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# Thermodynamic Behavior of (Methylcyclopentane + Ethyl Acetate) Binary Liquid Mixture: Density at Several Temperatures and Vapor–Liquid Equilibrium at 25, 50 and 101.3 kPa

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**Abstract:**

The density and isobaric phase equilibria of the binary system methylcyclopentane + ethyl acetate were investigated for the first time in this work. The density of the system was measured at 101 kPa from (288.15 to 308.15) K for the entire composition range thanks to a vibrating tube densimeter. Positive excess molar volumes were observed and correlated using a Redlich-Kister equation.

New isobaric vapor–liquid equilibrium data for the system methylcyclopentane + ethyl acetate were measured by means of a recirculation ebulliometer. The phase equilibrium was measured at 25, 50 and 101.3 kPa. Equilibrium compositions were determined indirectly, from density measurements of the liquid and condensed vapor phases. Some additional density and vapor–liquid equilibrium data measurements for the binary system ethyl acetate + methylcyclohexane were performed for comparison with previously published results and validation of the experimental protocol.

The methylcyclopentane + ethyl acetate binary mixture displays pronounced positive deviations from ideality and a positive azeotrope. Three thermodynamic consistency tests were employed to validate the produced data set. The reported data were successfully correlated by the NRTL model and the modified UNIFAC predictive model was also used. UNIFAC provides a very good description of the phase behavior at 101.3 kPa whereas predictions are less accurate at low pressures (25 and 50 kPa).

## 1. Introduction

Mixtures of esters and hydrocarbons are commonly encountered in many industrial fields, since several widely used solvents are among these types of compounds. Numerous studies have thus been published regarding the phase equilibria and thermodynamic properties of binary systems of esters with normal and branched alkanes.<sup>1-21</sup> Among those, an ester that features prominently is ethyl acetate, which is one of the most industrially employed short-chain esters. Mixtures of ethyl acetate with aromatic compounds and with unsubstituted naphthenes (mainly cyclohexane) have also been significantly studied.

Despite the numerous works featuring ethyl acetate, systems containing ethyl acetate and a branched naphthene (branched cyclic hydrocarbon such as methylcyclopentane, methylcyclohexane, ethylcyclohexane...) have received less attention. To our knowledge, methylcyclohexane + ethyl acetate<sup>22-26</sup> is the only studied binary system of this kind. And yet, the structural groups  $\text{CH}_{2,\text{cyclic}}$  and  $\text{CH}_{\text{cyclic}}$  can be found in many molecules, including heavy molecules, biomolecules and pharma-type molecules. The development of predictive thermodynamic models such as group contribution approaches for mixtures implies the regression of interaction parameters between groups, typically using accurate experimental data of binary mixtures containing these groups.<sup>27,28</sup> Too few experimental data available for certain types of binary mixtures may lead to unreliable or missing group-interaction parameters, limiting the applicability of predictive models to such mixtures.<sup>27,29,30</sup>

This work aims to increase the number of experimental vapor-liquid equilibrium (VLE) data for mixtures containing ethyl acetate and a branched naphthene. To do so, the VLE of the binary system methylcyclopentane (mC5) + ethyl acetate (EA) was measured under 25, 50 and 101.3 kPa using a recirculation ebulliometer. The density of the system mC5 + EA under

atmospheric pressure was also measured from (288.15 to 308.15) K at intervals of 5 K. To our knowledge, the density of this binary system has never been reported. While the system mC5 + EA has no known industrial application, it is an interesting candidate to expand the number of available data, since cyclopentane and methylcyclopentane may present a different behavior from the other cycloalkanes<sup>31</sup>.

In addition, the system EA + methylcyclohexane (mC6) was also studied for comparison with previously published data<sup>22-26</sup> and validation of the experimental protocol applied in this study.

A Redlich-Kister type equation<sup>32</sup> was employed to fit the excess molar volumes derived from the density data reported in this paper whereas the newly measured VLE data were correlated by means of the NRTL model.<sup>33</sup> The modified UNIFAC (Dortmund) predictive model<sup>34,35</sup> was also utilized to assess its ability to represent data pertaining to a binary system never measured before.

## 2. Materials and Methods

### 2.1. Materials

Suppliers and purities of the compounds used in this study are provided in Table 1. The purities stated by the manufacturers were confirmed by gas chromatography analyses. The chemicals were thus used without further purification. They were stored in the presence of molecular sieves and degassed before use.

**Table 1. Description of the Chemicals Used in This Study**

compound	abbreviation	CAS number	supplier	mole fraction purity <sup>b</sup>
ethyl acetate	EA	141-78-6	Sigma Aldrich	0.999
methylcyclopentane	mC5	96-37-7	Sigma Aldrich	0.993
methylcyclohexane	mC6	108-87-2	Alfa Aesar <sup>a</sup>	0.999

<sup>a</sup> ThermoFisher Scientific. <sup>b</sup> information provided by the manufacturers and confirmed by GC analyses.

### 2.2. Density Measurements

A vibrating tube density meter (DMA 4500 M, Anton Paar) was employed to measure pure component and mixture densities under atmospheric pressure ( $p = 101$  kPa) at five different temperatures ( $T$ ) ranging from (288.15 to 308.15) K. More details about the experimental method employed can be found in previous works.<sup>14,36</sup> 18 binary mixtures of known compositions were prepared for the system EA + mC6 and 19 for the system mC5 + EA so as to precisely describe the whole composition range. The binary mixtures were prepared using a precision balance (Meler Toledo, model ML204) with a weighing error ( $u_{\text{weighing}}$ ) of less than 0.0002 g. The standard uncertainty in composition was calculated through the following expression

$$u(x_1) = x_1(1 - x_1) \sqrt{\left(\frac{u(m_1)}{m_1}\right)^2 + \left(\frac{u(m_2)}{m_2}\right)^2} \quad (1)$$

in which  $x_1$  stands for the mole fraction of component 1 and  $m_1$  and  $m_2$  are the weighted masses of the pure components. The total mass ( $m_1 + m_2$ ) of each prepared mixture was between 8 and 9 g. The combined expanded uncertainty in mole fraction was found to be  $U(x_1) = 0.0001$ , corresponding to the combined standard uncertainty multiplied by a coverage factor of  $k = 2$  for a 95% level of confidence.

During the measurement period, the density meter was checked daily and was periodically calibrated at 298.15 K with dry air and ultrapure water. The device is also calibrated and maintained yearly by the manufacturer. The thermometer included in the measurement device was calibrated against a Pt-100 probe (MKT 10, Anton Paar GmbH) which had been previously calibrated according to ISO 17025. The expanded uncertainty of the temperature ( $U(T)$ ) measured by the device was 0.02 K ( $k = 2$ ). The density was measured with a standard uncertainty ( $u(\rho)$ ) of  $0.00005 \text{ g}\cdot\text{cm}^{-3}$  and the impurities of the chemicals were taken into account.<sup>37,38</sup>

The density uncertainty of a compound  $i$  was estimated using eq 2

$$u(\rho_i) = \sqrt{\left(\frac{u(\rho)}{\sqrt{3}}\right)^2 + \left(\rho_i \xi (1 - x_{\text{purity},i})\right)^2} \quad (2)$$

with  $\xi$  the postulated density difference between the pure component and its impurities.  $\xi$  was assumed to be 0.1, as recommended by Chirico et al.<sup>37</sup>

For binary mixtures, the combined density uncertainty was calculated according to

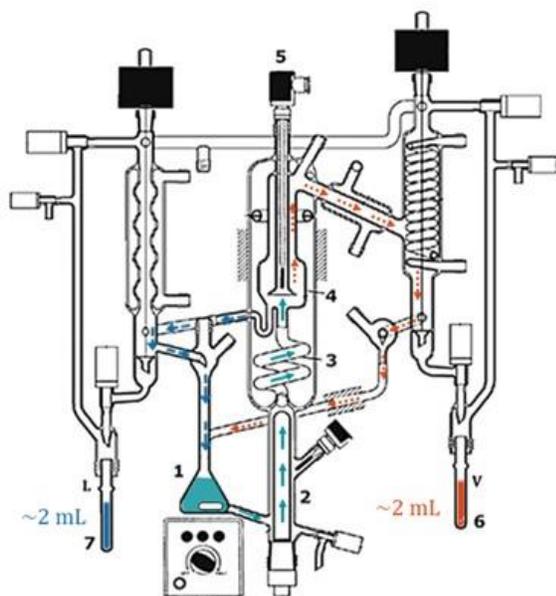
$$u(\rho_m) = \sqrt{u(\rho_1)^2 + u(\rho_2)^2 + u(x_1)^2} \quad (3)$$

The resulting combined standard uncertainties are  $u(\rho_i) = 0.00010 \text{ g}\cdot\text{cm}^{-3}$  for pure EA and pure mC6 and  $u(\rho_m) = 0.00014 \text{ g}\cdot\text{cm}^{-3}$  for the binary mixture EA + mC6, and  $u(\rho_i) = 0.00053 \text{ g}\cdot\text{cm}^{-3}$  for pure mC5 (due to its lower purity) and  $u(\rho_m) = 0.00060 \text{ g}\cdot\text{cm}^{-3}$  for the mC5 + EA mixture.

