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Ebulliometric Determination and Prediction of Vapor−Liquid Equilibria for Binary Mixtures of Ethanol and Ethyl Hexanoate

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ABSTRACT: The objective of this study is to measure vapor−liquid equilibria (VLE) data for an ethanol + fatty acid ethyl ester (FAEE) system. VLE data for the binary system ethanol + ethyl hexanoate were determined at pressures of (40.00 to 101.3) kPa using an ebulliometer, which could compensate for vapor hold-up. The hold-up compensable ebulliometer was designed for this study, and the experimental apparatus and procedure were verified by measuring the VLE data for ethanol + *p*-xylene at pressures of (40.00 to 101.3) kPa. The densities at 298.15 K for pure components investigated in this study were also measured by a densimeter. The experimental VLE data of the two binary mixtures, ethanol + *p*-xylene and ethanol + ethyl hexanoate, were represented by the Wilson and nonrandom two-liquid (NRTL) models. The analytical solutions of groups (ASOG) and modified universal functional activity coefficient (UNIFAC, Dortmund) group contribution models were also used to predict the VLE behavior of these binary mixtures. The VLE data could be applied for the production of a biodiesel fuel synthesized from fatty acid ethyl esters using supercritical ethanol without a catalyst.

INTRODUCTION

Fatty acid methyl esters (FAMEs), which have been widely produced as biodiesel fuel (BDF), have attracted increasing attention as an environmentally friendly alternative fuel to light oil. FAMEs produce exhaust with lower amount of sulfur oxide (SO_x) and graphite than light oil, and its particulate emissions are also low.[1,2] FAMEs can be synthesized from renewable biological sources such as vegetable oils and animal fats. Usually, FAMEs are synthesized from oil and methanol by alkali catalyzed transesterification. However, this process is time-consuming, as complicated separation processes are required for the removal of the alkali catalyst, and glycerol is produced as a byproduct. Furthermore, oil from biomass contains water and free fatty acids.[3−5] Water decreases the catalytic efficiency of transesterification, and the free fatty acid reacts with the alkali catalyst to form soap. Soap formation consumes the catalyst and reduces the catalytic efficiency, increases the viscosity and gel formation, and makes it difficult to separate the glycerol byproduct.[5] To overcome these issues, fatty acid ethyl ester (FAEE) synthesis using supercritical ethanol without a catalyst has been proposed.[6−9] FAEEs synthesized from ethanol by transesterification can be produced without fossil fuels because ethanol can be obtained from agricultural products. However, the FAEEs obtained by this procedure have low volatility, and ignition delay and combustion problems could occur when used as BDFs.[10,11] Therefore, ethanol addition has been considered to enhance the vapor pressure of FAEEs.[8] An increase in the amount of ethanol will enhance the vapor pressure through depression of the boiling point of the FAEEs, which can be related to the vapor−liquid equilibria (VLE) for the ethanol and FAEE mixture. Consequently, VLE data for these mixtures are important for the production of BDFs derived from FAEEs. However, reports on VLE data for such mixtures are scarce.

The objective of this study is the measurement of VLE for the binary mixture ethanol + FAEE. In this study, an ebulliometric method was used for the measurement of VLE for this mixture, because this method is relatively convenient for VLE measurements when it is not necessary to analyze the composition. Usually, ethanol and FAEEs have very different boiling points because the FAEEs have high normal boiling points. When the ebulliometric method is used for these mixtures, vapor hold-up has been identified as a major concern.[12−14] Therefore, an ebulliometer that could compensate for vapor hold-up was designed for this study. The system ethanol + *p*-xylene was selected to test the experimental apparatus and procedure at pressures of (40.00 to 101.3) kPa. This mixture was selected because it has a large boiling point difference. FAMEs and FAEEs typically contain between 8 and 24 carbons.[8,15,16] Because of the expected measurement limit of the ebulliometer for boiling points, ethyl hexanoate ($C_8H_{16}O_2$, CAS Registry No. 123-66-0) with eight carbons was selected as the FAEE for the ethanol + FAEE study.

