

## Publication IV

Helena Laavi, Juha-Pekka Pokki, Petri Uusi-Kyyny, Alexis Massimi, Younghun Kim, Erlin Sapei, and Ville Alopaeus. Vapor–Liquid Equilibrium, Excess Molar Enthalpies, and Excess Molar Volumes of Binary Mixtures Containing Ethyl Acetate, Butyl Acetate and 2-Butanol at 350 K. *J. Chem. Eng. Data*, 58 (4) 1011–1019, April 1, 2013.

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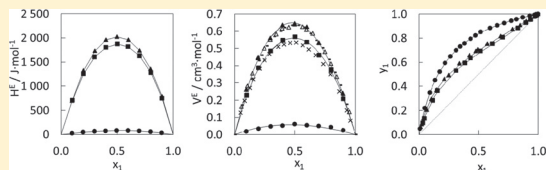


# Vapor–Liquid Equilibrium at 350 K, Excess Molar Enthalpies at 298 K, and Excess Molar Volumes at 298 K of Binary Mixtures Containing Ethyl Acetate, Butyl Acetate, and 2-Butanol

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**ABSTRACT:** Vapor–liquid equilibrium (VLE), excess molar enthalpies ( $H^E$ ), and excess molar volumes ( $V^E$ ) provide means of developing accurate thermodynamic models. In this work, new data of binary mixtures of ethyl acetate, butyl acetate, and 2-butanol are reported. Isothermal VLE data at 350 K were measured by using a circulation still for ethyl acetate + 2-butanol, for 2-butanol + butyl acetate, and for ethyl acetate + butyl acetate.  $H^E$  was measured at 298 K by using a SETARAM C80 calorimeter equipped with a flow mixing cell.  $V^E$  was measured at 298 K by using an Anton Paar DMA 512P densimeter. Liquid phase activity coefficients of the Wilson model and vapor phase fugacities of the Hayden–O’Connell correlation were regressed for a thermodynamic model based on the measured data. Model extrapolation agreed well with literature data. Redlich–Kister equation parameters were regressed by using only the measured  $V^E$  data.



## INTRODUCTION

Renewable fuels and bio based fuel additives are gaining more and more attention due to their ability to cut down greenhouse gas emissions. Ethyl acetate (EtOAc) and butyl acetate (BuOAc) are currently considered among promising candidates for bio based fuel additives.<sup>1,2</sup> Especially butyl acetate has a good potential for improving biodiesel properties because of its very low freezing point (199.65 K) and a high flash point (295 K).<sup>3</sup>

The use of both excess molar enthalpies ( $H^E$ ) and vapor–liquid equilibrium (VLE) data in thermodynamic modeling improves the model reliability and makes the model more extrapolative outside the original temperature range.<sup>4</sup> The suitability of this approach to nonideal systems was shown in our recent work.<sup>5</sup>

VLE data for the EtOAc and 2-butanol (2-BuOH) binary system at 101.32 kPa have been reported for the temperature range from 350.25 K to 372.39 K.<sup>6</sup> Excess volumes for the same system have been reported at 298.15 K,<sup>6,7</sup> 303.15 K,<sup>7</sup> and 308.15 K.<sup>7</sup> For the binary system of 2-BuOH and BuOAc, VLE data at 101.3 kPa have been reported for the temperature range from 372 K to 399 K<sup>8,9</sup> and excess volumes at 298.15 K.<sup>8</sup> Isobaric VLE data for the EtOAc and BuOAc binary system have been reported for the temperature range 350.75 K to 394.95 K.<sup>10</sup> No excess enthalpies are reported in open literature for these binary systems.

In this work, the properties of binary mixtures EtOAc, BuOAc, and 2-BuOH, which are common solvents in chemical industry, were studied. New isothermal VLE data were measured at 350 K, and  $H^E$  and  $V^E$  were measured at 298 K. First, VLE and  $H^E$  data were used for the regression of the liquid phase activity coefficients of the Wilson model. Vapor

phase fugacities were calculated based on the Hayden–O’Connell correlation. Then, the model was compared against literature data. Redlich–Kister equation parameters were regressed by using only the measured  $V^E$  data.

## MATERIALS

All chemicals were purchased from Sigma-Aldrich and their purities, water contents, and densities are listed in Table 1. A gas chromatograph (GC) was used to check the purity of the chemicals. High purity ( $x_{\text{EtOAc}} \geq 0.998$ ) EtOAc was dried over a molecular sieve (Merck, pore size 3 Å) after which no impurities were detected by GC. BuOAc ( $x_{\text{BuOAc}} \geq 0.995$ ) was distilled and dried over a molecular sieve (Merck, pore size 3 Å) after which the final mole fraction  $x$  of the chemical detected by GC was 0.9981. 2-BuOH was dried over a molecular sieve (Merck, pore size 3 Å) after which the final mole fraction  $x_{2\text{-BuOH}}$  was 0.9986 detected by GC. The water contents of the chemicals were low and determined using the Karl Fischer titrator (Mettler-Toledo DL38) applying one-component reagents (Hydrapoint Solvent G and Titrant 2 mgH<sub>2</sub>O·cm<sup>-3</sup>) technique. The pure component densities were measured by using the DMA512P Density Measuring Cell (Anton Paar) thermostatted with a Lauda E200 water immersion thermostat. The literature<sup>11</sup> values of densities for the pure chemicals are shown for comparison in Table 1.

Received: January 8, 2013

Accepted: March 19, 2013

Published: April 1, 2013

Table 1. Purity  $x$ , Water Content, and Density  $\rho$  at 298.4 K and at 0.1 MPa of Pure Liquid Components<sup>a</sup>

	CAS no.	$x_{\text{mit}}$	purification method	$x_{\text{final}}$	water content		$\rho_{\text{exp}}$	$\rho_{\text{lit}}^*$
					wt %	kg·dm <sup>-3</sup>	kg·dm <sup>-3</sup>	
EtOAc	141-78-6	0.998	drying over molecular sieves	1.0000	0.009	0.8939	0.8933	
BuOAc	123-86-4	0.995	distillation, drying over molecular sieves	0.9981	0.008	0.8756	0.8756	
2-BuOH	78-92-2	0.995	drying over molecular sieves	0.9986	0.021	0.8017	0.8021	

<sup>a</sup>  $x_{\text{mit}}$  and  $x_{\text{final}}$  are the initial and final mole fractions of the chemical;  $\rho_{\text{exp}}$  is the measured density, kg·dm<sup>-3</sup>;  $\rho_{\text{lit}}$  is the density from DIPPR,<sup>11</sup> kg·dm<sup>-3</sup>.