The combined standard uncertainties of the excess molar volumes,  $V_m^E$ , derived from the mixture's density data were calculated by propagating the standard uncertainties related to the mole fractions and the mixture densities. The standard uncertainties obtained are  $u(V_m^E) = 0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$  for EA + mC6 and  $u(V_m^E) = 0.09 \text{ cm}^3 \cdot \text{mol}^{-1}$  for mC5 + EA. The densities were measured under ambient pressure, i.e.,  $101 \pm 2 \text{ kPa}$ , corresponding to the average atmospheric pressure in Paris ( $\sim 45 \text{ m}$  above sea level).

### 2.3. VLE Measurements

VLE data were measured using a recirculation ebulliometer (Labodest VLE 602, ILUDEST, Germany). This commercial apparatus is routinely employed to acquire isobaric VLE data under low pressure and is extensively described in our previous works<sup>14,36</sup> and in many other studies.<sup>1,39-42</sup> Figure 1 depicts the experimental VLE device.



**Figure 1.** Dynamic ebulliometer used in this study. (1) mixing chamber containing a magnetic stirrer, (2) adjustable power quartz heater, (3) Cottrell pump, (4) separation chamber, (5) temperature probe, (6,7) vapor and liquid sampling port. The circulation of phases in the device is indicated by the arrows.

The principle of the apparatus is based on the continuous circulation of the vapor and liquid phases through the device, which comprises a Cottrell pump (3) and a separation chamber (4). About 105 mL of the studied mixture were introduced in the mixing chamber (1) and brought to a boil thanks to a quartz immersion heater (2). The heating power was adjusted to obtain a condensed vapor phase flow between one and two drops per second.

The pressure in the system was maintained by a vacuum pump and injections of pure gaseous nitrogen. A pressure sensor and transmitter model P-30 (WIKA, Germany) was used to measure the pressure with an accuracy of 0.3 kPa. The standard uncertainty related to the equilibrium pressure was estimated by considering the accuracy of the sensor and the inevitable pressure fluctuations in the device at steady state. Pressure fluctuations (0.1 kPa) were assumed to be symmetrical.<sup>43</sup> Hence, the combined standard uncertainty was estimated to be  $u(p) = 0.3$  kPa.

The equilibrium temperatures were measured using a Pt-100 resistance sensor (Temperaturmeßtechnik Geraberg, Germany) with a standard uncertainty of 0.06 K. Once the thermodynamic equilibrium was reached during experiments, temperature fluctuations of 0.05 K were noticed. The combined standard uncertainty is thus  $u(T) = 0.07$  K.

When a state of thermodynamic equilibrium was reached in the mixture (i.e., after at least 30 min of temperature stability), 2 mL of the liquid phase and 2 mL of the condensed vapor phase were collected (see Figure 1, (6,7)). Compositions of the liquid and the condensed vapor phases at equilibrium were determined indirectly, by density measurements at 298.15 K using the density meter described above. To do so, the density data measured with synthetic mixtures at 298.15 K were employed to generate a fourth-order polynomial involving the density and the molar composition of the studied binary systems:

$$x_1 = A \rho_m^4 + B \rho_m^3 + C \rho_m^2 + D \rho_m + E \quad (4)$$

The coefficients of the polynomial are provided in Table S1 in the Supporting Information, along with the calibration curve analysis in Figure S1. The coefficients in Table S1 allow to precisely estimate the molar fraction of a mixture  $x_1$ . Indeed, average deviations between experimental and calculated molar fraction are 0.0006 (EA + mC6) and 0.0004 (mC5 + EA) whereas maximum deviations are 0.0014 and 0.0012, respectively.

The combined uncertainty of each binary system was calculated considering the uncertainty of the density measurements, the uncertainty of the composition of the prepared synthetic mixtures and the purity of the components. The combined uncertainty of the liquid and vapor mole fraction were  $u(x_1) = u(y_1) = 0.002$  for the binary system EA + mC6 and  $u(x_1) = u(y_1) = 0.009$  for the binary mC5 + EA.

### 3. Results and Discussion

#### 3.1. Comparison Between Measured Pure Component Properties and Literature Values

Table 2 gives densities of the pure components measured in this study and literature data.

**Table 2. Measured Densities ( $\rho$ ) of Ethyl Acetate; Methylcyclopentane and Methylcyclohexane with Literature Values at Temperature  $T$  and Pressure  $p = 101$  kPa <sup>a</sup>**

$T/K$	$\rho/g\cdot cm^{-3}$					
	ethyl acetate		methylcyclopentane		methylcyclohexane	
	this work	literature	this work	literature	this work	literature
288.15	0.9066	0.90648 <sup>44</sup>	0.7526	0.75280 <sup>46 b</sup>	0.7736	0.77363 <sup>51,52</sup>
293.15	0.9005	0.90049 <sup>14</sup> 0.9005 <sup>19</sup> 0.900573 <sup>45</sup>	0.7479	0.74862 <sup>46</sup> 0.74854 <sup>47</sup> 0.74830 <sup>48 c</sup> 0.74664 <sup>49</sup> 0.748 <sup>50</sup>	0.7693	0.76931 <sup>31,51,52</sup> 0.7693 <sup>53</sup> 0.7690 <sup>54</sup>
298.15	0.8945	0.89456 <sup>25</sup> 0.89433 <sup>44</sup> 0.894473 <sup>45</sup>	0.7432	0.74393 <sup>46</sup> 0.74194 <sup>49</sup>	0.7650	0.76520 <sup>25</sup> 0.76499 <sup>51,52</sup>
303.15	0.8883	0.88829 <sup>14</sup>	0.7385	0.73948 <sup>47</sup>	0.7607	0.76125 <sup>26</sup>

		0.8882 <sup>19</sup>		0.73928 <sup>48</sup>		0.76065 <sup>51,52</sup>
		0.88804 <sup>26</sup>		0.73721 <sup>49</sup>		0.7607 <sup>53</sup>
		0.888347 <sup>45</sup>				0.7604 <sup>54</sup>
308.15	0.8821	0.88202 <sup>44</sup>	0.7337		0.7563	0.75603 <sup>55</sup>
		0.882172 <sup>45</sup>				

<sup>a</sup> Standard uncertainties:  $u(T) = 0.01$  K,  $u(p) = 1$  kPa,  $u(\rho) = 0.00010$  g·cm<sup>-3</sup> for ethyl acetate and methylcyclohexane and  $u(\rho) = 0.00053$  g·cm<sup>-3</sup> for methylcyclopentane (due to its lower purity). <sup>b</sup> At 288.71 K. <sup>c</sup> At 293.55 K.

