Vapor−Liquid Equilibrium of Mixtures Containing Adipic Acid, Glutaric Acid, Dimethyl Adipate, Dimethyl Glutarate, Methanol, and Water

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Isothermal vapor−liquid equilibrium (VLE) data were measured, with a static-type apparatus, for the binary systems of methanol + dimethyl adipate, methanol + dimethyl glutarate, and dimethyl glutarate + glutaric acid at (353.15 to 453.15) K. These systems showed slightly positive deviations from the ideal solution behavior without any azeotrope formation. Additionally, the saturated pressures of dimthyl adipate, dimethyl glutarate, methanol + adipic acid, and methanol + water + adipic acid were also determined experimentally in a temperature range of (323.15 to 463.15) K. While the new binary VLE data were correlated with the NRTL-HOC and the UNIQUAC-HOC models, respectively, to determine the optimal values of the model parameters, the saturated pressure data of the ternary system were used to test the validity of the VLE prediction by using the parameters determined from solid−liquid equilibrium data.

Introduction

Dimethyl adipate (DMA) and dimethyl glutarate (DMG) are the main constituents in dibasic esters (DBE) blends, which are commonly used as paint strippers and also potentially as green solvents to replace conventional organic solvents of high volatility and high toxicity in many industrial applications.[1,2]. DBE can be produced from esterification of methanol and dibasic acids, such as adipic acid and glutaric acid. These two acids are available from the intermediate streams in caprolactam plants. The process waste acids could be feasibly recovered as DMA and DMG by using reactive distillation technology.

To develop this reactive distillation process, we need the phase equilibrium properties of the mixtures containing the reactants and the products of the reactions of adipic acid with methanol and glutaric acid with methanol. The intermediates of the reactions, monomethyl adipate and monomethyl glutarate, are rather minor in the products.[3,4] The major species of these two reversible cascade reactions are adipic acid/methanol/dimethyl adipate/water and glutaric acid/methanol/dimethyl glutarate/water. The phase equilibrium properties of the binary or the ternary systems composed of these major components form a data basis for the determination or verification of the parameters in thermodynamic models. Table 1 compiles the phase equilibrium data sources for the related constituent binaries. These available equilibrium properties include vapor−liquid equilibrium (VLE), solid−liquid equilibrium (SLE), and binary and ternary liquid−liquid equilibrium (LLE).

Since water is partially miscible with DMA and DMG, the LLE data of water + methanol + dimethyl adipate or + dimethyl glutarate are useful in the design of decanter, which is one of the key units in the reactive distillation process. Stephenson and Stuart[10] reported the LLE data of water + dimethyl glutarate and water + dimethyl glutarate. Most recently, Hung et al.[9] provided the LLE data of water + methanol + dimethyl adipate, water + adipic acid monomethyl ester + dimethyl adipate, and water + methanol + dimethyl glutarate.

Table 1. Phase Equilibrium Data Sources for Adipic Acid/Methanol/Dimethyl Adipate/Water and Glutaric Acid/Methanol/Dimethyl Glutarate/Water

component *i*	component *j*	properties	source
methanol	adipic acid	SLE[a]	ref 5
		VP[b]	this work
dimethyl adipate	adipic acid	SLE	ref 6
water	adipic acid	SLE	ref 5
		VP	this work
methanol	dimethyl adipate	VLE	this work
water	methanol	VLE	ref 7
			ref 8
water	dimethyl adipate	LLE[c]	ref 9
methanol	glutaric acid	SLE	ref 6
dimethyl glutarate	glutaric acid	VLE	this work
water	glutaric acid	SLE	ref 5
methanol	dimethyl glutarate	VLE	this work
water	dimethyl glutarate	LLE	ref 9

[a] Solid−liquid equilibrium. [b] Saturation pressure (or bubble pressure). [c] Liquid−liquid equilibrium.

The VLE data are also essential to the design of the reactive distillation column. Unfortunately, the related VLE data are very scarce in the literature, except for those of water + methanol.[7,8] A few VLE data were also reported for water + adipic acid and water + glutaric acid, but those sources are not readily accessible. In the present study, isothermal VLE data were measured for three binary systems of methanol + dimethyl adipate, methanol + dimethyl glutarate, and dimethyl glutarate + glutaric acid, at temperatures ranging from (353.15 to 453.15) K. These VLE data were correlated with the NRTL-HOC[11,12] and the UNIQUAC-HOC[12,13] models, respectively.