## EQUIPMENT

**Excess Molar Enthalpy.** For excess molar enthalpies a flow mixing cell was inserted into a SETARAM C80 calorimeter.<sup>12</sup> The temperature accuracy of the calorimeter was 0.1 at 298 K. Two syringe pumps (ISCO 260D, ISCO 500D, accuracy 0.5 % of the set flow rate) controlled the chemical flows into the calorimeter. The calorimeter was calibrated by using two well-known recommended chemical reference systems: cyclohexane–hexane and methanol–water.<sup>13</sup> The calibration procedure followed the recommendations for this type of equipment.<sup>13,14</sup> Cyclohexane–hexane binary system was used to determine the sensitivity of the calorimeter and methanol–water binary system was used to check the accuracy of the calibration. The absolute average accuracy of the calorimeter was found to be 2.6 %.

**Excess Molar Volume.** DMA 512 P vibrating tube densimeter was used measuring the densities of the binary mixtures. The densimeter was calibrated with deionized and degassed water<sup>15</sup> and dry air<sup>16</sup> reference systems. The densimeter (uncertainty  $\pm 0.00016$  kg·dm<sup>-3</sup>) was attached to the outlet of the calorimeter unit and its temperature was controlled with a Lauda E200 water immersion thermostat. A Thermolyzer S2541 temperature meter with a Pt-100 probe calibrated at the Centre for Metrology and Accreditation was used to determine the temperature of the vibrating tube block. The calibration uncertainty was  $\pm 0.015$  K and the uncertainty of the temperature was estimated to  $\pm 0.02$  K. As seen in Table 1, the measured pure component densities corresponded well to the literature data.

**Vapor–Liquid Equilibrium.** Vapor–liquid equilibrium was measured with a circulation still. The design was based on Yerazunis equipment<sup>17</sup> with marginal modifications.<sup>18,19</sup> The liquid volume needed for running the apparatus was approximately 80 cm<sup>3</sup>. Pressure was measured with a pressure transducer PMP 4070 (Druck) connected to Red Lion panel meter with accuracy of 0.04 kPa. The pressure meter was compared against the Beamex MC2-PE field calibrator calibrated at the Centre for Metrology and Accreditation. The uncertainty of the whole pressure measurements system including the calibration uncertainty was less than  $\pm 0.17$  kPa. The temperature meter was a F200 Precision Thermometer (Automatic Systems Laboratories ASL) with an uncertainty of  $\pm 0.02$  K calibrated at the Centre for Metrology and Accreditation at calibration uncertainty of 0.015 K. The uncertainty of the whole temperature measurement system was less than  $\pm 0.05$  K.

Agilent 6850 gas chromatograph with a flame ionization detector (FID) was used for VLE composition analysis.

## EXPERIMENTAL PROCEDURE

**Excess Molar Enthalpy.** The procedure was similar to the one used in our previous work.<sup>5</sup> The feed pumps were let to equilibrate to the feed temperature for 60 min before the

experiment started. The total flow rate to the calorimeter was kept constant at 0.5 cm<sup>3</sup>·min<sup>-1</sup> by varying the flow rates of the feed pumps as recommended.<sup>12,14</sup> The calorimeter signal stabilized in approximately 20 min, after which at least 10 min was waited prior to recording the values of the experimental point.

**Excess Molar Volume.** Since the densimeter was located after the calorimeter unit, it also provided information whether the mixing in the calorimeter flow mixing cell could be assumed complete. The thermostat of the densimeter was activated at least one hour prior to the measurements to guarantee the temperature in demand. The densimeter signal was let to stabilize (30 to 45) min for each experimental point. However, the first 10 min were needed to get the flow with the adjusted composition to reach to the densimeter and the (20 to 35 min) were enough for stabilization of the signal.

**Vapor–Liquid Equilibrium.** The procedure is described in detail in our previous work.<sup>19</sup> Pure component 1 was introduced in the circulation still, and its vapor pressure was measured. Then, component 2 was introduced into the cell and it took approximately 30 min to achieve a constant temperature. The temperature was held constant for (30 to 45) min before sampling. After recording the pressure reading, the vapor and liquid samples were simultaneously withdrawn with a 1 cm<sup>3</sup> Hamilton Sample Lock syringe. Approximately half of the syringe volume was used for composition analysis by using a GC.

**Gas Chromatograph.** Compositions of liquid and condensed vapor phase samples were determined by gas chromatography. Liquid samples of 1  $\mu$ L were injected into GC. Prior to GC analysis, the condensed vapor and liquid phase samples of the circulation still equipment were diluted with 0.6 cm<sup>3</sup> of toluene. Agilent GC 2 cm<sup>3</sup> glass vials with aluminum crimp caps with PTFE/red rubber septa were used.

The following settings were used for the GC analysis for all measurements related to the circulation still apparatus. The front inlet temperature was set to 523 K and the pressure to 181.8 kPa over pressure, the split ratio was 500:1. The HP-1 (methyl siloxane: length 60 m, inner diameter 250  $\mu$ m, film thickness 1  $\mu$ m) capillary column was used. Helium was used as the carrier gas with a flow rate of 25 cm<sup>3</sup>·s<sup>-1</sup>. The initial temperature of the GC oven was 343 K and it was kept for 5 min after which the oven was heated for 5 min at a rate of 5 K·min<sup>-1</sup> to the final temperature of 368 K, which was kept for 5 min. The FID temperature was set to 523 K, hydrogen flow was set to 40 cm<sup>3</sup>·min<sup>-1</sup> and air flow was set to 450 cm<sup>3</sup>·min<sup>-1</sup>.

## MODELING

The Hayden–O'Connell (HOC) method was used for the modeling of the vapor phase fugacity coefficients.<sup>20,21</sup> The method predicts the second virial coefficients for the virial equation of state only by using the critical properties and molecular parameters of the components. The association

**Table 2. Physical Properties<sup>11</sup> and the Modeling Parameters<sup>20,21</sup> Used in the Hayden–O'Connell Correlation with Chemical Theory<sup>a</sup>**

	EtOAc	BuOAc	2-BuOH
RGYR/10 <sup>-10</sup> m	3.35	4.28	3.18
DMOM/D	1.78	1.84	1.66
v <sup>L</sup> /cm <sup>3</sup> ·mol <sup>-1</sup>	98.49	132.6	92.38
Association $\eta_{ii}$ and Solvation Parameters $\eta_{ij}$			
EtOAc	0.53	0.53	1.30
BuOAc	0.53	0.53	1.30
2-BuOH	1.30	1.30	1.75
Critical Properties			
$\omega$	0.3657	0.4394	0.568
Z <sub>c</sub>	0.255	0.251	0.252
P <sub>c</sub> /kPa	3830	3090	4179
T <sub>c</sub> /K	523.25	575.40	532.63
V <sub>c</sub> /cm <sup>3</sup> ·mol <sup>-1</sup>	286	395	268

<sup>a</sup>RGYR is the radius of gyration, 10<sup>-10</sup>m; DMOM is the dipole moment, D; v<sup>L</sup> is the molar volume of pure liquid, cm<sup>3</sup>·mol<sup>-1</sup>;  $\eta_{ii}$  are the association parameters (located in the diagonal of the table);  $\eta_{ij}$  are the solvation parameters.

parameters  $\eta_{ii}$  and solvation parameters  $\eta_{ij}$  were available for all components in literature.<sup>21</sup> These numerical values and other modeling parameters and physical properties of the components are presented in Table 2.