The density data reported in Table 2 are in very good agreement with those previously published except for mC5, for which small deviations can be observed between our data and some other works. Recent mC5 density data are not so abundant in the open literature and some discrepancies between authors can be seen. Furthermore, the purity of the samples employed by the authors in the cited references<sup>46-49</sup> is not always clearly mentioned. A purity issue could explain the significant gap between the mC5 densities measured by González et al.<sup>49</sup> and those reported in this paper and in other studies.<sup>46-48</sup>

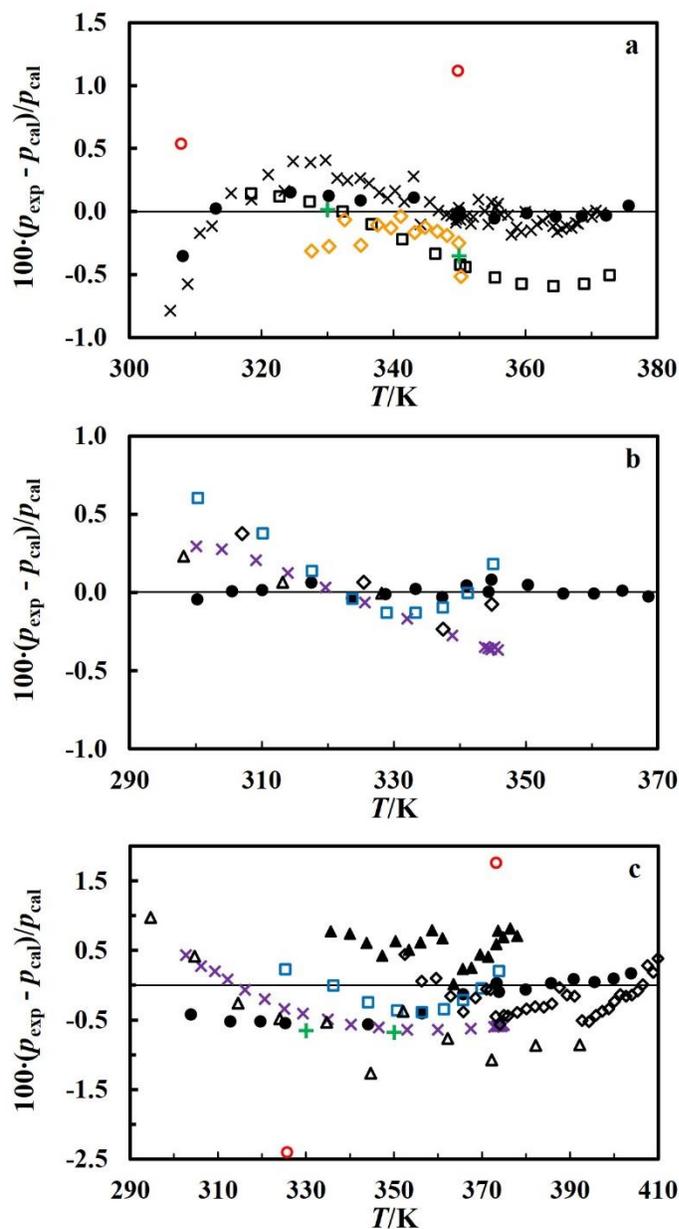
Bearing in mind the consistency tests that need to be performed for the data, vapor pressures of the pure components were measured from vacuum up to 200 kPa. The experimental vapor pressures are reported in Table 3 and are shown as deviation plots in Figure 2.

**Table 3. Measured Vapor Pressures for Pure Ethyl Acetate, Methylcyclopentane and Methylcyclohexane <sup>a</sup>**

ethyl acetate		methylcyclopentane		methylcyclohexane	
<i>T</i> /K	<i>p</i> /kPa	<i>T</i> /K	<i>p</i> /kPa	<i>T</i> /K	<i>p</i> /kPa
308.10	20.0	300.26	20.0	303.81	8.0
313.12	25.0	305.58	25.0	312.88	12.0
324.48	40.0	310.10	30.0	319.71	16.0
330.23	50.0	317.55	40.0	325.27	20.0
335.11	60.0	323.66	50.0	344.14	40.0
343.14	80.0	328.83	60.0	356.42	60.0
349.74	100.0	333.35	70.0	365.74	80.0
350.13	101.3	337.41	80.0	373.40	100.0
355.35	120.0	341.05	90.0	373.91	101.3

360.25	140.0	344.42	100.0	380.03	120.0
364.66	160.0	344.82	101.3	385.79	140.0
368.66	180.0	350.40	120.0	390.96	160.0
372.34	200.0	355.68	140.0	395.69	180.0
375.73	220.0	360.39	160.0	400.00	200.0
		364.66	180.0	403.98	220.0
		368.60	200.0		

<sup>a</sup> Combined standard uncertainties  $u$  are  $u(T) = 0.07$  K,  $u(p) = 0.3$  kPa.



**Figure 2.** Deviation plots of vapor pressures reported in this work from the Riedel equation and parameters listed in Table 4. ●: experimental data from this work. (a) ethyl acetate. ×: Fernández

et al.<sup>5</sup> ○: Zhao et al.<sup>22</sup> †: Wichterle and Linek<sup>23</sup> □: Ambrose et al.<sup>57</sup> ◇: Shaahmadi et al.<sup>58</sup> (b) methylcyclopentane. ×: Willingham et al.<sup>59</sup> □: Sapei et al.<sup>60</sup> △: Mentzer et al.<sup>61</sup> ◇: Ehrett and Weber<sup>62</sup> (c) methylcyclohexane. ○: Zhao et al.<sup>22</sup> †: Wichterle and Linek<sup>23</sup> ×: Willingham et al.<sup>59</sup> □: Sapei et al.<sup>60</sup> ◇: Pereiro et al.<sup>63</sup> △: Mokbel et al.<sup>64</sup> ▲: Loras et al.<sup>65</sup>

The modified Riedel equation was used to represent the vapor pressure of the pure compounds

$$\ln p_i^{vap} = A_i + B_i/T + C_i \ln T + D_i T^{E_i} \quad (5)$$

In which  $p_i^{vap}$  is expressed in Pa and  $T$  in K. The parameters of eq. 5 were fitted against the vapor pressures measured in this work or were obtained from the DIPPR database embedded in the Simulis Thermodynamics calculation server for thermophysical properties and phase equilibria (ProSim).<sup>56</sup> The parameters employed in this work are listed in Table 4.

**Table 4. Riedel Equation Parameters Used in This Work**

Compound	$A_i$	$B_i$	$C_i$	$D_i$	$E_i$	$T_{min}/K$	$T_{max}/K$	$\sigma_p/kPa^a$
ethyl acetate	23.5287	-4311.83	0.07582	$-7.15915 \times 10^{-17}$	6	308.1	375.7	0.06
methylcyclopentane	52.6322	-5175.77	-4.47007	$1.30231 \times 10^{-17}$	6	300.3	368.6	0.03
methylcyclohexane	92.6840	-7080.80	-10.69500	$8.13660 \times 10^{-6}$	2	146.6	572.1	0.16

<sup>a</sup> Standard deviation between experimental vapor pressures (Table 3) and calculated values using the Riedel equation

Most of the vapor pressures reported previously are in excellent agreement with results reported in this work and deviations are generally smaller than 0.5%. As shown in Figure 2, the data measured in this study are in good agreement with vapor pressures reported by Wichterle and Linek<sup>23</sup> for EA and mC6 whereas the boiling temperatures reported by Zhao et al.<sup>22</sup> appear to present significant discrepancies from other sources, particularly for mC6 (see Figure 2.c).

### 3.2. Density and Excess Molar Volumes of the Binary Systems

The system EA (1) + mC6 (2) was investigated for comparison with previously published results. Excess molar volumes were reported by Linek<sup>25</sup> at 298.15 K and by Rajasekhar<sup>26</sup> at 303.15 K. In both studies the densities were not provided and only excess molar volumes were reported.

In this work, the densities of the mixtures ( $\rho_m$ ) were measured at 288.15, 293.15, 298.15, 303.15 and 308.15 K for 18 mixtures ranging from  $x_1 = \{0.0351 \text{ to } 0.9496\}$  (mole fraction of component 1). Density data were then used to calculate the excess molar volumes using eq. 6

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (6)$$

$x_1$  and  $x_2$  are the mole fractions of the mixture whereas  $M_1$ ,  $M_2$  and  $\rho_1$ ,  $\rho_2$  are the pure component molar masses and densities, respectively. Table 5 lists experimental densities and excess molar volumes for the system EA (1) + mC6 (2) measured in this work.