For the mixtures containing high melting compounds, such as dibasic acids and DBE, the VLE experiment is relatively more difficult to be made as compared to the SLE measurement. As a consequence, the SLE experiment could be an alternative way to provide valuable information for determining the model parameters, if the VLE data are unavailable.[14] A series of SLE measurements has been conducted in our laboratory for water + adipic acid, dimethyl adipate + adipic acid, water + glutaric acid, methanol + adipic acid, and methanol + glutaric acid at

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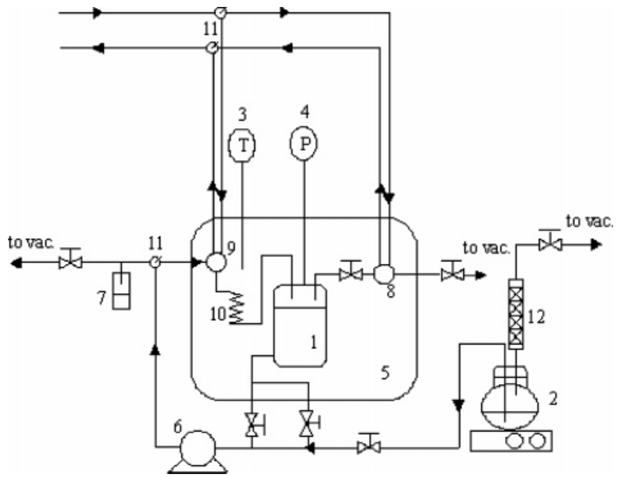

Figure 1. Schematic diagram of the isothermal VLE apparatus: 1, equilibrium cell; 2, degas bottle; 3, thermometer; 4, pressure transducer; 5, thermostatic bath; 6, liquid circulation pump; 7, liquid sampling vial; 8, gas sampling valve; 9, liquid sampling valve; 10, preheater; 11, three-way valve; 12, fractionation column.

atmospheric pressure.[5,6] These SLE data were correlated with several activity coefficient models, and the optimal values of the model parameters were reported by Tein[5] and by Chen.[6] The saturated pressures were also measured, in this study, for methanol + adipic acid and in methanol + water + adipic acid mixtures over (323.15 to 403.15) K in order to test the validity of VLE prediction by using the model parameters determined from the SLE data.

Experimental Section

Apparatus and Procedure. A static apparatus was employed in this study to measure the isothermal VLE data. The schematic diagram is illustrated in Figure 1, and its operating procedure has been described in detail by Hwang et al.[15] A round-bottom bottle (2) with a fractionation column (12) served as the degassing−feeding unit. During the course of degassing, the prepared solution was heated by a hot plate and stirred with a magnetic bar. The evaporated gas was withdrawn by vacuum. After the degassing step, the solution was transferred into a blind equilibrium cell (1) via a liquid pump (6) (model NSI-33R, operable up to 473 K, Milton Roy, USA). The cell was immersed in a thermostatic bath (5) (model EX-251 HT, stability = ± 0.03 K, Neslab, USA). Bath temperature was measured by a precision thermometer (3) (model 1560, Hart Scientific, USA) with a platinum RTD probe, which was calibrated periodically with a high-precision quartz thermometer to an uncertainty of ± 0.02 K. A pressure transducer (4) (model PDCR-912, Druck, UK) connected to a digital indicator (model DPI-261, Druck, UK) determined the equilibrium pressure to an uncertainty of ± 0.1 %.