The objective of this study is to measure the boiling points for ethanol + ethyl hexanoate at (40.00 to 101.3) kPa. The liquid−liquid equilibrium (LLE) data for the ternary mixture water + ethanol + ethyl hexanoate have been measured by Lin et al.[17] Also, the infinite dilution volatilities of ethyl hexanoate in water + ethanol were studied by using three static headspace methods.[18] However, VLE data for the binary mixture ethanol + ethyl hexanoate have not been reported previously. The experimental boiling point data for this binary mixture were represented using the Wilson[19] and nonrandom two-liquid (NRTL)[20] models. Predictions were made using the ASOG[21,22] and modified UNIFAC (Dortmund)[23−27] group contribution models, and the prediction accuracy was evaluated. Applications of these group contribution

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models to the prediction of phase equilibria have been reported by several authors.[28−30] These reports are relevant to the separation and purification processes of FAMEs, and to our knowledge predictions for mixtures containing FAEEs have not been discussed.

■ EXPERIMENTAL SECTION

Materials. Special grade ethanol and *p*-xylene were obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and special grade ethyl hexanoate from Kanto Chemical Co. (Tokyo, Japan). The ethanol was dried over 3A molecular sieves and the *p*-xylene and ethyl hexanoate over 13X molecular sieves. The purities were checked by a gas chromatograph equipped with a thermal conductivity detector and were found to be >0.999 (mass fraction). The normal boiling points (T_b) of the purified chemicals were measured using a hold-up compensable ebulliometer designed in this study (details are given in the Apparatus section). The densities (ρ) at 298.15 K were measured using a precision digital oscillating U-tube densimeter (DMA 4500, Anton Paar GmbH, Graz, Austria), with a reproducibility of 10^{-2} kg·m^{-3}. The measured ρ and T_b and literature values are shown in Table 1.[31−35] For ethanol and *p*-xylene, the experimental T_b and ρ agreed with the literature values. For ethyl hexanoate, the experimental T_b and ρ agreed with data from Serijam et al.[33] and Sheu et al.,[34] respectively.

The Antoine constants of the materials investigated in this study are summarized in Table 2. These constants were determined from the experimental vapor pressure data. The average deviations between the experimental values and those calculated using the Antoine constants in the literature[36,37] were within 0.11 kPa. Except for ethyl hexanoate, the vapor pressures calculated using the Antoine constants determined in this study deviated from those in the literature[38] by 0.09 kPa on average.

Table 1. Normal Boiling Points (T_b), Densities (ρ) at 298.15 K, and Liquid Molar Volumes at 298.15 K, v_i^L, of the Pure Components Used in This Study

	T_b/K		ρ (298.15 K)/kg·m^{-3}		$v_i^L \cdot 10^6$
component	exptl	lit.	exptl	lit.	m^3·mol^{-1}
ethanol	351.44	351.443[a]	785.18	784.93[a]	58.67
p-xylene	411.48	411.509[a]	856.68	856.61[a]	123.93
ethyl hexanoate	440.57	441.2[b]	865.59	866.29[d]	166.61
		440.06[c]		866.38[e]	

[a] Reference 31. [b] Reference 32. [c] Reference 33. [d] Reference 34. [e] Reference 35.

Apparatus. A schematic diagram of the experimental apparatus is shown in Figure 1. The ebulliometer designed in this study to compensate for vapor hold-up included one ebulliometer (1) for trapping the vapor and another ebulliometer (2) for measuring the boiling points of a vapor−liquid mixture. Each boiling flask has a capacity of about 200 cm^3, and both ebulliometers share a condenser (C). The benefits of an ebulliometer that can compensate for vapor hold-up are described in previous papers.[12−14] One feature of this system is that the compensation for the vapor hold-up is achieved by moving the trapped condensate of ebulliometer (1) to ebulliometer (2). The ebulliometers (1, 2) in this study were based on that of Moon et al.,[39] except the boiling flask and mixing trap were combined in the ebulliometer in the present study. The combination of the boiling flask and mixing trap enabled the enhancement of the circulation of the liquid phase from the mixing trap to boiling flask. Equilibrium temperatures were measured with a calibrated platinum resistance thermometer (3) connected to a personal computer (7) via a data logger (6) (34970A, Agilent Technologies, Inc., Santa Clara, CA). The accuracy was estimated to be ± 0.01 K. The pressure in the apparatus was established by a pressure controller DPI515 (5) supplied by Druck Co. (Kirchentellinsfurt, Germany). The uncertainty in the pressure was estimated to be ± 0.03 kPa.