The liquid activity coefficients were regressed by using the Wilson model<sup>22</sup> where the temperature dependence of adjustable parameters ( $\lambda_{ij}$  and  $\Lambda_{ij}$ ) was given by the polynomials (eq 1) to (eq 4)

$$\lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}T \quad (1)$$

$$\lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}T \quad (2)$$

$$\Lambda_{12} = \frac{v_1^L}{v_1^L} \exp\left(-\frac{\lambda_{12}}{T}\right) \quad (3)$$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp\left(-\frac{\lambda_{21}}{T}\right) \quad (4)$$

where  $\lambda_{ij}$  are the model parameters (K);  $a_{0,ij}$  (K), and  $a_{1,ij}$  (°) are the binary interaction parameters;  $T$  is the temperature (K);  $\Lambda_{ij}$  are the model parameters (°); and  $v_i^L$  are the molar volumes of the pure liquid component (cm<sup>3</sup>·mol<sup>-1</sup>). The values of the binary interaction parameters are collected in Table 11.

**Table 3. Excess Molar Enthalpy  $H^E$ , Excess Molar Volume  $V^E$ , and Density  $\rho$  at 298 K and at 0.1 MPa of Binary Systems of EtOAc, BuOAc, and 2-BuOH<sup>a</sup>**

$x_1$	$u(x_1)$	$H^E$	$u(H^E)$	$\rho$	$V^E$	$u(V^E)$	$T$
		J·mol <sup>-1</sup>	J·mol <sup>-1</sup>	kg·dm <sup>-3</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>	K
EtOAc (1)–2-BuOH (2)							
0.9008	0.0005	784.2	10.1	0.8831	0.2407	0.0211	298.39
0.8007	0.0010	1351.2	17.4	0.8731	0.3713	0.0208	298.39
0.7017	0.0013	1740.4	22.5	0.8628	0.5334	0.0189	298.39
0.6019	0.0016	1959.8	25.3	0.8530	0.6239	0.0161	298.39
0.5012	0.0017	2023.6	26.1	0.8437	0.6448	0.0129	298.39
0.4017	0.0017	1959.1	25.3	0.8345	0.6362	0.0100	298.39
0.3014	0.0016	1731.9	22.3	0.8258	0.5589	0.0081	298.39
0.2003	0.0013	1319.4	17.0	0.8172	0.4478	0.0081	298.39
0.1005	0.0008	698.3	9.0	0.8092	0.2614	0.0112	298.39
BuOAc (1)–2-BuOH (2)							
0.9003	0.0006	745.4	9.6	0.8689	0.2067	0.0256	298.43
0.8013	0.0011	1272.6	16.4	0.8621	0.3771	0.0235	298.43
0.7011	0.0017	1621.3	20.9	0.8554	0.4600	0.0202	298.43
0.6004	0.0021	1818.7	23.5	0.8483	0.5354	0.0157	298.43
0.5020	0.0025	1873.3	24.2	0.8412	0.5660	0.0103	298.43
0.4004	0.0028	1803.3	23.3	0.8337	0.5461	0.0045	298.43
0.3004	0.0029	1601.0	20.7	0.8260	0.4833	0.0007	298.40
0.2008	0.0026	1250.9	16.1	0.8181	0.3856	0.0032	298.42
0.1008	0.0018	709.7	9.2	0.8100	0.2274	0.0005	298.42
EtOAc (1)–BuOAc (2)							
0.0991	0.0001	23.2	0.3	0.8769	0.0176	0.0256	298.46
0.1982	0.0003	43.7	0.6	0.8782	0.0338	0.0249	298.46
0.2993	0.0004	59.4	0.8	0.8797	0.0457	0.0245	298.46
0.3993	0.0006	70.0	0.9	0.8813	0.0506	0.0243	298.46
0.4982	0.0007	76.0	1.0	0.8829	0.0591	0.0243	298.46
0.5994	0.0007	74.7	1.0	0.8848	0.0543	0.0244	298.46
0.6985	0.0007	67.0	0.9	0.8867	0.0488	0.0244	298.45
0.7988	0.0007	52.4	0.7	0.8889	0.0421	0.0241	298.46
0.8995	0.0004	30.0	0.4	0.8913	0.0241	0.0228	298.46

<sup>a</sup> $x_1$  is the mole fraction of the component 1;  $H^E$  is the excess molar enthalpy at 298 K, J·mol<sup>-1</sup>;  $\rho$  is the density of which the standard uncertainty  $u(\rho) = 0.0002$ , kg·dm<sup>-3</sup>;  $V^E$  is the excess molar volume, cm<sup>3</sup>·mol<sup>-1</sup>;  $T$  is the temperature at which the excess volumes have been measured of which the standard uncertainty  $u(T) = 0.02$ , K. The values of the uncertainties  $u(x_1)$ ,  $u(H^E)$ , and  $u(V^E)$  are given in the table.

The total objective function ( $F$ ) of the data regression was the sum of the objective functions presented in (eq 5) and in (eq 6) for VLE and  $H^E$  data sets, respectively.

$$F_{\text{VLE}} = \sum_{i=1}^{\text{NP}} \left( \frac{p_{\text{calc},i} - p_{\text{meas},i}}{p_{\text{meas},i}} \right)^2$$

at bubble point pressure at  $x_{\text{meas}}$  and  $T_{\text{meas}}$  (5)

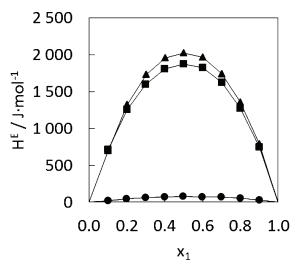
$$F_{\text{HE}} = \sum_{i=1}^{\text{NP}} \left( \frac{H_{\text{calc},i}^E - H_{\text{meas},i}^E}{H_{\text{meas},i}^E} \right)^2$$

at  $x_{\text{meas}}$  and  $T_{\text{meas}}$  (6)

where NP is the number of experimental points,  $p$  is the pressure (kPa),  $x$  is the liquid mole fraction,  $T$  is the temperature (K), and  $H^E$  is the excess molar enthalpy ( $\text{J}\cdot\text{mol}^{-1}$ ).