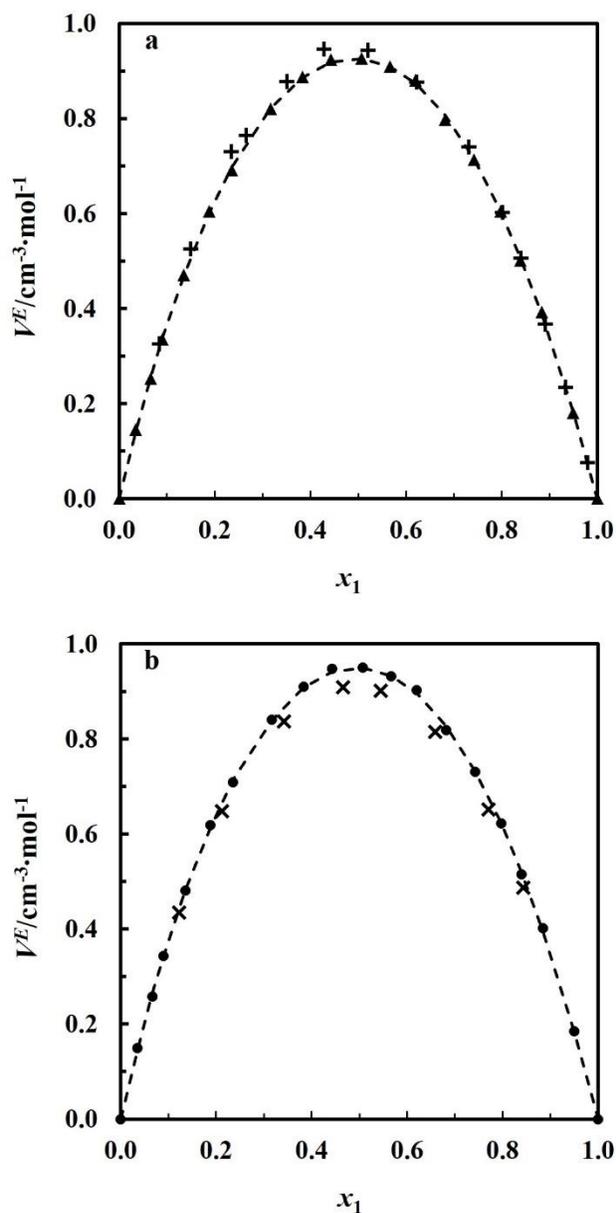
**Table 5. Experimental Densities ( $\rho$ ) and Calculated Excess Molar Volumes ( $V_m^E$ ) for EA (1) + mC6 (2) Binary Mixtures at Mole Fraction  $x_1$  in EA at Temperature  $T$  and  $p = 101 \text{ kPa}$  <sup>a</sup>**

$x_1$ /mol·mol <sup>-1</sup>	$T = 288.15 \text{ K}$		$T = 293.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 303.15 \text{ K}$		$T = 308.15 \text{ K}$	
	$\rho$ /g·cm <sup>-3</sup>	$V_m^E$ /cm <sup>-3</sup> ·mol <sup>-1</sup>								
0.0000	0.77364	0.00	0.76934	0.00	0.76502	0.00	0.76068	0.00	0.75634	0.00
0.0351	0.77638	0.14	0.77203	0.14	0.76766	0.15	0.76326	0.15	0.75887	0.15
0.0666	0.77902	0.24	0.77462	0.25	0.77020	0.25	0.76576	0.26	0.76130	0.27
0.0901	0.78101	0.32	0.77656	0.33	0.77210	0.34	0.76762	0.34	0.76313	0.35
0.1353	0.78498	0.45	0.78048	0.46	0.77596	0.47	0.77141	0.48	0.76684	0.49
0.1881	0.78992	0.58	0.78532	0.59	0.78071	0.61	0.77608	0.62	0.77142	0.64
0.2353	0.79460	0.66	0.78996	0.68	0.78527	0.69	0.78055	0.71	0.77582	0.73
0.3167	0.80313	0.78	0.79833	0.80	0.79350	0.82	0.78865	0.84	0.78378	0.86
0.3831	0.81057	0.84	0.80566	0.87	0.80072	0.89	0.79575	0.91	0.79075	0.94
0.4427	0.81762	0.88	0.81261	0.90	0.80756	0.92	0.80249	0.95	0.79738	0.98
0.5074	0.82577	0.88	0.82065	0.90	0.81549	0.93	0.81030	0.95	0.80508	0.98
0.5667	0.83363	0.86	0.82841	0.88	0.82314	0.91	0.81785	0.93	0.81251	0.96
0.6201	0.84102	0.84	0.83570	0.86	0.83034	0.88	0.82495	0.90	0.81951	0.93
0.6818	0.85021	0.76	0.84479	0.78	0.83931	0.80	0.83380	0.82	0.82825	0.84

0.7423	0.85957	0.68	0.85403	0.69	0.84844	0.71	0.84282	0.73	0.83714	0.75
0.7973	0.86860	0.58	0.86297	0.59	0.85728	0.61	0.85154	0.62	0.84578	0.64
0.8390	0.87585	0.48	0.87014	0.49	0.86437	0.50	0.85855	0.52	0.85270	0.53
0.8841	0.88388	0.37	0.87807	0.38	0.87221	0.39	0.86631	0.40	0.86036	0.41
0.9496	0.89640	0.17	0.89048	0.18	0.88448	0.18	0.87844	0.19	0.87235	0.19
1.0000	0.90658	0.00	0.90054	0.00	0.89445	0.00	0.88830	0.00	0.88211	0.00

<sup>a</sup> Expanded uncertainties are  $U(T) = 0.02$  K,  $U(p) = 2$  kPa and  $U(x_1) = 0.0001$  mol·mol<sup>-1</sup> ( $k = 2$ , level of confidence  $\approx$

0.95). Combined standard uncertainties are  $u(\rho) = 0.00014$  g·cm<sup>-3</sup> and  $u(V_m^E) = 0.02$  cm<sup>3</sup>·mol<sup>-1</sup>.



**Figure 3.** Excess molar volumes of the binary system EA (1) + mC6 (2). (a) At 298.15 K. ▲: data from this work. +: Linek<sup>25</sup>. (b) At 303.15 K. ●: data from this work. ×: Rajasekhar and

Reddy<sup>26</sup>. Dashed lines: Redlich-Kister equation (eq. 7) with parameters reported in the Supporting Information (Table S2).

A Redlich-Kister expression was used to correlate the excess molar volumes

$$\frac{V_m^E}{x_1(1-x_1)} = a_0 + a_1(2x_1 - 1) + a_2(2x_1 - 1)^2 + a_3(2x_1 - 1)^3 \quad (7)$$

The fitted parameters  $a_0$ ,  $a_1$ ,  $a_2$  and  $a_3$  are given in Table S2 (Supporting Information).

Excess molar volumes from this work for EA + mC6 binary mixtures are plotted in Figure 3 along with existing literature data<sup>25,26</sup>. A good agreement is observed between our data and the literature.

As far as we know, the density of the binary system mC5 + EA has never been reported.

Experimental densities and excess molar volumes for the mC5 + EA mixture are gathered in Table 6 and plotted in Figure 4.

**Table 6. Experimental Densities ( $\rho$ ) and Calculated Excess Molar Volumes ( $V_m^E$ ) for mC5**

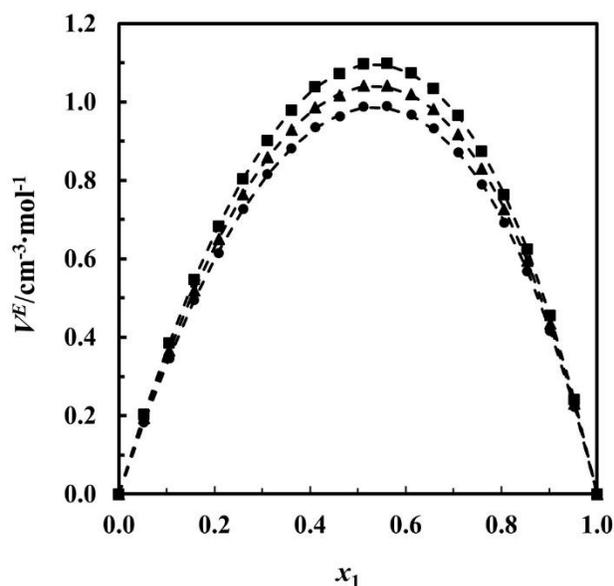
**(1) + EA (2) Mixtures at Mole Fraction  $x_1$  in mC5 at Temperature  $T$  and  $p = 101$  kPa <sup>a</sup>**