Procedures. The boiling points of the charged mixtures were measured using the ebulliometer as follows:

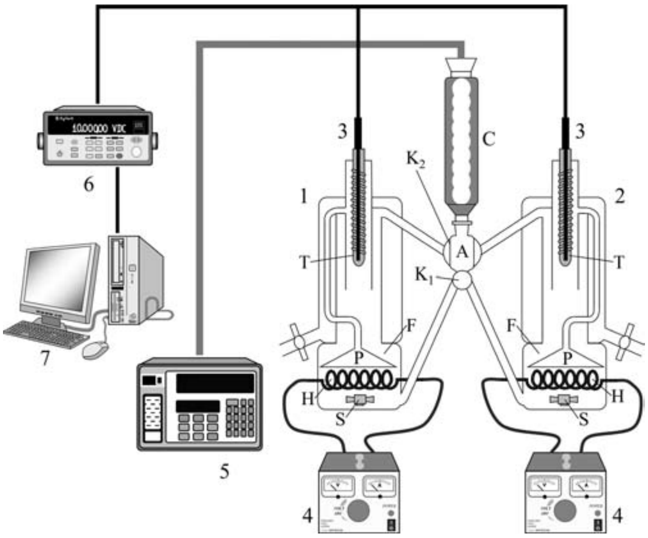

Figure 1. VLE measurement apparatus: 1, 2, ebulliometers; 3, thermometer; 4, volt slider; 5, pressure controller; 6, data logger; 7, personal computer; A, vapor collector; C, condenser; F, boiling flask; H, heater; K_1, K_2, three-way tap; P, cottrell pump; S, stirrer; T, thermometer well.

Table 2. Determined Antoine Equation Constants[a] of the Pure Components Determined in This Study

				$\lvert\Delta P_i^S\rvert_{av}$ [b]		$\lvert\Delta P_i^S\rvert_{av}$ [c]	
component	A	B	C	kPa	lit. (Antoine constant)	kPa	lit. (vapor pressure)
ethanol	7.18077	1555.91	−50.786	0.11	36	0.07	36
p-xylene	5.98089	1365.22	−68.032	0.06	36	0.09	36
ethyl hexanoate	6.82892	2016.18	−22.568	0.07	37		

[a] $\log(P_i^S/\text{kPa}) = A - B/([(T/\text{K})] + C)$. [b] $\lvert\Delta P_i^S\rvert_{av} = (\sum_{k=1}^{NDP} \lvert P_{i,exptl} - P_{i,calcd}\rvert_k)/NDP$, where $P_{i,exptl}$ is the experimental vapor pressure and $P_{i,calcd}$ is the calculated vapor pressure using Antoine constants from the literature. [c] $\lvert\Delta P_i^S\rvert_{av} = (\sum_{k=1}^{NDP} \lvert P_{i,lit} - P_{i,calcd}\rvert_k)/NDP$, where $P_{i,lit}$ is the literature vapor pressure and $P_{i,calcd}$ is the calculated vapor pressure using the Antoine constants determined in this study.

Table 3. Experimental Boiling Points, Liquid-Phase Mole Fraction (x_1), and Temperature (T), for Ethanol (1) + *p*-Xylene (2)

40.00 kPa		53.33 kPa		66.66 kPa		79.99 kPa		93.32 kPa		101.3 kPa	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	379.81	0.0000	388.96	0.0000	396.45	0.0000	402.82	0.0000	408.40	0.0000	411.48
0.1000	339.47	0.1000	347.29	0.1000	353.52	0.1000	359.33	0.1000	364.14	0.1000	369.38
0.2000	335.39	0.1501	344.42	0.1501	350.52	0.1501	355.63	0.1501	359.98	0.2000	361.88
0.3007	334.54	0.2000	342.87	0.2000	349.05	0.2000	354.37	0.2000	359.14	0.2499	359.43
0.4000	333.19	0.2499	342.41	0.3007	347.09	0.2499	353.17	0.3007	355.86	0.3000	358.12
0.4997	332.04	0.3007	341.67	0.4000	345.78	0.3007	351.39	0.4000	354.43	0.4000	355.90
0.6000	331.51	0.4000	340.31	0.4997	344.14	0.4000	350.32	0.4997	352.97	0.4999	355.45
0.7000	330.87	0.4997	338.65	0.6000	343.57	0.4997	348.85	0.6000	352.21	0.6000	353.98
0.7999	330.53	0.6000	338.15	0.7000	342.89	0.6000	348.18	0.7000	351.41	0.7000	353.46
0.9000	329.95	0.7000	337.48	0.7999	342.31	0.7000	347.45	0.7999	350.63	0.8000	352.65
1.0000	329.69	0.7999	337.06	0.9000	341.62	0.7999	346.75	0.9000	349.87	0.9000	351.90
		0.9000	336.39	1.0000	341.23	0.9000	346.03	1.0000	349.39	1.0000	351.44
		1.0000	336.07			1.0000	345.60				