## RESULTS

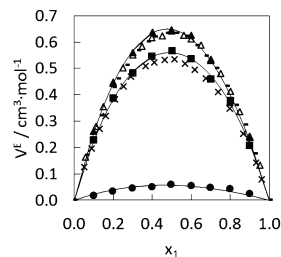
**Excess Molar Enthalpy, Density, and Excess Molar Volume.** Results of the measurements for excess molar



**Figure 1.** Excess molar enthalpies  $H^E$  at 298 K as a function of molar fraction  $x_1$  of binary systems of  $\blacktriangle$ , EtOAc (1) + 2-BuOH (2);  $\blacksquare$ , 2-BuOH (1) + BuOAc (2);  $\bullet$ , EtOAc (1) + BuOAc (2); —, comparison with the model presented in this work.

enthalpies, densities, and excess molar volumes for the binary mixtures of EtOAc, BuOAc, and 2-BuOH are presented in Table 3.

The experimental excess molar enthalpies  $H^E$  ( $\text{J}\cdot\text{mol}^{-1}$ ) were regressed together with the measured VLE data by using the Wilson model<sup>22</sup> for liquid phase activities and HOC method with chemical theory correlation<sup>20,21</sup> for vapor phase fugacities. The values of  $H^E$  are highly positive and of the same magnitude for the acetate-alcohol binary mixtures. Unlike these two systems, the  $H^E$  for the binary mixture of the two acetates is substantially lower as can be seen in Figure 1. This indicates that the acetate-alcohol binary mixtures deviate more from ideality than the binary mixture of the two acetates. The model corresponds well to the experimental values.



**Figure 2.** Excess molar volumes  $V^E$  at 298 K as a function of molar fraction  $x_1$  of binary systems of  $\blacktriangle$ , EtOAc (1) + 2-BuOH (2);  $\blacksquare$ , 2-BuOH (1) + BuOAc (2);  $\bullet$ , EtOAc (1) + BuOAc (2); —, comparison with the model presented in this work; —, EtOAc (1) + 2-BuOH (2) from literature;<sup>6</sup>  $\Delta$ , EtOAc (1) + 2-BuOH (2) from literature;<sup>7</sup>  $\times$ , 2-BuOH (1) + BuOAc (2) from literature.<sup>8</sup>

The excess molar volumes  $V^E$  ( $\text{cm}^3\cdot\text{mol}^{-1}$ ) were regressed using the Redlich–Kister equation<sup>23</sup> (eq 7)

$$V^E = x_1(1 - x_1) \sum_{i=0}^m A_i(2x_1 - 1)^i$$

(7)

where  $x_i$  is the mole fraction of the component 1 and  $m$  is the highest index of summation. The values of the parameters  $A_i$  determined by a least-squares analysis are listed in Table 4 together with the standard deviations. The total number of the parameters for each system was optimized so that the most accurate results were obtained but overfitting was avoided. The graphs of the Redlich–Kister equation with the experimental excess molar volumes are illustrated in Figure 2. The definition of the excess molar volume is given in equation (eq 8)

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}$$

(8)

where  $x_i$  is the molar fraction,  $M_i$  is the molar mass ( $\text{g}\cdot\text{mol}^{-1}$ ), and  $\rho_i$  the density ( $\text{g}\cdot\text{cm}^{-3}$ ) of the component  $i$ .

The excess molar volumes are positive for all studied binary systems. The acetate-alcohol binary mixtures have nearly the same and substantially higher  $V^E$  than the acetate mixture that behaves almost ideally. The EtOAc + 2-BuOH binary system has slightly higher value ( $0.65 \text{ cm}^3\cdot\text{mol}^{-1}$ ) for  $V^E$  than the BuOAc + 2-BuOH binary system ( $0.57 \text{ cm}^3\cdot\text{mol}^{-1}$ ). The Redlich–Kister model follows accurately the experimental points and the standard deviations between the model and the measured data are less or equal to  $0.013 \text{ cm}^3\cdot\text{mol}^{-1}$ . For the binary system of EtOAc + 2-BuOH, the highest deviation from the data of Hernandez and Ortega<sup>6</sup> is only 2 % and from the data of Resa et al.<sup>7</sup> 4 %. For the binary system of 2-BuOH + BuOAc, the highest deviation from the data of Gonzalez and Ortega<sup>8</sup> is 5 %.

**Table 4.** Parameters  $A_i$  of the Redlich–Kister Equation for the Excess Molar Volume  $V^E$ <sup>a</sup>

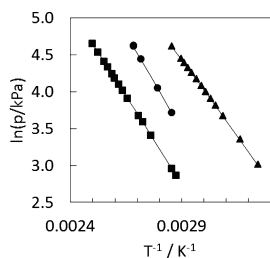
	$A_0$	$A_1$	$A_2$	$S$
	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{cm}^3\cdot\text{mol}^{-1}$
EtOAc (1)–2-BuOH (2)	2.593	−0.229	0.112	0.013
BuOAc (1)–2-BuOH (2)	2.240	−0.089	0.290	0.006
EtOAc (1)–BuOAc (2)	0.227	−0.034		0.002

<sup>a</sup> $A_0$  to  $A_2$  are the Redlich–Kister equation (eq 7) parameters for excess molar volume  $V^E$ ,  $\text{cm}^3\cdot\text{mol}^{-1}$ ;  $S$  is the standard deviation  $S = ((1/N) \sum_{i=1}^N (V_{\text{experiments}}^E - V_{\text{Redlich-Kister}}^E)^2)^{1/2}$ ,  $\text{cm}^3\cdot\text{mol}^{-1}$ ;  $N$  is the number of experiments.

**Table 5.** Vapor Pressures  $p$  at Temperature  $T$  of EtOAc, BuOAc, and 2-BuOH<sup>a</sup>

$T/K$		$p/kPa$
	EtOAc	
350.02		100.68
345.08		85.33
343.35		80.41
341.41		75.18
337.13		64.61
339.47		70.22
334.64		58.96
332.5		54.49
330.08		49.73
327.66		45.34
323.99		39.28
316.23		28.59
308.33		20.29
	BuOAc	
400.14		104.28
396.20		92.99
392.05		82.23
389.51		76.01
386.64		69.55
384.68		65.36
382.10		60.18
379.41		55.17
376.29		49.75
369.50		39.45
367.04		36.18
362.03		30.20
350.12		19.17
347.83		17.44
	2-BuOH	
350.15		40.99

<sup>a</sup> $T$  is the temperature of which the standard uncertainty  $u(T) = 0.05$ , K;  $p$  is the pressure of which the standard uncertainty  $u(p) = 0.04$ , kPa.