A liquid circulation loop was equipped for promoting the equilibration as well as taking liquid sample. The liquid outlet from the cell penetrated the wall of thermostatic bath and then connected to the liquid pump (6). The temperature of circulated liquid was regulated by a preheater (10) before returning to the cell. The pump head and the parts outside the thermostatic bath were wrapped with heating tapes and well-insulated to avoid solidifying the circulated solutions. While the liquid sample can be collected in a vial (7) via the sampling port or taken online by a sampling valve (9) (model TN-202, 5 μL, operable up to 573 K, Valco, USA), the vapor sample can also be taken online by a six-port sampling valve (8) (model 2-2919, operable up to 573 K, Valco, USA) with a 0.25 cm^3 sampling loop. These two sampling valves were immersed in the thermostatic bath to keep the samples at the equilibrium temperature. The compositions of samples were analyzed by gas chromatography (model 8700, China Chromatography, Taiwan) with a thermal conductivity detector (TCD). A stainless steel column packed with 20 % SE-30 (80/100 mesh, 4.27 m × 0.3175 cm and i.d. of 2 mm) was used in the sample analysis for methanol + dimethyl adipate, and another stainless steel column packed with 3 % OV-101 (80/100 mesh, 1 m × 0.3175 cm and i.d. of 2 mm) was used for dimethyl glutarate-containing systems. High-purity helium (99.99 %) served as a carrier gas. Four to five samples were replicated at each experimental condition. The average area fraction was converted into mole fraction via calibration equations, which were determined by gas chromatography analysis for various standard mixtures of known mole fractions prepared by mass. Because the concentrations of the heavy components in the vapor samples of the investigated systems are too dilute to be determined accurately by online gas chromatography, only liquid samples were analyzed in the present study. The uncertainty of the reported mole fractions was estimated to within ± 0.003.

Materials. Methanol (99.8 mass %) was purchased from Sigma-Aldrich (USA). Adipic acid (99+ mass %), glutaric acid (99+ mass %), DMA (99+ mass %), and DMG (98+ mass %) were supplied by Arcos, USA. Deionized distilled water was prepared in our laboratory. No impurity peaks were detected from chromatographic analysis. All the chemicals were used without further purification.

Results and Discussions

Experimental Data. Vapor pressure of the constituents is the most important property for development of a reactive distillation process. Among the major components of these two esterification systems, the vapor pressure data of DMG and DMA are unavailable in literature. To provide those essential thermodynamic data, we conducted the vapor pressure measurement for DMG and DMA in temperature ranges of (393.15 to 463.15) K and (353.15 to 443.15) K, respectively. Table 2 reports the experimental results, and Figure 2 illustrates the variation of vapor pressures with temperature over the entire experimental range. The new vapor pressure data were correlated with the Antoine equation. The determined coefficients are given in Table 2.

The static apparatus was subsequently used in the measurement of VLE data ($P-T-x_i$) for three binary systems unavailable in the literature (methanol + dimethyl adipate, methanol + dimethyl glutarate, and dimethyl glutarate + glutaric acid) within temperature ranges of (353.15 to 403.15) K, (393.15 to 433.15) K, and (433.15 to 453.15) K, respectively. Tables 3 to 5 compile the VLE data, and Figures 3 to 5 present the VLE phase diagrams for these three binary systems. All the binary systems exhibit slightly positive deviations from the Raoult's law, and no azeotropes were found in any system. These new binary VLE data will be used in the determination of model parameters later.

As mentioned earlier, the NRTL model parameters have been determined from the SLE data for adipic acid + methanol and adipic acid + water.[5] In order to test the validity of VLE calculation using those parameters determined from the SLE data, saturation pressures were also measured for the two binary mixtures of methanol + adipic acid with mole ratios of 10:1 and 15:1 and for a ternary mixture of methanol + water + adipic acid with a mole ratio of 10:3:1, which are approximately in accordance with the feed compositions of the esterification of adipic acid with methanol. The measurements were implemented

Table 2. Vapor Pressures of Dimethyl Glutarate and Dimethyl Adipate

T/K	P^{sat}_{exptl}/kPa	P^{sat}_{calcd} [a]/kPa	$10^2\Delta P^{sat}$ [b]	T/K	P^{sat}_{exptl}/kPa	P^{sat}_{calcd} [a]/kPa	$10^2\Delta P^{sat}$ [b]
Dimethyl Glutarate				Dimethyl Adipate			
393.15	8.85	8.85	0.0	353.15	0.51	0.51	0.0
413.15	19.14	18.85	−1.5	373.15	1.26	1.26	0.0
423.15	25.31	25.50	0.8	383.15	1.92	1.92	0.0
433.15	32.89	33.21	1.0	403.15	4.33	4.21	−2.8
443.15	41.36	41.94	1.4	413.15	5.93	6.06	2.2
453.15	51.72	51.60	−0.2	423.15	8.37	8.61	2.9
463.15	63.01	62.11	−1.4	433.15	12.30	12.03	−2.2
				443.15	16.66	16.59	−0.4
$10^2\Delta P^{sat}/P^{sat}$ [c]			0.9	$10^2\Delta P^{sat}/P^{sat}$ [c]			1.3