$x_1$ /mol·mol <sup>-1</sup>	$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K	
	$\rho$ /g·cm <sup>-3</sup>	$V_m^E$ /cm <sup>-3</sup> ·mol <sup>-1</sup>								
0.0000	0.90658	0.00	0.90054	0.00	0.89445	0.00	0.88830	0.00	0.88211	0.00
0.0523	0.89571	0.18	0.88975	0.19	0.88371	0.19	0.87764	0.20	0.87151	0.20
0.1054	0.88510	0.35	0.87919	0.36	0.87322	0.37	0.86722	0.37	0.86116	0.38
0.1572	0.87502	0.50	0.86919	0.51	0.86330	0.52	0.85736	0.53	0.85138	0.55
0.2088	0.86540	0.62	0.85962	0.63	0.85379	0.65	0.84793	0.66	0.84201	0.68
0.2595	0.85617	0.73	0.85047	0.74	0.84471	0.77	0.83891	0.78	0.83307	0.80
0.3105	0.84723	0.82	0.84160	0.84	0.83590	0.86	0.83018	0.88	0.82441	0.90
0.3606	0.83876	0.88	0.83319	0.90	0.82756	0.93	0.82190	0.95	0.81619	0.98
0.4105	0.83055	0.94	0.82504	0.96	0.81948	0.99	0.81389	1.01	0.80825	1.04
0.4620	0.82243	0.96	0.81697	0.99	0.81149	1.02	0.80596	1.04	0.80039	1.07
0.5114	0.81476	0.99	0.80939	1.01	0.80397	1.04	0.79851	1.07	0.79301	1.10
0.5609	0.80736	0.99	0.80206	1.01	0.79671	1.04	0.79132	1.07	0.78589	1.10
0.6115	0.80007	0.97	0.79484	0.99	0.78956	1.02	0.78424	1.05	0.77889	1.07
0.6585	0.79350	0.93	0.78833	0.96	0.78313	0.98	0.77788	1.01	0.77259	1.03
0.7100	0.78656	0.87	0.78147	0.89	0.77633	0.92	0.77116	0.94	0.76595	0.97
0.7588	0.78023	0.79	0.77520	0.81	0.77015	0.83	0.76504	0.85	0.75991	0.87

0.8056	0.77437	0.69	0.76942	0.71	0.76443	0.73	0.75940	0.74	0.75433	0.76
0.8539	0.76854	0.57	0.76366	0.58	0.75875	0.60	0.75379	0.61	0.74880	0.62
0.9021	0.76299	0.42	0.75819	0.42	0.75334	0.43	0.74845	0.44	0.74354	0.45
0.9528	0.75743	0.22	0.75271	0.23	0.74794	0.23	0.74312	0.24	0.73829	0.24
1.0000	0.75259	0.00	0.74792	0.00	0.74322	0.00	0.73847	0.00	0.73371	0.00

<sup>a</sup> Expanded uncertainties are  $U(T) = 0.02$  K,  $U(p) = 2$  kPa and  $U(x_1) = 0.0001$  ( $k = 2$ , level of confidence  $\approx 0.95$ ).

Combined standard uncertainties are  $u(\rho) = 0.00060$  g·cm<sup>-3</sup> and  $u(V_m^E) = 0.09$  cm<sup>3</sup>·mol<sup>-1</sup>.



**Figure 4.** Excess molar volumes of the binary system mC5 (1) + EA (2). ●: 288.15 K; ▲: 298.15 K; ■: 308.15 K; dashed lines: Redlich-Kister equation (eq. 7) with parameters reported in the Supporting Information (Table S2).

Regardless of the temperature, positive excess molar volumes are observed for the system mC5 + EA, similarly to the binary system EA + mC6. This indicates a volume expansion due to the prevalence of repulsion forces between the molecules involved in the mixture. In general, alkanes + short chain ester mixtures including alkanes + EA exhibit a similar behavior.

It is worth noting that the excess molar volume of the binary system EA + mC5 for a given molar fraction is significantly higher than that of the EA + mC6 mixture. Considering equimolar mixtures, the excess molar volume of the system EA + mC5 is roughly 12% higher than that of the system EA + mC6, regardless of the temperature. This could perhaps be attributed to the

smaller size of the mC5 ring, which could induce a negative impact on the interstitial accommodation.

### 3.3. VLE of the Binary System EA (1) + mC6 (2) at 20 kPa

The VLE of the mixture EA + mC6 was measured under 20 kPa for comparison with  $(T, x, y)$  data published by Zhao et al.<sup>22</sup> and experimental azeotropic coordinates  $(T_{az}, x_{1,az})$  at 20.15 kPa reported by Gmehling and Bölts.<sup>24</sup> The experimental VLE data obtained in this study are reported in Table 7. The compositions of the liquid and condensed vapor phases ( $x_1$  and  $y_1$ ) were determined by density measurements at 298.15 K and under atmospheric pressure (Table S3).

**Table 7. Experimental Isobaric Vapor-Liquid Equilibrium Data for the System Ethyl Acetate (1) – Methylcyclohexane (2) at  $p = 20$  kPa <sup>a</sup>**

$T$ /K	$x_1$ /mol·mol <sup>-1</sup>	$y_1$ /mol·mol <sup>-1</sup>	$\gamma_1$	$\gamma_2$	$G^E/RT$
325.27	0.000	0.000		1.000	0.000
319.11	0.057	0.259	2.859	0.998	0.058
316.53	0.097	0.362	2.607	0.998	0.092
314.72	0.137	0.429	2.357	1.009	0.125
312.95	0.188	0.494	2.129	1.025	0.162
311.77	0.237	0.537	1.930	1.050	0.193
310.61	0.298	0.578	1.736	1.094	0.228
309.83	0.354	0.609	1.592	1.140	0.249
308.49	0.484	0.666	1.349	1.294	0.278
308.14	0.534	0.687	1.281	1.364	0.277
307.78	0.606	0.714	1.192	1.499	0.266
307.46	0.680	0.748	1.128	1.650	0.242
307.39	0.702	0.757	1.109	1.714	0.233
307.30	0.759	0.785	1.068	1.884	0.203
307.25	0.795	0.805	1.048	2.014	0.181
307.24	0.833	0.829	1.030	2.170	0.154
307.30	0.879	0.863	1.014	2.394	0.117

307.37	0.903	0.886	1.010	2.478	0.097
307.57	0.942	0.924	1.001	2.740	0.059
307.73	0.963	0.948	0.997	2.919	0.037
308.10	1.000	1.000	1.000		0.000

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.3$  kPa,  $u(T) = 0.07$  K,  $u(x) = u(y) = 0.002$  mol·mol<sup>-1</sup>.  $T$ , equilibrium

temperature,  $x_1$  and  $y_1$ , liquid and vapor-phase ethyl acetate mole fraction, respectively.  $\gamma_i$ , activity coefficient,  $G^E/RT$ , dimensionless Gibbs function.

In this work, activity coefficients  $\gamma_i$  for a binary mixture containing pure compounds  $i$  and  $j$  were calculated with eq. 8 using the truncated virial EOS