**Figure 3.** Temperature dependency of the vapor pressure of pure components: ▲, EtOAc; ■, BuOAc; ●, 2-BuOH; —, DIPPR<sup>11</sup> correlation.

**Pure Component Vapor Pressure.** Pure component vapor pressures were measured before the VLE measurements of the binary systems. The vapor pressure data of 2-butanol have already been published in our earlier work<sup>5</sup> and here is an extension of the vapor pressure up to 350 K. The vapor pressures are shown in Table 5 and illustrated graphically in Figure 3.

The vapor pressure correlation is presented in equation (eq 9)

**Table 6.** Coefficients  $A$  to  $C$  for the Vapor Pressure Correlation and the Absolute Average Pressure Deviation  $|\overline{\Delta p}|$  from the Literature<sup>11</sup> from Temperature  $T_{\min}$  to  $T_{\max}$ <sup>a</sup>

	EtOAc	BuOAc	2-BuOH
this work			
$A$	7.2202	7.0111	8.2682
$B$	2751.9	2998.8	2980.0
$C$	-60.838	-76.745	-90.353
$T_{\min}/K$	308.3	347.8	350.2
$T_{\max}/K$	350.0	400.1	372.7
$ \overline{\Delta p} /kPa$	0.41	0.04	0.75

<sup>a</sup> $A$ ,  $B$ , and  $C$  are the parameters for the (eq 9) in this work;  $T_{\min}$  (K) is the minimum temperature for the vapor pressure correlation;  $T_{\max}$  is the maximum pressure for the vapor pressure correlation;  $|\overline{\Delta p}|$  (kPa) is the absolute average pressure deviation from the DIPPR<sup>11</sup> reference.

**Table 7.** Measured  $x$ ,  $y$ ,  $T$ , and  $p$  Data for the Binary System of EtOAc (1) + 2-BuOH (2)<sup>a</sup>

$x_1$	$y_1$	$T/K$	$p/kPa$
0.000	0.000	350.15	40.99
0.016	0.064	350.09	42.77
0.025	0.084	350.08	43.66
0.042	0.137	350.07	45.52
0.069	0.207	350.08	48.32
0.107	0.297	350.07	52.09
0.152	0.371	350.08	55.86
0.215	0.459	350.08	61.14
0.253	0.490	350.07	64.03
0.341	0.589	350.08	70.13
0.425	0.656	350.07	75.22
0.479	0.690	350.08	77.80
0.497	0.703	350.08	79.09
0.577	0.753	350.08	82.86
0.688	0.817	350.07	88.18
0.787	0.874	350.07	92.71
0.850	0.909	350.08	95.40
0.901	0.939	350.08	97.52
0.941	0.963	350.08	99.02
0.968	0.980	350.08	100.09
0.982	0.988	350.07	100.48
1.000	1.000	350.02	100.68

<sup>a</sup> $x_1$  is the EtOAc liquid phase mole fraction of which the standard uncertainty  $u(x_1) = 0.001$ ;  $y_1$  is the EtOAc vapor phase mole fraction of which the standard uncertainty  $u(y_1) = 0.001$ ;  $T$  is the temperature of which the standard uncertainty  $u(T) = 0.05$ , K;  $p$  is the pressure of which the standard uncertainty  $u(p) = 0.17$ , kPa.

$$\ln\left(\frac{p}{\text{MPa}}\right) = A - \frac{B}{\left(\frac{T}{K}\right) + C} \quad (9)$$

where  $p$  is the vapor pressure (MPa),  $T$  is the temperature (K), and  $A$ ,  $B$ , and  $C$  are the parameters of the equation. The coefficients ( $A$  to  $C$ ) are given in Table 6. The (eq 9) with these parameters was used as the vapor pressure correlation of the VLE model presented in this work. The objective function used for the (eq 9) was the minimum of the sum of the absolute relative deviations between measured and calculated values (eq 10).

**Table 8.** Measured  $x$ ,  $y$ ,  $T$ , and  $p$  Data for the Binary System of 2-BuOH (1) + BuOAc (2)<sup>a</sup>

$x_1$	$y_1$	$T/K$	$p/kPa$
0	0	350.12	19.17
0.034	0.095	350.08	20.55
0.048	0.134	350.09	21.03
0.119	0.282	350.08	23.94
0.158	0.363	350.08	25.12
0.315	0.529	350.08	29.36
0.386	0.593	350.07	31.04
0.436	0.634	350.07	32.15
0.518	0.691	350.08	33.83
0.616	0.752	350.08	35.54
0.704	0.805	350.08	36.94
0.833	0.883	350.08	38.61
0.898	0.927	350.08	39.42
0.935	0.954	350.08	39.9
0.973	0.98	350.08	40.33
0.99	0.993	350.08	40.5
1	1	350.15	40.99

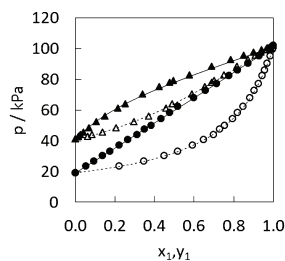
<sup>a</sup> $x_1$  is the 2-BuOH liquid phase mole fraction of which the standard uncertainty  $u(x_1) = 0.001$ ;  $y_1$  is the 2-BuOH vapor phase mole fraction of which the standard uncertainty  $u(y_1) = 0.001$ ;  $T$  is the temperature of which the standard uncertainty  $u(T) = 0.05$ , K;  $p$  is the pressure of which the standard uncertainty  $u(p) = 0.17$ , kPa.