[a] Calculated from the Antoine equation: $\ln P^{sat} = A - [(B)/(T + C)]$ with Antoine constants as follows: $A = 7.4650$, $B = 633.4508$, and $C = -273.2725$ for dimethyl glutarate; $A = 17.9128$, $B = 7255.259$, and $C = 37.1978$ for dimethyl adipate. The units of P^{sat} and T are kPa and K, respectively. [b] $\Delta P^{sat} = (P^{sat}_{calcd} - P^{sat}_{exptl})/(P^{sat}_{exptl})$. [c] $\Delta P^{sat}/P^{sat} = (1)/(n)\sum_{i=1}^{n}((|P^{sat}_{calcd} - P^{sat}_{exptl}|)/(P^{sat}_{exptl}))_i$, where n is the number of data points.

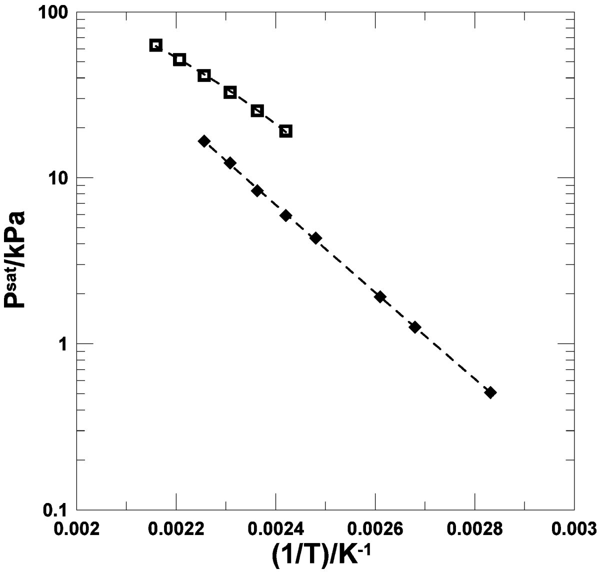

Figure 2. Variation of vapor pressures with temperature for dimethyl glutarate and dimethyl adipate: □, experimental dimethyl adipate; ■, experimental dimethyl glutarate; - - -, calculated Antoine equation.

Table 3. Vapor−Liquid Equilibrium Data for Methanol (1) + Dimethyl Adipate (2)

T/K	P/kPa	x_1	T/K	P/kPa	x_1	T/K	P/kPa	x_1
353.15	180.5	1.0	373.15	352.8	1.0	403.15	840.1	1.0
	172.6	0.936		335.4	0.945		787.6	0.934
	158.3	0.833		287.8	0.802		684.1	0.794
	153.7	0.786		260.5	0.669		585.8	0.664
	148.1	0.749		234.8	0.583		516.2	0.574
	141.0	0.687		223.8	0.550		425.4	0.468
	137.4	0.671		198.9	0.478		302.6	0.322
	125.9	0.599		145.0	0.332		289.3	0.309
	108.6	0.489		141.6	0.320		256.5	0.274
	80.5	0.328		92.9	0.196		183.3	0.194
	53.4	0.199		45.1	0.093		180.8	0.193
	30.4	0.100		1.26	0.0		85.9	0.089
	0.51	0.0					4.33	0.0

Table 4. Vapor−Liquid Equilibrium Data for Methanol (1) + Dimethyl Glutarate (2)

T/K	P/kPa	x_1	T/K	P/kPa	x_1	T/K	P/kPa	x_1
393.15	8.85	0.0	413.15	19.1	0.0	433.15	32.9	0.0
	37.1	0.036		43.2	0.032		76.5	0.038
	72.1	0.087		149.2	0.109		148.5	0.084
	149.2	0.205		241.8	0.202		236.1	0.124
	243.5	0.340		335.9	0.282		479.7	0.269
	324.5	0.482		495.2	0.426		623.5	0.335
	377.9	0.570		587.4	0.496		738.2	0.400
	453.5	0.693		741.7	0.644		923.1	0.509
	510.8	0.787		889.7	0.814		1227.7	0.687
	564.8	0.880		965.4	0.872		1298.9	0.722
	641.3	1.0		1087.3	1.0		1509.4	0.842
							1754.9	1.0