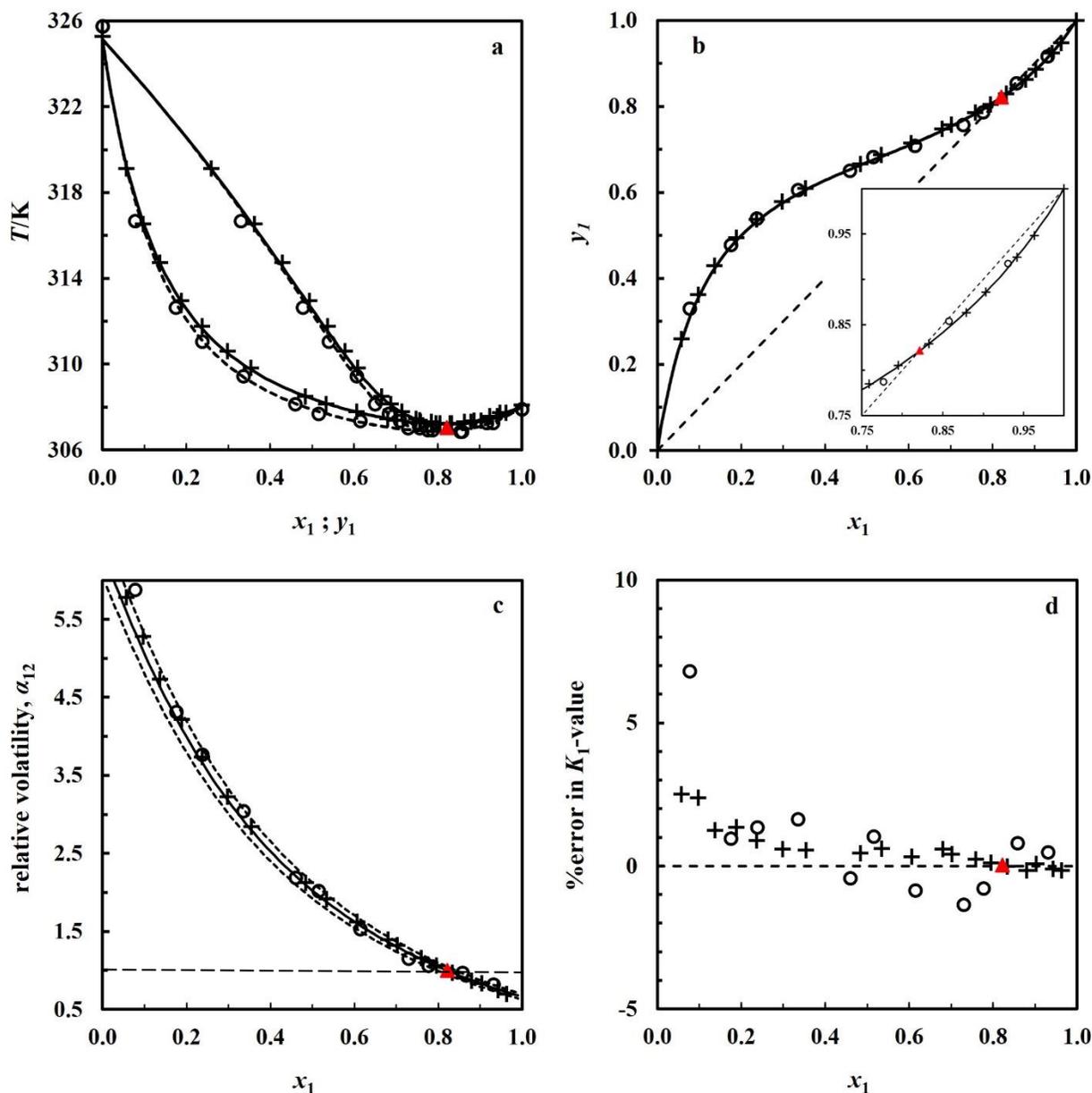
$$\gamma_i = \frac{y_i p}{x_i p_i^{vap}} \exp \left[ \frac{(B_{ii} - V_i^{liq})(p - p_i^{vap}) + p(1 - y_i)^2 (2B_{ij} - B_{ii} - B_{jj})}{RT} \right] \quad (8)$$

$p$  is the pressure of the isobaric VLE measurement,  $x_i$  is the liquid-phase mole fraction and  $y_i$  is the vapor-phase mole fraction.  $V_i^{liq}$  is the molar volume of the pure component  $i$  at the equilibrium temperature,  $T$ . The Rackett equation<sup>66</sup> was used to calculate the pure component molar volumes and the Tsonopoulos approach<sup>67</sup> was employed to estimate the second virial coefficients  $B_{ii}$ ,  $B_{jj}$  and  $B_{ij}$ . Although the Rackett equation was chosen to rigorously calculate  $V_i^{liq}$  at each equilibrium temperature, we also tested another method using our density measurements to calculate the liquid molar volumes of the pure components. The density measurements were conducted at temperatures lower than most equilibrium temperatures, but the difference is not significant. The experimental liquid molar volumes are in good agreement with values obtained with the Rackett equation. Additionally, the activity coefficients obtained using equation 8 are nearly unchanged for the entire data set, whichever the method employed.

Finally, the excess Gibbs energy ( $G^E$ ) for a binary mixture is defined by

$$G^E = RT \sum x_i \ln \gamma_i \quad (9)$$

The experimental results from this work for the system EA + mC6 at 20 kPa are plotted in Figure 5 with previously published data. The relative volatilities ( $\alpha_{12}$ ) and absolute volatilities ( $K_1$ ) of EA from this work and from the literature are also plotted and compared with values calculated with the NRTL model, as suggested by Mathias<sup>68,69</sup> to evaluate VLE data obtained by indirect concentration measurements.



**Figure 5.** Isobaric VLE of the binary system EA (1) + mC6 (2) at 20 kPa. (a)  $T_{xy}$  diagram. Solid lines: NRTL model; dashed lines: UNIFAC. (b)  $y_1$ - $x_1$  chart. (c) Relative volatilities. Solid line:

NRTL model; dashed lines:  $\pm 5\%$  deviations. (d) Percent errors of NRTL model  $K_1$ -values.  $\oplus$ : data from this work;  $\circ$ : Zhao et al.<sup>22</sup>;  $\blacktriangle$  Gmehling and Böltz<sup>24</sup> azeotropic point.

The  $T_{xy}$  diagram shown in Figure 5 (a) does not allow to compare the measured VLE data to those reported by Zhao et al.<sup>22</sup> since the boiling point of mC6 at 20 kPa reported by Zhao differs noticeably (of roughly 0.5 K) from the one measured in this work and from most of the literature data. Yet, when  $y_1$  is plotted against  $x_1$  (see Figure 5 (b)), a good agreement can be observed between the equilibrium compositions reported by Zhao and those from this work. Moreover, the data measured near the azeotropic point are consistent with the azeotropic coordinates reported by Gmehling and Böltz<sup>24</sup> at 20.15 kPa. Indeed,  $T_{az} = 307.05$  K and  $x_{1,az} = y_{1,az} = 0.8215$  were found by Gmehling whereas  $T_{az}$  and  $x_{1,az}$  for our data were estimated to be 307.24 K and 0.822.

Figure 5 indicates that the relative volatilities ( $\alpha_{12}$ ) obtained from our data are in agreement with the NRTL model within  $\pm 5\%$  deviation (average deviation = 1.7%; maximum deviation = 3.6%), whereas deviations in the  $K$ -value of EA do not exceed 2.5% (average deviation = 0.7%). Figure 5 also illustrates that the data reported by Zhao present an uncertainty that is slightly higher than those reported in this work. The average deviation of the VLE data set measured by Zhao is 1.5% for the  $K$ -value of EA and 4.2% for the relative volatilities.

### 3.4. VLE of the Binary System mC5 (1) + EA (2)

The VLE of the binary system mC5 + EA was measured at 25, 50 and 101.3 kPa using the experimental method previously described for the system EA + mC6 at 20 kPa. Considering the non-ideality of the vapor phase, activity coefficients derived from VLE data were estimated through the method outlined in section 3.3. (virial EOS and Tsonopoulos correlation). Table 8 lists the experimentally determined VLE data for the binary mixture mC5 + EA. The measured density values of the liquid and condensed vapor phases are listed in Table S4 (Supporting Information).

Experimental VLE data are plotted in Figure 6 with isobaric phase diagrams (left graphs). Activity coefficients are also plotted in the figure (right graphs).

**Table 8. Experimental Isobaric Vapor-Liquid Equilibrium Data for the Methylcyclopentane (1) – Ethyl Acetate (2) System at  $p = 25, 50$  and  $101.3$  kPa <sup>a</sup>**

$T$ /K	$x_1$ /mol·mol <sup>-1</sup>	$y_1$ /mol·mol <sup>-1</sup>	$\gamma_1$	$\gamma_2$	$G^E/RT$
<b><math>p = 25</math> kPa</b>					
313.12	0.000	0.000		1.000	0.000
311.55	0.025	0.087	2.775	1.001	0.027
309.90	0.055	0.173	2.670	1.004	0.058
308.53	0.088	0.245	2.491	1.009	0.088
307.26	0.127	0.313	2.317	1.014	0.119
306.04	0.175	0.376	2.119	1.029	0.155
305.33	0.213	0.412	1.962	1.050	0.182
304.37	0.275	0.463	1.774	1.087	0.218
303.85	0.320	0.496	1.668	1.114	0.237
302.74	0.474	0.582	1.382	1.257	0.274
302.50	0.532	0.609	1.301	1.337	0.276
302.37	0.589	0.635	1.231	1.430	0.269
302.28	0.642	0.661	1.180	1.532	0.259
302.27	0.695	0.687	1.133	1.662	0.242
302.35	0.742	0.713	1.098	1.795	0.220
302.49	0.783	0.741	1.074	1.915	0.197
303.00	0.860	0.801	1.035	2.231	0.142
303.20	0.886	0.822	1.023	2.429	0.121
303.81	0.930	0.877	1.013	2.662	0.081
304.51	0.962	0.927	1.006	2.823	0.046
305.58	1.000	1.000	1.000		0.000
<b><math>p = 50</math> kPa</b>					
330.23	0.000	0.000		1.000	0.000
326.96	0.066	0.171	2.337	1.005	0.060
326.70	0.070	0.182	2.366	1.006	0.065
325.68	0.097	0.234	2.270	1.009	0.087
324.81	0.126	0.277	2.130	1.017	0.110
324.00	0.156	0.323	2.061	1.018	0.128