**Table 9.** Measured  $x$ ,  $y$ ,  $T$ , and  $p$  Data for the Binary System of EtOAc (1) + BuOAc (2)<sup>a</sup>

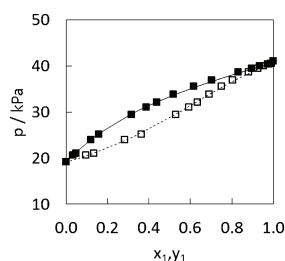
$x_1$	$y_1$	$T/K$	$p/kPa$
0.000	0.000	350.12	19.17
0.053	0.221	350.07	23.36
0.094	0.346	350.03	26.72
0.138	0.449	350.06	30.07
0.176	0.518	350.07	33.11
0.222	0.594	350.12	36.83
0.265	0.648	350.05	40.48
0.313	0.697	350.11	44.00
0.349	0.730	350.14	47.33
0.382	0.755	350.12	50.03
0.434	0.795	350.11	54.38
0.476	0.822	350.10	58.26
0.519	0.850	350.08	62.19
0.599	0.882	350.04	67.80
0.658	0.905	350.10	72.60
0.715	0.926	350.06	77.09
0.777	0.945	350.08	82.25
0.819	0.957	350.12	85.95
0.873	0.971	350.11	90.33
0.931	0.985	350.05	94.87
0.985	0.997	350.06	99.46
1.000	1.000	350.02	100.68

<sup>a</sup> $x_1$  is the EtOAc liquid phase mole fraction of which the standard uncertainty  $u(x_1) = 0.001$ ;  $y_1$  is the EtOAc vapor phase mole fraction of which the standard uncertainty  $u(y_1) = 0.001$ ;  $T$  is the temperature of which the standard uncertainty  $u(T) = 0.05$ , K;  $p$  is the pressure of which the standard uncertainty  $u(p) = 0.17$ , kPa.

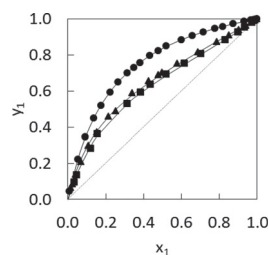
$$F_{\text{vap.pres.}} = \frac{\sum_{i=1}^{\text{NP}} \left( \frac{|p_{\text{calc},i} - p_{\text{meas},i}|}{p_{\text{meas},i}} \right)}{\text{NP}} \quad (10)$$



**Figure 4.** Pressure–composition diagram at 350 K:  $\blacktriangle$ , liquid mole fraction;  $\triangle$ , vapor mole fraction for EtOAc (1) + 2-BuOH (2); and  $\bullet$ , liquid mole fraction;  $\circ$ , vapor mole fraction for EtOAc (1) + BuOAc (2); —, liquid phase comparison with the model presented in this work; - -, vapor phase comparison with the model presented in this work.



**Figure 5.** Pressure–composition diagram at 350 K:  $\blacksquare$ , liquid mole fraction;  $\square$ , vapor mole fraction for 2-BuOH (1) + BuOAc (2); —, liquid phase comparison with the model presented in this work; - -, vapor phase comparison with the model presented in this work.



**Figure 6.** Composition diagram for at 350 K:  $\blacktriangle$ , measurements of EtOAc (1) + 2-BuOH (2);  $\blacksquare$ , measurements of 2-BuOH (1) + BuOAc (2); and  $\bullet$ , measurements of EtOAc (1) + BuOAc (2); —, comparison with the model presented in this work.

where NP is the number of experimental points and  $p$  is the pressure (kPa).

The correlation of DIPPR<sup>11</sup> was used for the comparison of the measured vapor pressures. Within the applied temperature ranges, the vapor pressure correlation based on measured vapor pressures agreed well with the DIPPR<sup>11</sup> vapor pressure correlation as can be seen from Table 6.

**Vapor–Liquid Equilibrium.** The measured VLE results are presented in Tables 7, 8, and 9. The pressure–composition diagrams for the binary mixtures of EtOAc + 2-BuOH and for EtOAc + BuOAc are presented in Figure 4, and the pressure–composition diagram for the binary system of 2-BuOH + BuOAc is presented in Figure 5. The  $xy$ -composition diagrams for all binary systems are presented in Figure 6.



**Table 10. Results of the Consistency Tests (Area, Infinite Dilution, and Point) for Circulation Still Measurements of the Binary Systems of Ethyl Acetate, Butyl Acetate, and 2-Butanol by Using the Hayden–O'Connell Method<sup>a</sup>**

	EtOAc (1) + 2-BuOH (2)	2-BuOH (1) + BuOAc (2)	EtOAc (1) + BuOAc (2)
Area Test			
area	-0.003	-0.008	-0.013
deviation/%	1.4	3.5	86.8
Infinite Dilution Test			
$x_1 \rightarrow 0/\%$	6.3	3.7	not applicable
$x_1 \rightarrow 1/\%$	8.2	5.7	not applicable
Point Test			
$ \overline{\Delta y} $	0.006	0.005	0.002 (0.006 <sup>b</sup> )
$ \overline{\Delta p} /\text{kPa}$	0.69	0.15	0.18 (0.30 <sup>b</sup> )

<sup>a</sup> $x_1$  is the component 1 liquid mole fraction;  $y$  is the component 1 vapor mole fraction;  $|\overline{\Delta p}|$  is the absolute average pressure deviation between the measured and calculated pressure, kPa. <sup>b</sup>For comparison, point test results by assuming ideal liquid and ideal vapor.

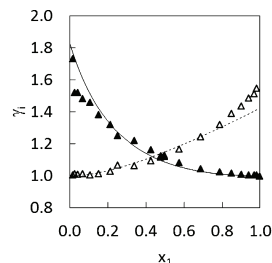
The consistency of the measured VLE data was first evaluated by using the area test.<sup>24–26</sup> Second, the infinite dilution test<sup>24–26</sup> was applied to the measured data. Third, the point test was applied.<sup>27</sup> The results of the consistency tests for the circulation still measurements are given in Table 10. The binary system of EtOAc + BuOAc showed very ideal behavior. The total area of the first consistency test was less than 0.03 which was considered as the passing criterion for the test<sup>28</sup> even though the relative error exceeded other criteria.<sup>24,25</sup> Moreover, for the binary system of EtOAc + BuOAc the infinite dilution test did not give appropriate results since the activity coefficients were close to unity over the whole composition range.<sup>29</sup> Consequently, the logarithms of the activity coefficients were close to zero and minor errors produced relatively high deviations in the test function.

The regressed Wilson model parameters and the deviations of the objective functions are listed in Table 11. As seen in the table, the model corresponds well to the experimental data. The binary system of EtOAc and BuOAc behaves almost ideally so the vapor pressures were also modeled by using ideal vapor and the activity coefficients were set to one for ideal liquid. The rigorous VLE model was then compared to the ideal vapor and ideal liquid based model to study the importance of accurate modeling. The average absolute deviation of the vapor phase mole fraction increased from  $|\overline{\Delta y}|_{\text{HOC}} = 0.002$  to  $|\overline{\Delta y}|_{\text{ideal}} = 0.006$  when ideal vapor and ideal liquid assumption was used. Similarly the absolute average pressure deviation increased from