Table 5. Vapor−Liquid Equilibrium Data for Dimethyl Glutarate (1) + Glutaric Acid (2)

T/K	P/kPa	x_1	T/K	P/kPa	x_1	T/K	P/kPa	x_1
433.15	0.17	0.0	443.15	0.32	0.0	453.15	0.55	0.0
	5.00	0.078		7.62	0.137		6.30	0.098
	7.90	0.143		11.75	0.218		10.39	0.186
	9.77	0.215		16.32	0.324		15.22	0.289
	10.68	0.242		20.54	0.452		18.09	0.343
	16.00	0.439		25.53	0.580		27.46	0.514
	17.15	0.478		29.17	0.669		32.20	0.598
	20.50	0.609		33.07	0.765		38.53	0.673
	25.93	0.800		41.36	1.0		42.23	0.751
	32.89	1.0					51.72	1.0

at temperatures from (323.15 to 403.15) K. While temperatures were higher than 403.15 K, esterification of adipic acid with methanol was detected by gas chromatography analysis due to the appearance of extraneous peaks of water and esters in some instances at the end of measurement, even without in the presence of catalyst. Table 6 presents the experimental results, indicating that the saturated pressures of these three systems vary from (47.0 to 721.9) kPa. Since the loaded liquid mixtures almost occupied all the space of the equilibrium cell, the reported equilibrium pressures are close to the bubble pressures. Figure 6 shows the variation of the saturated vapor pressures with temperature. These experimental data will be compared in next section with the VLE calculated results by using the parameters determined from VLE data and SLE data, respectively.

VLE Data Correlation

The ϕ−γ method was applied in the present study to correlate the new binary VLE data. The NRTL[11] and the UNIQUAC[13] models were employed to represent the nonideality of liquid mixtures, and a two-term virial equation with the second virial coefficient estimated from the correlation of Hayden and O'Connell[12] was used to describe the nonideality of vapor mixtures simultaneously. These two models are denoted as NRTL-HOC and UNIQUAC-HOC, respectively. Table 7 gives the physical properties and the parameters for each constituent compound. These values were taken from Aspen Plus databank and were used in VLE calculations. The optimal values of the binary parameters were obtained from bubble pressure calculation by the minimization of the following objective function π:

$$\pi = \sum_{k=1}^{n} (P_{calcd} - P_{exptl})_k^{\ 2} \tag{1}$$

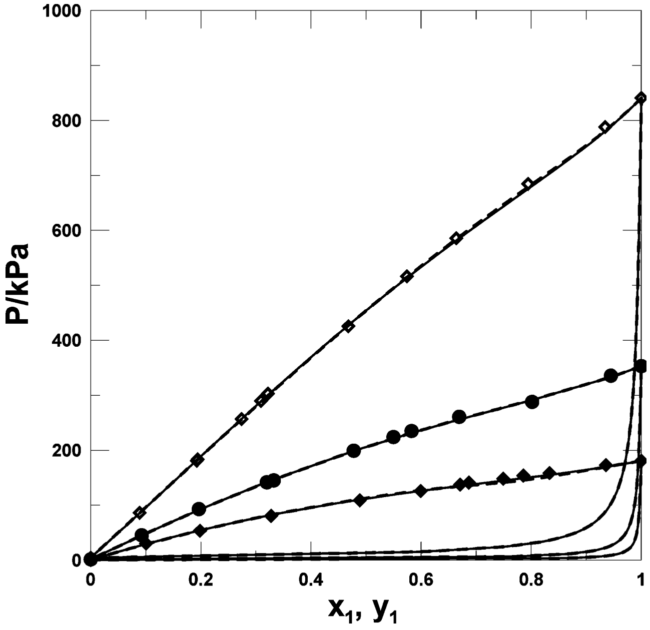

Figure 3. VLE phase diagram for methanol (1) + dimethyl adipate (2): □, experimental at 353.15 K; ●, experimental at 373.15 K; ◆, experimental at 403.15 K; —, calculated NRTL-HOC; - - -, calculated UNIQUAC-HOC. Each lower branch of the curve represents the calculated results of the vapor phase.