323.08	0.199	0.370	1.910	1.035	0.157
322.24	0.248	0.419	1.786	1.052	0.182
321.53	0.306	0.459	1.624	1.092	0.209
320.97	0.362	0.496	1.513	1.132	0.229
320.16	0.485	0.566	1.325	1.249	0.251
319.94	0.541	0.595	1.258	1.320	0.251
319.85	0.582	0.616	1.214	1.380	0.247
319.82	0.619	0.634	1.176	1.445	0.240
319.81	0.683	0.670	1.126	1.568	0.224
319.99	0.763	0.717	1.071	1.788	0.190
320.10	0.791	0.735	1.055	1.891	0.175
320.33	0.825	0.762	1.040	2.011	0.154
320.63	0.857	0.792	1.029	2.127	0.132
320.89	0.882	0.817	1.022	2.246	0.114
321.66	0.927	0.873	1.010	2.448	0.075
323.66	1.000	1.000	1.000		0.000

**$p = 101.3$  kPa**

350.13	0.000	0.000		1.000	0.000
348.46	0.033	0.085	2.364	0.998	0.026
346.70	0.073	0.174	2.295	0.995	0.056
345.72	0.101	0.224	2.194	0.996	0.075
344.82	0.137	0.271	2.006	1.004	0.099
343.65	0.184	0.331	1.885	1.014	0.128
342.76	0.232	0.380	1.760	1.029	0.153
341.85	0.299	0.433	1.597	1.064	0.184
341.33	0.349	0.469	1.504	1.093	0.200
340.63	0.447	0.527	1.346	1.176	0.222
340.38	0.494	0.553	1.287	1.226	0.228
340.27	0.535	0.577	1.243	1.268	0.227
340.22	0.583	0.601	1.190	1.337	0.222
340.21	0.645	0.634	1.134	1.442	0.211
340.25	0.695	0.664	1.100	1.541	0.198
340.32	0.731	0.686	1.078	1.630	0.186
340.44	0.765	0.710	1.062	1.718	0.173
340.72	0.823	0.755	1.040	1.912	0.147
341.66	0.878	0.810	1.016	2.088	0.103
341.99	0.900	0.836	1.012	2.177	0.089

344.82

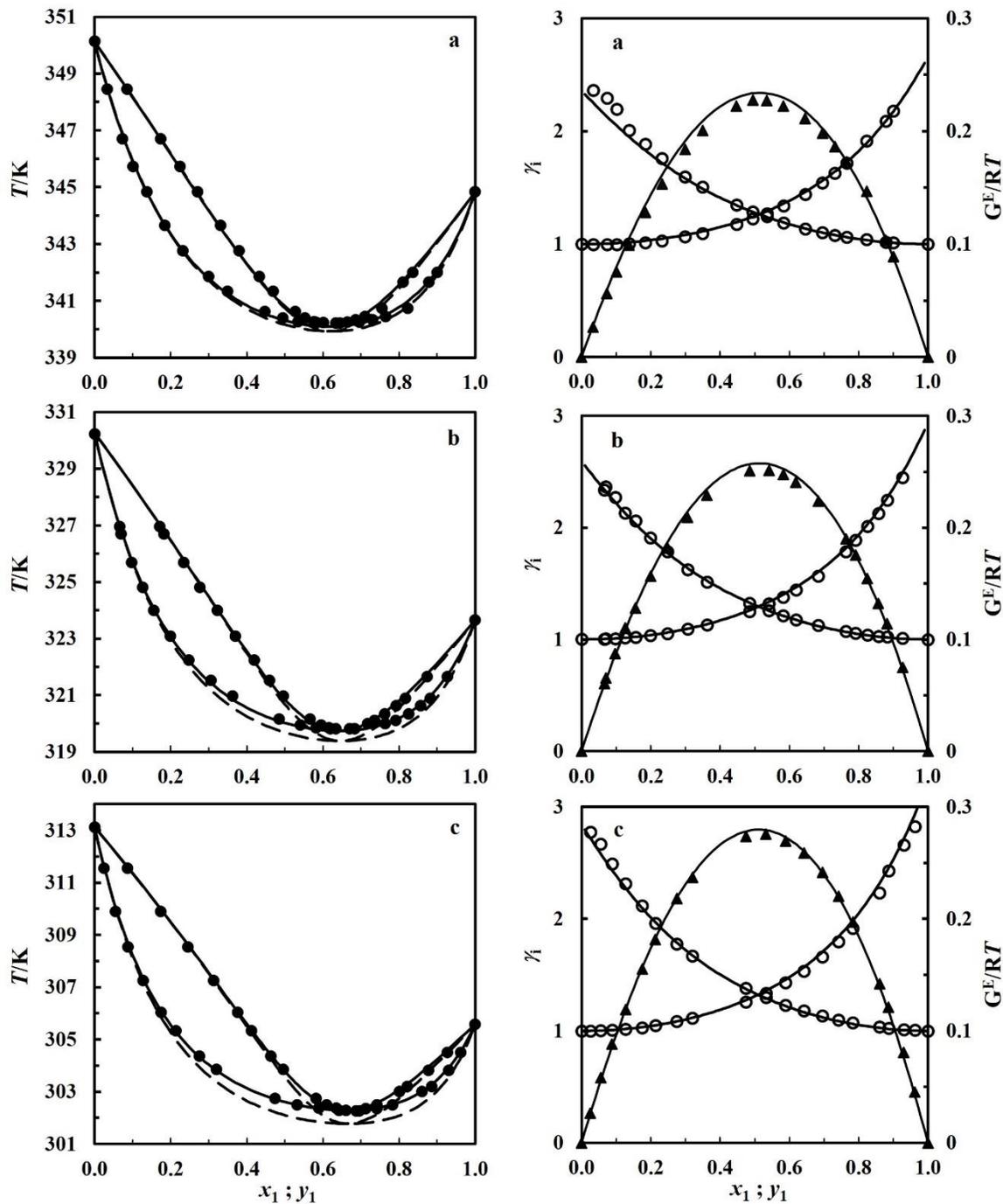
1.000

1.000

1.000

0.000

<sup>a</sup> Standard uncertainties  $u$  are  $u(p) = 0.3$  kPa,  $u(T) = 0.07$  K,  $u(x) = u(y) = 0.009$  mol·mol<sup>-1</sup>.  $T$ , equilibrium temperature,  $x_1$  and  $y_1$ , liquid and vapor-phase methylcyclopentane mole fraction, respectively.  $\gamma_i$ , activity coefficient,  $G^E/RT$ , dimensionless Gibbs function.



**Figure 6.** Isobaric phase diagrams (left charts) and plots of the experimental activity coefficients (right charts) of the binary system mC5 (1) + EA (2). Symbols: experimental data. Solid lines: curves calculated using the NRTL model. Dashed lines: bubble and dew curves predicted using UNIFAC. (a) 101.3 kPa. (b) 50 kPa. (c) 25 kPa.

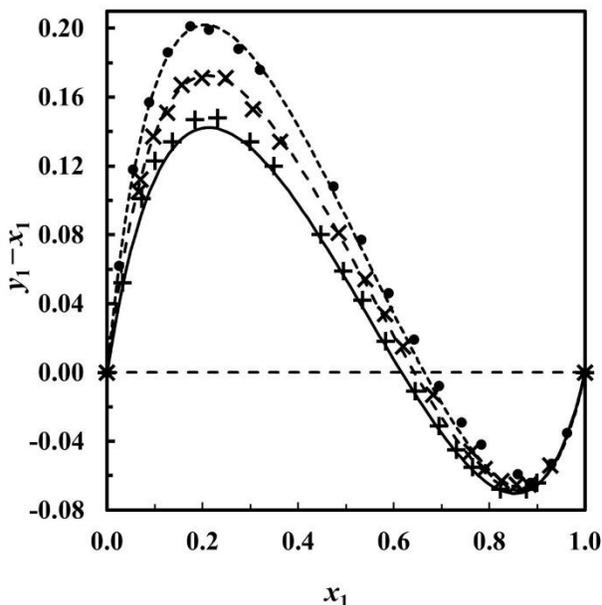
Additional plots with the experimental relative and absolute volatilities obtained for the system mC5 + EA are provided in Figure S2 of the Supporting Information and compared to the results of the NRTL model. Figure S2 confirms the accuracy of the experimental method with a relatively low scattering of the data. Among the 58 experimental data represented, only two present a %error in  $K_1$ -value higher than 2.5% and the average %error does not exceed 0.8%.