Step 1. A mixture (approximately 100 cm^3) with a known composition was charged into each ebulliometer. The liquid mole fraction was determined gravimetrically using a Mettler digital balance (model AX504, Mettler-Toledo Inc., Columbus, OH) with a sensitivity of 0.1 mg and a maximum load of 510 g. The uncertainty in the mole fraction was estimated to be ± 0.0001. The system pressure was set to the desired pressure using the pressure controller. For measurement, the three-way taps K_1 and K_2 were switched to ebulliometer (1), and the mixture in the ebulliometer (1) was brought to the boiling point. After reaching a steady state, K_1 and K_2 were closed, and heating was stopped simultaneously. This trapped the vapor above K_1, where it then condensed.

Step 2. After switching K_1 and K_2 to ebulliometer (2), the condensate trapped above K_1 was moved to ebulliometer (2). The mixture in ebulliometer (2) was then brought to the boiling point. The vapor hold-ups in step 1 and step 2 were equal. The boiling point steady-state was achieved when the temperature in the ebulliometer changed by less than ± 0.02 K for 2 min. The uncertainty in the experimental boiling point was estimated to be ± 0.03 K. After reaching equilibrium, the boiling point measurement was performed at a higher system pressure.

For the measurement of boiling point at 101.3 kPa, the ebulliometer was open to the atmosphere, and the atmospheric pressure in the ebulliometer was measured using a Fortin barometer with an accuracy of ± 0.013 kPa (± 0.1 mmHg). The experimental boiling points were corrected to 101.3 kPa by the following equation,[40] because the atmospheric pressure fluctuated slightly during the measurements:

$$T = T_{\mathrm{exptl}} + \frac{1}{2.303\sum_{i=1}^{\mathrm{NC}} B_i x_i/(T_{\mathrm{exptl}} + C_i)^2}\,\frac{101.3 - P_{\mathrm{exptl}}}{P_{\mathrm{exptl}}} \qquad (1)$$

where NC is the number of components; T_{exptl}/K is the experimental temperature at the actual atmospheric pressure, P_{exptl}/kPa; B_i and C_i are the Antoine constants of component i, as listed in Table 3; and x_i is the mole fraction in the liquid phase.

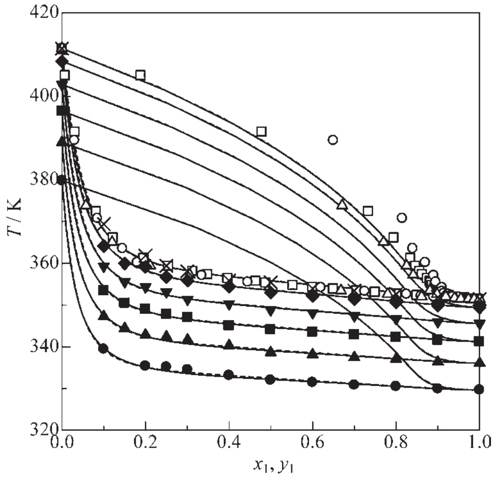

Figure 2. Temperature—composition relationships for ethanol (1) + *p*-xylene (2). This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ×, 101.3 kPa; ○, Yakushina and Koshelkov;[41] △, Galska-Krajewska;[42] □, Sánchez-Russinyol et al.;[43] —, Wilson; - - -, NRTL.

■ RESULTS AND DISCUSSION

Before measurement of the VLE data for the ethanol + ethyl hexanoate mixture, the apparatus and procedure for VLE measurement designed in this study were checked by measuring VLE data for the binary mixture ethanol + *p*-xylene and a comparison to known literature values. In the ethanol + ethyl hexanoate mixture, ethanol and ethyl hexanoate have very different normal boiling points. Therefore, the test system must cover a wide boiling point range. The ethanol + *p*-xylene system has a VLE temperature range of (351 to 411) K at 101.3 kPa. VLE data for this mixture at 101.3 kPa have been reported by several authors.[41−43] The experimental results for the

Table 4. Experimental Boiling Points, Liquid-Phase Mole Fraction (x_1), and Temperature (T) for Ethanol (1) + Ethyl Hexanoate (2)