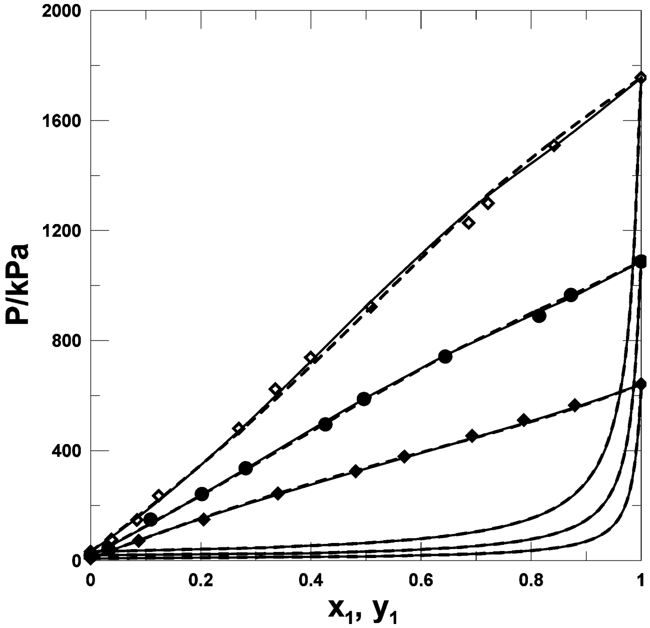

Figure 4. VLE phase diagram for methanol (1) + dimethyl glutarate (2): □, experimental at 393.15 K; ●, experimental at 413.15 K; ◆, experimental at 433.15 K; —, calculated NRTL-HOC; - - -, calculated UNIQUAC-HOC. Each lower branch of the curve represents the calculated results of the vapor phase.

where n is the number of data points and the subscripts calcd and exptl refer to calculated and experimental values, respectively. The optimization algorithm is similar to that of Prausnitz et al.[16] Table 8 lists the correlated results, and the smoothed curves in Figures 3 to 5 are the calculated results from the NRTL-HOC and the UNIQUAC-HOC models. The results reveal that the NRTL-HOC model yielded slightly better correlation.

The applicability of the model parameters determined from SLE data for VLE calculation was also tested with the saturated pressure data of the ternary mixture of methanol + water + adipic acid with the mole ratio of 10:3:1 as given in Table 6. Among these three constituent binaries, the NRTL parameters of water + methanol were taken from Aspen Plus databank, and those of methanol + adipic acid and water + adipic acid were determined from SLE data.[5] The values of the model parameters are reported in Table 9. With these parameters, the NRTL-HOC model predicted the saturated pressures of methanol + water + adipic acid to an average absolute deviation (AAD) of 2.1 %, while the model correlated the saturated pressure (VLE) data of the ternary mixture to an AAD of 0.4 %. Figure 6 compares the predicted and the correlated results with the experimental values. It appears that the predicted bubble pressures by using the parameters obtained from SLE data agreed reasonably with the experimental values.

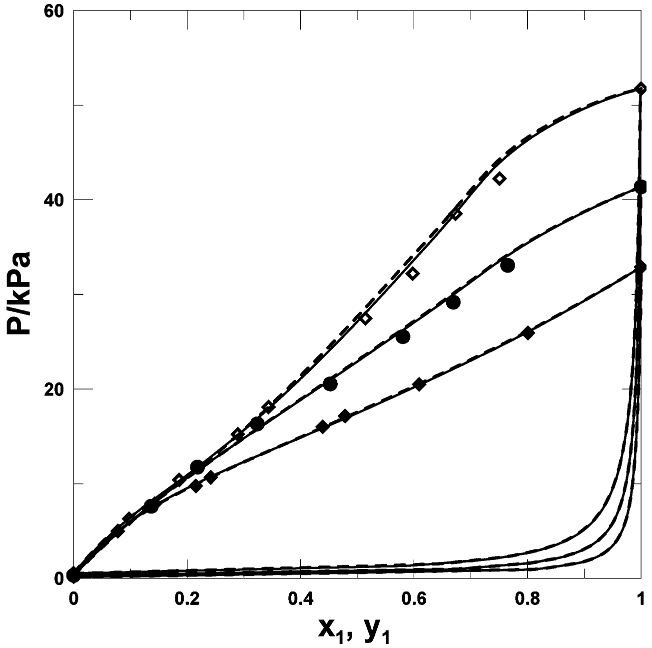

Figure 5. VLE phase diagram for dimethyl glutarate (1) + glutaric acid (2): □, experimental at 433.15 K; ●, experimental at 443.15 K; ◆, experimental at 453.15 K; —, calculated NRTL-HOC; - - -, calculated UNIQUAC-HOC. Each lower branch of the curve represents the calculated results of the vapor phase.

