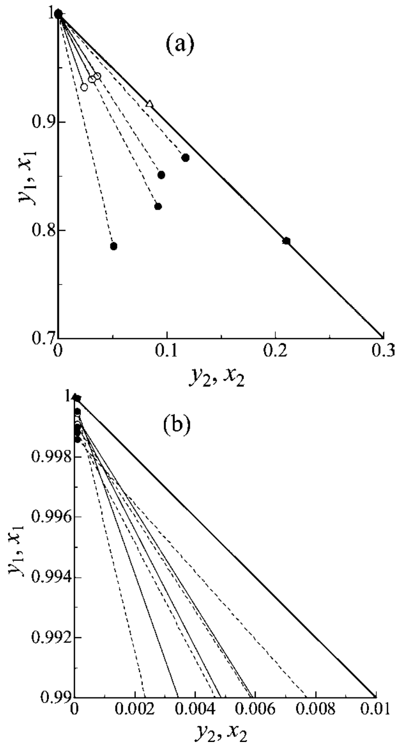

Figure 2. Phase equilibria for the methanol (1) + C18 FAMEs (2) + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) system at p = 8.0 MPa: (a) liquid−vapor equilibria; (b) equilibrium compositions in the vapor; ○−○, T = 523 K; ●- - -●, T = 548 K; ▲, binary data at T = 523 K; △, binary data at T = 548 K.

Table 4. Binary Parameters for the Methanol (1) + C18 FAMEs (2) + 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) System in the PR EOS

T/K	k_{12}	l_{12}	β_{12}	k_{13}	l_{13}	β_{13}	k_{23}	l_{23}	β_{23}
				conventional mixing rule					
523	0.101	0.147	1.00	0.076	0.182	1.00	0.426	0.415	1.00
548	0.119	0.147	1.00	0.051	0.182	1.00	0.386	0.415	1.00
				exponent-type mixing rule					
523	0.346	0.689	3.24	0.082	0.186	1.01	0.417	0.396	0.985
548	0.325	0.689	3.24	0.054	0.186	1.01	0.477	0.396	0.985

tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol have limited solubilities in methanol. The mole fractions of methanol in the vapor phase are very close to unity, while the pressure increases to 8 MPa, which is near the critical pressure of methanol (8.097 MPa). The solubilities of C18 FAMEs and 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol in vapor increase.

The phase equilibria at 8.0 MPa are shown in Figure 2. It shows the influence of temperature on phase equilibria at constant pressure. The influence of temperature is contrary to that of changing pressure. The two-phase area expands with increasing temperature. Noticeably, the influence of pressure and temperature on the vapor composition seems to be less significant than that on the liquid composition, as shown in Figures 1 and 2.

In addition to the measured data, Figures 1 and 2 show the tile lines connecting the equilibrium data in the liquid and vapor phases. Characteristically, the gradient of the equilibrium tie lines gradually changes from one side line of the triangle to the other. This means that the phase behavior for the ternary system tends to be close to that of the binary system of 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol + methanol with increasing 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol mole fraction in the feed.

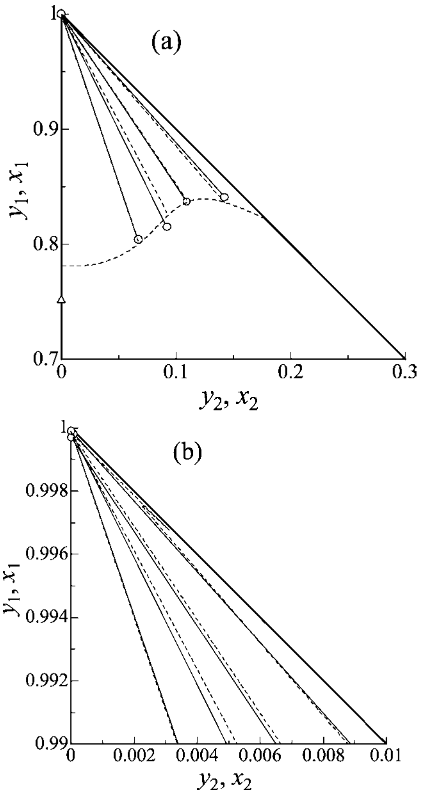

Figure 3. Phase equilibria for the methanol (1) + C18 FAMEs (2) + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) system at T = 523 K and p = 6.0 MPa: (a) liquid−vapor equilibria; (b) equilibrium compositions in the vapor; ○−○, experimental data for the ternary system; △, experimental data for the binary system; - - -, correlated results by the exponent-type mixing rule.

Table 5. Correlated Deviations of Phase Equilibria for the Methanol (1) + C18 FAMEs (2) + 2,5,7,8-Tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) System[a,b,c]

T/K	p/MPa	$E^{y,1}$	$E^{x,1}$	$E^{y,2}$	$E^{x,2}$
523	6.0	0.61	1.14	0.042	0.49
523	8.0	0.46	1.28	0.075	0.23
548	6.0	1.00	4.78	0.67	2.27
548	8.0	1.37	1.83	0.57	1.58

[a]

$$E^y = \frac{1}{3N_d}\left(\sum_{i=1}^{N_d}\sum_{j=1}^{3}|y_{j,\text{calc}}^{(i)} - y_{j,\text{exp}}^{(i)}|\right)\cdot 100.$$

[b]

$$E^x = \frac{1}{2N_d}\left(\sum_{i=1}^{N_d}|x_{1,\text{calc}}^{(i)} - x_{1,\text{exp}}^{(i)}| + \sum_{i=1}^{N_d}|x_{3,\text{calc}}^{(i)} - x_{3,\text{exp}}^{(i)}|\right)\cdot 100.$$

[c] N_d: number of data. Superscripts 1: conventional mixing rule; 2: exponent-type mixing rule.

In the correlations, the binary parameters for methanol + C18 FAMEs and methanol + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol were determined from the phase equilibrium data for each binary system.[6] The data for the ternary system obtained in this work were used for the determinations of the binary parameters for C18 FAMEs + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol pairs. The optimized values of the binary parameters are listed in Table 4. Figure 3 shows the correlated results by the exponent-type mixing rule for methanol + C18 FAMEs + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol systems at 523 K and 6.0 MPa. Table 5 lists the correlated results at all conditions studied in this work. As shown in Table

5, the results using the exponent-type mixing rule represent the experimental data better than those using the conventional mixing rule.

Conclusion

In this work, phase equilibria of methanol (1) + C18 FAMEs (2) + 2,5,7,8-tetramethyl-2-(5,9,13-trimethyltetradecyl)chroman-6-ol (3) systems were measured by a flow-type apparatus. The experimental data indicated that the two-phase region shrinks with increasing pressure. However, with increasing temperature, the two-phase area expands. The Peng−Robinson equation of state was used for the correlations of the phase equilibrium data obtained in this work. An exponent-type mixing rule was adopted for the energy parameter of the equation of state. The correlation accuracies by the exponent-type mixing rule are better than those by the conventional mixing rule.

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