40.00 kPa		53.33 kPa		66.66 kPa		79.99 kPa		93.32 kPa		101.3 kPa	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	408.31	0.0000	417.74	0.0000	425.39	0.0000	431.86	0.0000	437.53	0.0000	440.57
0.0501	384.52	0.1001	382.39	0.0501	402.56	0.0501	408.96	0.1001	401.71	0.0501	418.52
0.1001	371.26	0.2001	366.27	0.1001	390.53	0.1001	396.15	0.1999	386.08	0.1001	404.83
0.2001	356.64	0.3001	355.49	0.2001	373.46	0.1999	381.35	0.3001	374.92	0.1999	388.82
0.3001	347.77	0.3999	349.92	0.3001	363.17	0.3001	369.43	0.3997	366.56	0.3001	378.01
0.3999	342.37	0.5000	345.66	0.3999	356.09	0.3999	362.50	0.5000	361.18	0.3997	369.05
0.5000	338.61	0.6000	343.10	0.5000	351.39	0.4998	356.53	0.6000	357.85	0.5000	363.61
0.6000	336.21	0.6998	340.86	0.6000	348.62	0.6000	353.62	0.6998	355.37	0.6000	360.07
0.6998	334.13	0.7999	338.87	0.6998	346.55	0.6998	351.31	0.7999	353.08	0.7000	357.19
0.7999	332.21	0.9000	336.92	0.7999	344.21	0.8000	349.05	0.8997	351.37	0.8000	355.13
0.9000	330.55	1.0000	336.07	0.9000	342.21	0.9000	347.06	1.0000	349.39	0.9000	353.32
1.0000	329.69			1.0000	341.23	1.0000	345.60			1.0000	351.44

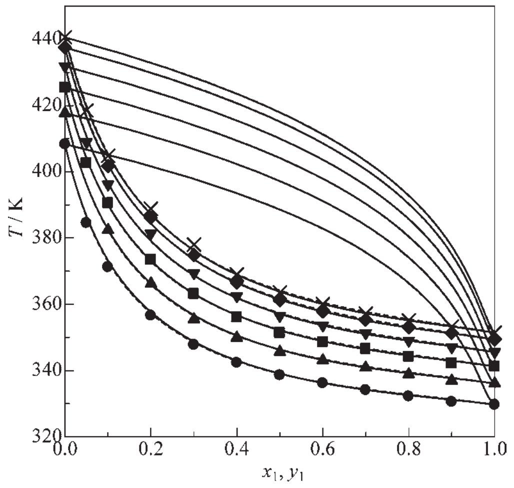

Figure 3. Temperature−composition relationships for ethanol (1) + ethyl hexanoate (2). This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ×, 101.3 kPa; —, Wilson; - - -, NRTL.

boiling point of ethanol (1) + p-xylene (2) at (40.00 to 101.3) kPa are listed in Table 3, and a comparison of these data with literature values is presented in Figure 2. As can be seen in Figure 2, the experimental results agreed with the literature data at 101.3 kPa. Our boiling point data agreed with data from Sánchez-Russinyol et al.,[43] which is thermodynamically consistent with the point test of Van Ness et al.,[44] modified by Fredenslund et al.[45,46] In view of these results, the experimental apparatus designed in this study was applied to VLE measurements for the ethanol + ethyl hexanoate binary mixture.

The experimental VLE data for ethanol (1) + ethyl hexanoate (2) at (40.00 to 101.3) kPa are listed in Table 4 and illustrated in Figure 3. Figure 3 shows that this mixture does not have azeotropic behavior at all experimental pressures. When the mole fraction in the liquid phase, x_1, was changed from 0 (pure ethyl hexanoate) to 0.4, the boiling point decreased by about 70 K at all experimental pressures. In addition, we confirmed that the two-phase region was not found through visual analysis of this mixture. In addition, the two-phase region was not also observed in the literature by Lin et al.