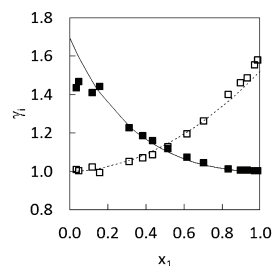
**Table 11. Wilson Model Parameters  $a_{ij}$  and Model Deviations of Vapor Mole Fraction  $y$ , Pressure  $p$ , and Excess Molar Enthalpy  $H^E$  from the Measured Values for the Binary Systems of Ethyl Acetate, Butyl Acetate, and 2-Butanol<sup>a</sup>**

	EtOAc (1) – 2-BuOH (2)	2-BuOH (1) – BuOAc (2)	EtOAc (1) – BuOAc (2)
$a_{0,12}$	212.67	539.191	45.8102
$a_{0,21}$	999.821	704.832	-23.7442
$a_{1,12}$	0.176711	-0.675454	-0.217909
$a_{1,21}$	-3.01116	-2.34942	0.269515
$ \overline{y} $	0.006	0.005	0.002
$ \overline{p} /\text{kPa}$	0.69	0.15	0.18
$ \overline{H^E} /\text{J}\cdot\text{mol}^{-1}$	24.5	13.0	0.5

<sup>a</sup> $a_{0,ij}$ ,  $a_{1,ij}$  are the Wilson model binary interaction parameters for (eq 1) and (eq 2);  $y$  is the vapor phase mole fraction;  $T$  is the temperature, K;  $p$  is the pressure, kPa;  $H^E$  is the excess molar enthalpy,  $\text{J}\cdot\text{mol}^{-1}$ .



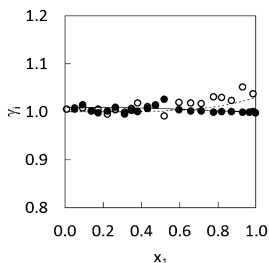
**Figure 7. Activity coefficients for EtOAc (1) + 2-BuOH (2) at 350 K as a function of molar fraction  $x_1$ :  $\blacktriangle$ , EtOAc;  $\triangle$ , 2-BuOH; —, comparison of the EtOAc activity coefficients with the model presented in this work; - -, comparison of the 2-BuOH activity coefficients with the model presented in this work.**



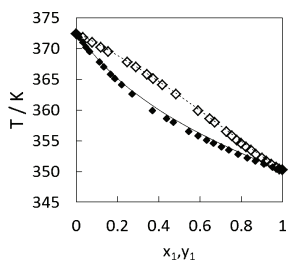
**Figure 8. Activity coefficients at 350 K for 2-BuOH (1) + BuOAc (2) as a function of molar fraction  $x_1$ :  $\blacksquare$ , 2-BuOH;  $\square$ , BuOAc; —, comparison of the 2-BuOH activity coefficients with the model presented in this work; - -, comparison of the BuOAc activity coefficients with the model presented in this work.**

$|\overline{\Delta p}|_{\text{HOC}} = 0.18$  kPa to  $|\overline{\Delta p}|_{\text{ideal}} = 0.30$  kPa. As a conclusion, the ideal vapor with ideal liquid assumption sufficiently models the vapor pressures of the binary system of EtOAc and BuOAc. However, the modeling of other thermodynamic properties, such as excess enthalpies, requires more accurate approach.

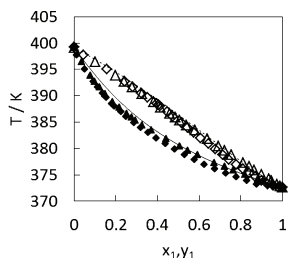
Modeled activity coefficients based on the VLE and the  $H^E$  measurements are presented in Figures 7, 8, and 9. As seen in the figures, the model well describes the measured data. In the case of the nonideal binary mixtures of an acetate and 2-BuOH, the highest deviations from experiments are found at both ends of the composition range. In the case of the closely ideal binary system of EtOAc – BuOAc, the activity coefficients are nearly unity throughout the whole composition range and the model shows the same trend.



**Figure 9.** Activity coefficients at 350 K for EtOAc (1) + BuOAc (2) as a function of molar fraction  $x_1$ : ●, EtOAc; ○, BuOAc; —, comparison of the EtOAc activity coefficients with the model presented in this work; - -, comparison of the BuOAc activity coefficients with the model presented in this work.



**Figure 10.** Equilibrium temperature as a function of composition: A comparison of literature data<sup>6</sup> and the model of this work for at 101.32 kPa for EtOAc (1) + 2-BuOH (2): ◆ (liquid), ◇ (vapor) literature data;<sup>6</sup> —, liquid phase comparison with the model presented in this work; - -, vapor phase comparison with the model presented in this work.

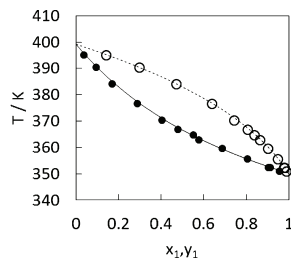


**Figure 11.** Equilibrium temperature as a function of composition: A comparison of literature data<sup>8,9</sup> and the model of this work for at 101.32 kPa for 2-BuOH (1) + BuOAc (2): ◆ (liquid), ◇ (vapor) literature data;<sup>8</sup> ▲ (liquid), Δ (vapor) literature data;<sup>9</sup> —, liquid phase comparison with the model presented in this work; - -, vapor phase comparison with the model presented in this work.

The model of this work for the binary systems of EtOAc, BuOAc, and 2-BuOH was also compared against the literature data.<sup>6–10</sup> The model corresponds well to the isobaric literature data (Figures 10, 11, and 12) even though isothermal data was used in the model parameter regression.

## CONCLUSIONS

Excess molar enthalpies ( $H^E$ ) and excess molar volumes ( $V^E$ ) were measured at 298.15 K for the binary systems consisting of ethyl acetate (EtOAc), butyl acetate (BuOAc), and 2-butanol



**Figure 12.** Equilibrium temperature as a function of composition: A comparison of literature data<sup>10</sup> and the model of this work for at 101.32 kPa for EtOAc (1) + BuOAc (2): ● (liquid); ○ (vapor) literature data;<sup>10</sup> —, liquid phase comparison with the model presented in this work; - -, vapor phase comparison with the model presented in this work.

(2-BuOH). Redlich–Kister equation parameters were provided for  $V^E$ .

Isothermal VLE was measured at 350 K for all binary systems by using a circulation still. No azeotropic behavior was observed.

The Hayden–O'Connell method was applied to vapor phase fugacity coefficients and the Wilson model to liquid phase activity coefficients. The VLE model successfully correlated the new experimental VLE and  $H^E$  data and the existing VLE data in the literature for all the binary systems.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge Academy of Finland and H.L. acknowledges the Research Foundation of Helsinki University of Technology, and Jenny and Antti Wihuri Foundation for financial support.