Table 6. Saturation Pressures for Mixtures Containing Methanol, Water, and Adipic Acid

	P^{sat}/kPa		
T/K	mix A[a]	mix B[b]	mix C[c]
323.15	53.0	49.7	47.0
333.15	76.0	72.3	67.6
343.15	119.6	104.7	95.4
353.15	167.0	150.9	133.5
363.15	228.0	212.0	188.8
373.15	307.9	290.4	263.6
383.15	417.6	390.7	356.8
393.15	553.1	523.4	473.2
403.15	721.9	676.7	614.0

[a] Mix A: mixture with the mole ratio of methanol:adipic acid = 15:1. [b] Mix B: mixture with the mole ratio of methanol:adipic acid = 10:1. [c] Mix C: mixture with the mole ratio of methanol:water:adipic acid = 10:3:1.

Conclusions

Isothermal VLE data have been determined experimentally for three binary systems of methanol + dimethyl adipate, methanol + dimethyl glutarate, and dimethyl glutarate + glutaric

Table 7. Physical Properties and Parameters for Constituent Compounds[a]

	T_c[b]	P_c[c]		μ[e]	σ[f]			
	K	kPa	ω[d]	Debye	10^{-1}nm	η[g]	r[h]	q[h]
water	647.3	22055	0.345	1.8	0.615	1.7	0.92	1.40
methanol	512.5	8084	0.566	1.7	1.552	1.6	1.43	1.43
adipic acid	809.0	3530	1.051	2.3	4.976	0	5.27	4.60
glutaric acid	807.0	4040	0.959	2.6	4.591	0	4.60	4.07
dimethyl adipate	663.0	2530	0.700	2.2	5.150	0	6.47	5.62
dimethyl glutarate	653.0	2780	0.615	2.5	4.710	0	5.83	5.08

[a] Values taken from Aspen Plus databank. [b] Critical temperature. [c] Critical pressure. [d] Acentric factor. [e] Dipole moment. [f] Radius of gyration. [g] Association parameter in the HOC model. [h] Parameters in the UNIQUAC model.

Table 8. Correlated Results for Binary Mixtures

	NRTL-HOC					UNIQUAC-HOC						
mixture[a]	T/K	b_{12}[b]/K	b_{21}[b]/K	α[b]	$10^2\Delta P/P$[c]	a_{12}[b]	a_{21}[b]	b_{12}[b]/K	b_{21}[b]/K	c_{12}[b]	c_{21}[b]	$10^2\Delta P/P$
M1	353.15	470.571	−110.953	0.3	5.8	0.249	−40.679	1144.910	−390.265	−0.568	6.946	5.7
	373.15	528.240	−194.371	0.3	4.2	0.249	−40.679	1218.327	−510.357	−0.568	6.946	4.2
	403.15	632.858	−307.953	0.3	2.2	0.249	−40.679	1308.225	−687.670	−0.568	6.946	2.1
M2	393.15	74.620	62.700	0.3	2.4	0	0	110.839	−374.224	0	0	2.5
	413.15	862.405	−419.564	0.3	4.4	0	0	−53.340	−156.882	0	0	4.6
	433.15	1101.919	−532.292	0.3	3.5	0	0	−168.355	−41.416	0	0	4.2
M3	433.15	−298.583	763.256	0.3	1.7	0	0	168.242	−289.061	0	0	1.6
	443.15	−359.557	636.619	0.3	3.0	0	0	171.485	−247.855	0	0	3.2
	453.13	−701.936	1267.461	0.3	3.0	0	0	360.417	−605.558	0	0	3.4

[a] M1: methanol (1) + dimethyl adipate (2). M2: methanol (1) + dimethyl glutarate (2). M3: dimethyl glutarate (1) + glutaric acid (2). [b] $\tau_{ij} = \exp[a_{ij} + (b_{ij}/T) + c_{ij} \ln T]$ and α is the nonrandomness parameter in the NRTL model. [c] $\Delta P/P = (1)/(n)\sum_{i=1}^{n}((|P_{\text{calcd}} - P_{\text{exptl}}|)/(P_{\text{exptl}}))_k$, where n is the number of data points.