■ DATA REDUCTION AND PREDICTION

In this study, the experimental boiling point data were correlated using the Wilson and NRTL models. For the correlations, liquid-phase activity coefficients of component i, γ_i, were calculated using the following equation and assuming ideal gas behavior, and we have not found the second virial coefficient data or the critical pressure[47−49] needed for the Tsonopoulos method,[50,51] which are required for the calculation of the vapor-phase fugacity coefficients of ethyl hexanoate:

$$\gamma_i = \frac{Py_i}{P_i^S x_i} \tag{2}$$

where x_i and γ_i are the equilibrium mole fractions of component i in the liquid and vapor phase, respectively; P/kPa is the total pressure; and P_i^S/kPa is the saturated vapor pressure of pure component i. P_i^S in eq 2 was expressed by the Antoine equation with the Antoine constants listed in Table 3. The liquid molar volumes $\nu_i^L/\mathrm{m^3 \cdot mol^{-1}}$ required for the Wilson model were treated as constant and were determined from the density at 298.15 K. The values of ν_i^L are listed in Table 1. The mixture nonrandomness parameter, α_{12}, in the NRTL equation was changed from 0.2 to 0.5, and the value of 0.5 was applied for both binary mixtures, considering the correlation accuracies of the boiling points. The binary parameters $\lambda_{ij} - \lambda_{ii}$ for the Wilson model and $g_{ij} - g_{jj}$ for the NRTL model were expressed according to the following polynomial temperature expression, considering the temperature range of the VLE investigated in this study:

$$\text{Wilson}: \quad \lambda_{ij} - \lambda_{ii}/\mathrm{J \cdot mol^{-1}} = A_{ij}^{\mathrm{Wilson}} + B_{ij}^{\mathrm{Wilson}}(T/\mathrm{K}) \tag{3}$$

$$\text{NRTL}: \quad g_{ij} - g_{jj}/\mathrm{J \cdot mol^{-1}} = A_{ij}^{\mathrm{NRTL}} + B_{ij}^{\mathrm{NRTL}}(T/\mathrm{K}) \tag{4}$$

The parameters A_{ij} and B_{ij} for each model were fitted using the Marquardt method[52] for each system, independent of the pressure. The following objective function (F_{obj}) was minimized during the optimization of the binary Wilson and NRTL

Table 5. Parameters and Deviations between the Experimental and Calculated Boiling Points (ΔT) for the Ethanol (1) + *p*-Xylene (2) and Ethanol (1) + Ethyl Hexanoate (2) Systems Using the Wilson and NRTL Models[a]

Ethanol (1) + *p*-Xylene (2)					
Wilson			NRTL (α_{12} = 0.5)		
parameter	*ij* = 12	*ij* = 21	parameter	*ij* = 12	*ij* = 21
$A_{ij}^{\text{Wilson}}/\text{J}\cdot\text{mol}^{-1}$	$9.84692\cdot10^{3}$	$1.05070\cdot10^{4}$	$A_{ij}^{\text{NRTL}}/\text{J}\cdot\text{mol}^{-1}$	$9.78565\cdot10^{3}$	$1.27323\cdot10^{4}$
$B_{ij}^{\text{Wilson}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	−8.27497	$-2.86954\cdot10^{1}$	$B_{ij}^{\text{NRTL}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$-1.98033\cdot10^{1}$	$-2.31310\cdot10^{1}$
P/kPa	$\lvert\Delta T\rvert_{\text{av}}$/K	$\lvert\Delta T\rvert_{\text{max}}$/K	*P*/kPa	$\lvert\Delta T\rvert_{\text{av}}$/K	$\lvert\Delta T\rvert_{\text{max}}$/K
40.00	0.22	0.96	40.00	0.23	0.67
53.33	0.35	0.95	53.33	0.37	0.89
66.66	0.32	0.90	66.66	0.34	0.76
79.99	0.33	0.80	79.99	0.37	0.78
93.32	0.38	1.03	93.32	0.42	1.12
101.3	0.52	1.44	101.3	0.54	1.28
overall	0.35	1.44	overall	0.38	1.28

Ethanol (1) + Ethyl Hexanoate (2)					
Wilson			NRTL (α_{12} = 0.5)		
parameter	*ij* = 12	*ij* = 21	parameter	*ij* = 12	*ij* = 21
$A_{ij}^{\text{Wilson}}/\text{J}\cdot\text{mol}^{-1}$	$5.73389\cdot10^{3}$	$2.26176\cdot10^{3}$	$A_{ij}^{\text{NRTL}}/\text{J}\cdot\text{mol}^{-1}$	$9.02229\cdot10^{3}$	$3.88889\cdot10^{3}$
$B_{ij}^{\text{Wilson}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$-1.10158\cdot10^{1}$	−2.03618	$B_{ij}^{\text{NRTL}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$-1.61086\cdot10^{1}$	$-1.30238\cdot10^{1}$
P/kPa	$\lvert\Delta T\rvert_{\text{av}}$/K	$\lvert\Delta T\rvert_{\text{max}}$/K	*P*/kPa	$\lvert\Delta T\rvert_{\text{av}}$/K	$\lvert\Delta T\rvert_{\text{max}}$/K
40.00	0.72	2.16	40.00	0.65	1.98
53.33	0.38	1.29	53.33	0.44	1.08
66.66	0.42	1.50	66.66	0.53	1.62
79.99	0.56	2.18	79.99	0.67	2.28
93.32	0.40	1.73	93.32	0.48	1.74
101.3	0.44	1.77	101.3	0.64	1.68
overall	0.49	2.18	overall	0.57	2.28