## REFERENCES

- (1) Ruiz, D. A. Fuel Additive. U.S. Patent Application 20090178331, July 16, 2009.
- (2) Burgazli, J.; Burton, J.; Daniels, D. Fuel Composition with enhanced low temperature properties. U.S. Patent Application 20100005706, January 14, 2010.
- (3) Ali, S. H.; Al-Rashed, O.; Azeez, F. A.; Merchant, S. Q. Potential biofuel additive from renewable sources - Kinetic study of formation of butyl acetate by heterogeneously catalyzed transesterification of ethyl acetate with butanol. *Bioresour. Technol.* **2011**, *21*, 10094–10103.
- (4) Sandler, S. I. *Chemical and engineering Thermodynamics*; John Wiley & Sons, Inc.: New York, USA, 1999.
- (5) Laavi, H.; Zaitseva, A.; Pokki, J.-P.; Uusi-Kyyny, P.; Kim, Y.; Alopaeus, V. Vapor–Liquid Equilibrium, Excess Molar Enthalpies, and Excess Molar Volumes of Binary Mixtures Containing Methyl Isobutyl Ketone (MIBK) and 2-Butanol, tert-Pentanol, or 2-Ethyl-1-hexanol. *J. Chem. Eng. Data* **2012**, *57*, 3092–3101.
- (6) Hernández, P.; Ortega, J. Vapor–Liquid Equilibria and Densities for Ethyl Esters (Ethanoate to Butanoate) and Alkan-2-ol (C3–C4) at 101.32 kPa. *J. Chem. Eng. Data* **1997**, *42* (6), 1090–1100.
- (7) Resa, J. M.; González, C.; Juez, M.; Ortiz De Landaluce, S. Density, refractive index and speed of sound for mixtures of ethyl acetate with 2-butanol and 3-methyl-1-butanol: Vapor-liquid equilibria.

- brium of the ethyl acetate + 3-methyl-1-butanol system. *Fluid Phase Equilib.* **2004**, *2*, 175–180.
- (8) González, E.; Ortega, J. Vapor-Liquid equilibria at 101.32 kPa in mixtures formed by the first four butyl alkanooates and butan-2-ol. *Fluid Phase Equilib.* **1996**, *124*, 161–175.
- (9) Feng, L.-C.; Chou, C.-H.; Tang, M.; Chen, Y. P. Vapor-Liquid Equilibria of Binary Mixtures 2-Butanol + Butyl Acetate, Hexane + Butyl Acetate, and Cyclohexane + 2-Butanol at 101.3 kPa. *J. Chem. Eng. Data* **1998**, *43*, 658–61.
- (10) Shono, H.; Kanazawa, N.; Hashitani, M.; Komatsu, H.; Hirata, M. Vapor-Liquid equilibrium in extractive distillation of ethyl acetate-ethanol system. *Kogyo Kagaku Zasshi* **1969**, *72*, 815–819.
- (11) DIPPR, Design institute for physical property data/AIChE In DIPPR Project 801- Full version, 2005/2008/2009. [http://www.knovel.com/web/portal/browse/display?\\_EXT\\_KNOVEL\\_DISPLAY\\_bookid=1187&VerticalID=0](http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1187&VerticalID=0)].
- (12) SETARAM Technical note 12 - C80 Flow mixing cell; SETARAM: Caluire, France, March 3, 2010.
- (13) Wadsö, L.; Goldberg, R. N. Standards in isothermal micro-calorimetry (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 1625–1639.
- (14) Polednicek, M. *Développement d'appareillages pour l'acquisition des données thermodynamiques dans les systèmes d'intérêt environnemental et énergétique*, Doctoral dissertation, Blaise Pascal University: Clermont-Ferrand, France, 2000.
- (15) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.
- (16) Lemmon, E. W.; Jacobsen, R. T.; Penoncello, S. G.; Friend, D. G. Thermodynamic Properties of Air and Mixtures of Nitrogen, Argon, and Oxygen From 60 to 2000 K at Pressures to 2000 MPa. *J. Phys. Chem. Ref. Data* **2000**, *29*, 331–385.
- (17) Yerazunis, S.; Plowright, J., D.; Smola, F., M. Vapor-Liquid Equilibrium Determination by a New Apparatus. *AIChE J.* **1964**, *10*, 660–665.
- (18) Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapor-Liquid Equilibrium for the Binary Systems of 3-Methylpentane + 2-Methyl-2-propanol at 331 K and + 2-Butanol at 331 K. *J. Chem. Eng. Data* **2001**, *46*, 754–758.
- (19) Sapei, E.; Zaytseva, A.; Uusi-Kyyny, P.; Keskinen, K. I.; Aittamaa, J. Vapor-liquid equilibrium for binary system of thiophene + 2,2,4-trimethylpentane at 343.15 and 353.15 K and thiophene + 2-ethoxy-2-methylpropane at 333.15 and 343.15 K. *Fluid Phase Equilib.* **2007**, *261*, 115–121.
- (20) Hayden, G. J.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–216.
- (21) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer calculations for multicomponent vapour-liquid and liquid-liquid equilibria*; Prentice Hall Inc.: Englewood Cliffs, NJ, 1980.
- (22) 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.
- (23) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem. Res.* **1948**, *40*, 345–348.
- (24) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic consistency test of vapor-liquid equilibrium data: - Methanol + water, benzene + cyclohexane and ethyl methyl ketone + water. *Fluid Phase Equilib.* **1990**, *56*, 269–284.
- (25) Kurihara, K.; Egawa, Y.; Ochi, K.; Kojima, K. Evaluation of thermodynamic consistency of isobaric and isothermal binary vapor-liquid equilibrium data using the PAI test. *Fluid Phase Equilib.* **2004**, *219*, 75–85.
- (26) Kurihara, K.; Egawa, Y.; Iino, S.; Ochi, K.; Kojima, K. Evaluation of thermodynamic consistency of isobaric and isothermal binary vapor-liquid equilibrium data using the PAI test II, alcohol + n-alkane, +aromatic, +cycloalkane systems. *Fluid Phase Equilib.* **2007**, *257*, 151–162.
- (27) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt/Main, Germany, 1977; Vol. 1, Part 1.
- (28) Kang, J. W.; Diky, V.; Chirico, R. D.; Magee, J. W.; Muzny, C. D.; Abdulagatov, I.; Kazakov, A. F.; Frenkel, M. Quality Assessment Algorithm fo Vapor-Liquid Equilibrium Data. *J. Chem. Eng. Data* **2012**, *55*, 3631–3640.
- (29) Eubank, P. T.; Lamonte, B. G. Consistency Tests for Binary VLE Data. *J. Chem. Eng. Data* **2000**, *45*, 1040–1048.