Table 9. Calculated Results of Saturated Pressures for Ternary Mixtures of Methanol + Water + Adipic Acid with the NRTL-HOC Model

data source	mixture (1) + (2)	a_{12}	a_{21}	b_{12}/K	b_{21}/K	α	$10^2\Delta P^{\text{sat}}/P^{\text{sat}}$ [a]
VLE binary	water + methanol	−0.693.0[b]	2.7322[b]	172.9871[b]	−617.2687[b]	0.3[b]	2.1
SLE binary	methanol + adipic acid	0	0	−660.6	370.3	0.1	
SLE binary	water + adipic acid	0	0	1170	−416.7	0.3	
VLE binary	water + methanol	−0.693.0[b]	2.7322[b]	172.9871[b]	−617.2687[b]	0.3[b]	0.4
VLE binary	methanol + adipic acid	100.0[c]	5.1040[c]	102747.8[c]	43228.3[c]	0.3[c]	
VLE ternary	water + adipic acid	−0.2069[d]	208.3595[d]	−11.2289[d]	208.3595[d]	0.4[d]	

[a] Calculated results for the ternary system of methanol + water + adipic acid, where $\Delta P^{\text{sat}}/P^{\text{sat}} = (1)/(n)\sum_{k=1}^{n}((|P_{\text{calcd}}^{\text{sat}} - P_{\text{exptl}}^{\text{sat}}|)/(P_{\text{exptl}}^{\text{sat}}))_k$. [b] Parameters were taken from Aspen Plus databank. [c] Parameters were determined from saturation pressures of methanol + adipic acid with mole ratio of 10:1. [d] Parameters were determined from saturation pressures of methanol + water + adipic acid with mole ratio of 10:3:1.

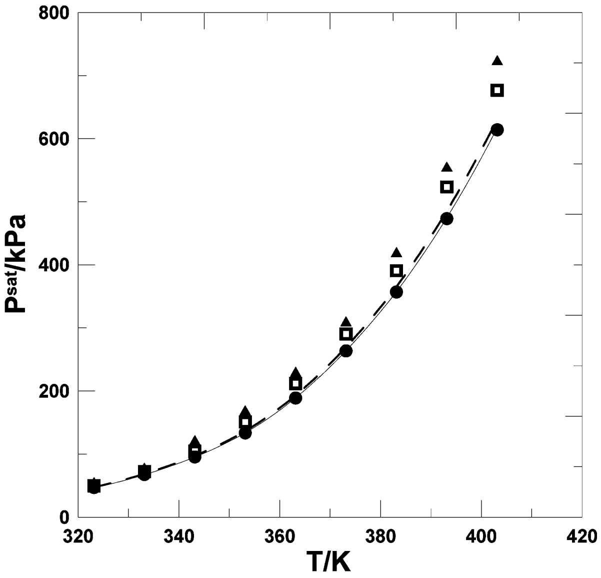

Figure 6. Variation of saturated pressures with temperature for the mixtures containing methanol, water, and adipic acid. The smoothed curves were calculated from the NRTL-HOC model: □, experimental MeOH:adipic acid = 15:1; ■, experimental MeOH:adipic acid = 10:1; ●, experimental MeOH: water:adipic acid = 10:3:1; —, calculated parameters for adipic acid-containing pairs determined from VLE data; - - -, calculated parameters for adipic acid-containing pairs determined from binary SLE data.

acid. Positive deviations from the ideal solution behavior and no azeotropes were found in these three investigated binary systems. The NRTL-HOC and the UNIQUAC-HOC models are capable of accurately correlating the binary VLE data, and the NRTL-HOC model yielded slightly better results. The saturation pressures have also been measured for pure compounds of dimethyl adipate and dimethyl glutarate, two binary mixtures of methanol + adipic acid with mole ratios of 10:1 and 15:1, and a ternary mixture of methanol + water + adipic acid with the mole ratio of 10:3:1. The NRTL-HOC model with the parameters of methanol + adipic acid and water + adipic acid determined from SLE data can predict the bubble pressures of methanol + water + adipic acid to an AAD of 2.1 %.

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