[a] $\lvert\Delta T\rvert = \lvert T_{\text{exptl}} - T_{\text{calcd}}\rvert$; $\lvert\Delta T\rvert_{\text{av}} = (\sum_{k=1}^{\text{NDP}}\lvert\Delta T\rvert_k)/\text{NDP}$, where NDP is the number of data points.

parameters:

$$F_{\text{obj}} = \sum_{k=1}^{\text{NDP}} (T_{\text{exptl}} - T_{\text{calcd}})_k^2 \qquad (5)$$

where NDP is the number of experimental data points; and T_{exptl}/K and T_{calcd}/K are the experimental and calculated boiling points, respectively. The fitted parameters for the Wilson and NRTL models and the absolute deviations between the experimental and calculated boiling points at each experimental pressure are listed in Table 5. Relatively good agreement between the experimental and calculated boiling points was obtained for both binary mixtures from the average deviations between the experimental and calculated boiling points, $\lvert\Delta T\rvert_{\text{av}}$. From Figure 2, large differences of the vapor phase composition in the ethanol + *p*-xylene system can be observed among the literature values from Figure 2. The correlated results by the Wilson and NRTL models nearly agree with the data by Sánchez-Russinyol et al.[43] Average deviations of the vapor phase composition between their experimental and our calculated values were 0.014 mol fraction in both models. According to Sánchez-Russinyol et al., their deviations between their experimental and correlated vapor mole fractions by three activity coefficient models (Wilson, NRTL, and UNIQUAC) are within 0.011 mole fraction. Therefore, our calculation accuracies are nearly same to their correlation ones.

The VLE predictions for the binary mixtures ethanol + *p*-xylene and ethanol + ethyl hexanoate were performed using the analytical solutions of groups (ASOG) and modified universal funcitonal activity coefficient (UNIFAC, Dortmund) group contribution models. In the ASOG model, the group interaction parameters m_{kl} and n_{kl} were obtained from Tochigi et al.[20] In the modified UNIFAC (Dortmund) model, the van der Waals volumes R_k and surface areas Q_k of the functional group and the group interaction parameters a_{nm}, b_{nm}, and c_{nm} were taken from Gmehling et al.[22] Deviations between the experimental and the predicted data are presented in Table 6, and the predicted diagrams are shown in Figures 4 and 5. In the ethanol + *p*-xylene mixture, these models provide a relatively good prediction accuracy from a comparison of $\lvert\Delta T\rvert_{\text{av}}$ between the data reduction in Table 5 and the prediction in Table 6. For the ethanol + ethyl hexanoate mixture, the predicted boiling points were lower than the experimental ones in the region of $x_1 < 0.4$. The prediction accuracy is represented by the maximum deviation between the experimental and the predicted boiling point ($\lvert\Delta T\rvert_{\text{max.}}$), which was 9.2 K for ASOG and 10.0 K for modified

Table 6. Deviations between the Experimental and Predicted Boiling Points (ΔT) for Ethanol (1) + *p*-Xylene (2) and Ethanol (1) + Ethyl Hexanoate (2) Using the ASOG and Modified UNIFAC (Dortmund) Models[a]

Ethanol (1) + *p*-Xylene (2)					
ASOG			modified UNIFAC (Dortmund)		
P/kPa	$\|\Delta T\|_{av}$/K	$\|\Delta T\|_{max.}$/K	P/kPa	$\|\Delta T\|_{av}$/K	$\|\Delta T\|_{max.}$/K
40.00	0.56	2.83	40.00	0.57	3.31
53.33	0.67	3.16	53.33	0.67	3.55
66.66	0.82	3.64	66.66	0.67	3.93
79.99	0.88	3.57	79.99	0.56	3.75
93.32	0.97	3.83	93.32	0.65	3.87
101.3	0.72	1.42	101.3	0.33	1.32
overall	0.77	3.83	overall	0.58	3.93

Ethanol (1) + Ethyl Hexanoate (2)					
ASOG			modified UNIFAC (Dortmund)		
P/kPa	$\|\Delta T\|_{av}$/K	$\|\Delta T\|_{max.}$/K	P/kPa	$\|\Delta T\|_{av}$/K	$\|\Delta T\|_{max.}$/K
40.00	1.86	5.08	40.00	2.31	6.16
53.33	2.07	7.26	53.33	2.44	8.03
66.66	2.61	8.09	66.66	2.90	8.62
79.99	2.98	9.18	79.99	3.22	9.98
93.32	2.94	8.99	93.32	3.16	9.61
101.3	2.19	9.04	101.3	3.31	9.58
overall	2.44	9.18	overall	2.89	9.98

[a] $|\Delta T| = |T_{exptl} - T_{calcd}|$; $|\Delta T|_{av} = (\Sigma_{k=1}^{NDP}|\Delta T|_k)/NDP$, where NDP is the number of data points.

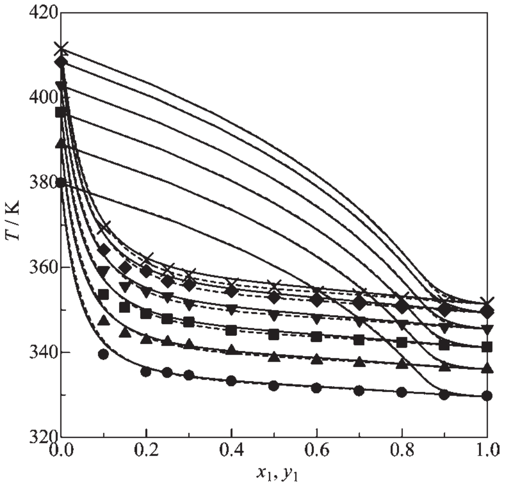

Figure 4. Predicted results of the VLE for ethanol (1) + *p*-xylene (2). This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ×, 101.3 kPa; —, ASOG; - - -, modified UNIFAC (Dortmund).

UNIFAC (Dortmund). The predicted results of the ethanol + ethyl hexanoate mixture indicate these group contribution models could be used for understanding a brief behavior of VLE data for mixtures containing ethanol and FAEE, for example, the enhancement of the vapor pressure of FAEEs by adding ethanol.

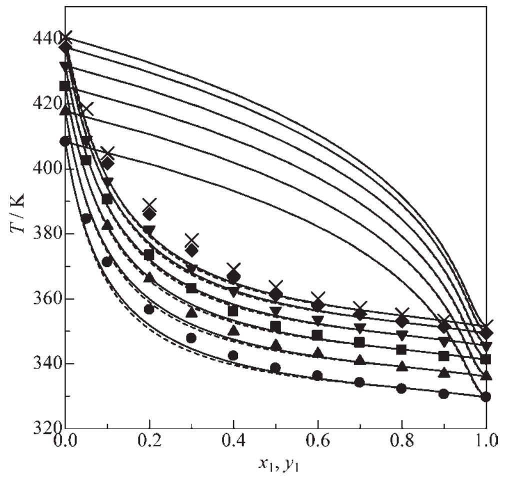

Figure 5. Predicted results of the VLE for ethanol (1) + ethyl hexanoate (2). This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ×, 101.3 kPa; —, ASOG; - - -, modified UNIFAC (Dortmund).

■ CONCLUSIONS

VLE data for a binary mixture of ethanol + ethyl hexanoate were measured at (40.00 to 10.3) kPa using an ebulliometer that could compensate for vapor hold-up. The experimental apparatus and procedure were verified by measuring the VLE data for ethanol + *p*-xylene at pressures of (40.00 to 101.3) kPa. The VLE data of ethanol + ethyl hexanoate showed no azeotropic point at all of the pressures investigated. The densities at 298.15 K for three pure components, for example, ethanol, *p*-xylene, and ethyl hexanoate, were also measured and were compared with the literature values. The experimental VLE data for the two binary mixtures were correlated by the Wilson and NRTL models, and reasonable correlation accuracy was obtained with both models. VLE predictions were also performed using the modified UNIFAC (Dortmund) model, and this model gave qualitative prediction results. The boiling point decreased as the amount of ethanol in the mixture increased. This knowledge and the qualitative representation of these behaviors should be useful for applications of FAEEs to BDF.

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