As illustrated by Figure 6, the binary system mC5 + EA presents significant positive deviations from ideality and a positive (pressure maximum, temperature minimum) azeotrope. This is a very common behavior, which is frequently encountered for binary mixtures of EA + alkanes and EA + naphthenic compounds (EA + cyclohexane, EA + methylcyclohexane). Figure 6 also demonstrates the capability of the NRTL model to correctly represent the phase equilibrium of the mixture. The azeotropic point is located in the naphthene-rich part of the isobaric diagram. The azeotropic coordinates were determined using the experimental data and linear interpolations and are reported in Table 9.

**Table 9. Experimental and Estimated With UNIFAC Azeotropic Temperature,  $T_{az}$ , Azeotropic Composition,  $x_{1,az}$ , and Difference Between the Pure Components Saturation Temperatures,  $\Delta T_{sat}$ , for the mC5 (1) + EA (2) system at  $p = 25, 50$  and  $101.3$  kPa**

$p$ /kPa	experimental		UNIFAC		
	$T_{az}$ /K	$x_{1,az}$ /mol·mol <sup>-1</sup>	$T_{az}$ /K	$x_{1,az}$ /mol·mol <sup>-1</sup>	$\Delta T_{sat}$ /K
25	302.27	0.679	301.78	0.665	7.54
50	319.81	0.653	319.38	0.646	6.57
101.3	340.21	0.621	339.93	0.621	5.31

Table 9 highlights a slight decrease of the azeotropic composition with an increase of the pressure. This appears clearly in Figure 7, in which  $y_1-x_1$  is plotted against  $x_1$  for the three pressures studied.



**Figure 7.**  $y_1-x_1$  plotted versus  $x_1$  for the system mC5 (1) + EA (2). ●: 25 kPa; ×: 50 kPa; +: 101.3 kPa. Continuous curves: curves calculated using the NRTL model.

This shifting of the azeotropic composition is a consequence of a decrease in the difference between the saturation temperatures ( $\Delta T_{\text{sat}}$ ) of the pure components. Indeed, between 25 and 101.3 kPa,  $\Delta T_{\text{sat}}$  decreases by 2.23 K, as reported in Table 9. Moreover, the respective position of the saturation curves at low pressure and the pure components' critical coordinates reveal that the studied binary system undoubtedly presents a Bancroft point near 800 kPa. The shifting of the azeotropic composition observed in this work at low pressure is likely to continue at higher pressures because of the Bancroft point.

## 4. Consistency Tests and VLE modeling

### 4.1. Thermodynamic Consistency Tests

Three different methods were employed for testing the consistency of the VLE data measured in this study. These methods are frequently used and are described elsewhere.<sup>70-73</sup>

The first is the Fredenslund test, as described by Wisniak et al.<sup>70</sup>. Legendre polynomials with four or five terms were used to fit the experimental data and the classical criterion  $\Delta y \leq 0.01$  was selected to validate the test.

Then, the Wisniak L-W test<sup>70,71</sup>, which combines a point test and an area test, was used with the following conditions:  $0.92 < L_i/W_i < 1.08$  and  $D < 3$ .

Finally, the area test described by Kojima et al.<sup>72</sup> and adopted by Kang et al.<sup>73</sup> for their quality assessment algorithm was employed in this study with the constraint  $|A^*| < 3$ . In this study, the area test was performed neglecting the heat of mixing effect (i.e. the  $\varepsilon$  term) and a third order polynomial equation was used for the integration of the experimental data.

The results of the above-mentioned consistency tests are provided in Table 10.

**Table 10. Results of the Consistency Tests**

Binary System	Fredenslund Test $\Delta y \leq 0.01$	L-W Point Test $0.92 < L_i/W_i < 1.08$	L-W Area Test $D < 3$	Kojima Area Test $ A^*  < 3$
EA + mC6 (20 kPa)	0.006	$0.992 < L_i/W_i < 1.078$	0.16	1.51
mC5 + EA (25 kPa)	0.003	$0.991 < L_i/W_i < 1.003$	0.29	1.87
mC5 + EA (50 kPa)	0.002	$0.976 < L_i/W_i < 0.984$	1.14	0.92
mC5 + EA (101.3 kPa)	0.005	$0.960 < L_i/W_i < 0.981$	1.85	2.02

The different data sets produced in this study pass the consistency tests. The experimental data provided in Tables 7 and 8 can thus be considered accurate and consistent.

## 4.2. VLE Data Modeling

The NRTL model was chosen to correlate the measured data. The equation involving the NRTL binary interaction parameters regressed in this work is

$$\tau_{ij} = \frac{g_{ij} - g_{ji}}{RT} = \frac{A_{ij}^0 + A_{ij}^T(T - 273.15)}{RT} \quad (9)$$

The interaction parameters were determined using the objective function (OF) detailed below

$$\text{OF} = \sum_{i=1}^N \left[ \left( \frac{x_1^{\text{exp}} - x_1^{\text{calc}}}{\sigma_x} \right)^2 + \left( \frac{y_1^{\text{exp}} - y_1^{\text{calc}}}{\sigma_y} \right)^2 + \left( \frac{T^{\text{exp}} - T^{\text{calc}}}{\sigma_T} \right)^2 \right] \quad (10)$$

$N$  is the number of data points included in the data set and  $\sigma$  is the standard deviation of the data set. The OF was minimized using the generalized reduced gradient algorithm available in the Microsoft Excel Solver tool linked to the Simulis Thermodynamics package. The NRTL binary interaction parameters obtained are given in Table 11.

**Table 11. Regressed NRTL Binary Interaction Parameters for the EA + mC6 and mC5 + EA Binary Systems**

Binary System	$A_{12}^0$ /J·mol <sup>-1</sup>	$A_{21}^0$ /J·mol <sup>-1</sup>	$A_{12}^T$ /J·mol <sup>-1</sup> ·K <sup>-1</sup>	$A_{21}^T$ /J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\alpha_{12}^{\text{NRTL}}$
EA (1) + mC6 (2) <sup>a</sup>	1566.21	1870.81			0.47
mC5 (1) + EA (2) <sup>b</sup>	1902.93	1662.93	-0.913	-6.850	0.47

<sup>a</sup> Parameters regressed against data at  $p = 20$  kPa. <sup>b</sup> Parameters regressed against data at  $p = 25, 50$  and  $101.3$  kPa.

Only the temperature-independent NRTL interaction parameters were adjusted for the system EA + mC6, since only one set of experimental data (at 20 kPa) is reported here for this system. In contrast, the experimental data for the system mC5 + EA extend over approximately 50 K. Temperature-dependent interaction parameters were thus considered for this system and are reported in Table 11.

A default value of 0.3 is frequently used for the non-randomness parameter  $\alpha_{12}^{\text{NRTL}}$ . However, de Klerk and Schwarz<sup>74</sup> recently pointed out that, for certain types of binary VLE phase behavior (such as minimum temperature azeotropic binary systems), the larger value of 0.47 was

more suitable. The two values of 0.30 and 0.47 were thus tested and a  $\alpha_{12}^{\text{NRTL}} = 0.47$  was finally selected, as it allowed to obtain slightly better results than 0.3.

The average absolute deviations between the experimental data and the calculated values are listed in Table 12 for each data set. The NRTL model allows a very good description of the phase behavior of the studied systems.

**Table 12. Average Deviations in Vapor Phase Mole Fraction and Equilibrium Temperature Between Experimental Data and NRTL and UNIFAC Model Predictions**

Binary System Data Set	NRTL		UNIFAC (Dortmund)	
	$\Delta y$ /mol·mol <sup>-1</sup>	$\Delta T$ /K	$\Delta y$ /mol·mol <sup>-1</sup>	$\Delta T$ /K
EA + mC6 20 kPa	0.0033	0.05	0.0057	0.38
mC5 + EA 25 kPa	0.0042	0.05	0.0090	0.34
mC5 + EA 50 kPa	0.0026	0.06	0.0059	0.26
mC5 + EA 101.3 kPa	0.0034	0.08	0.0038	0.16

The modified UNIFAC (Dortmund) group contribution method<sup>34,35</sup> was also used to evaluate its predictive abilities. UNIFAC provides an adequate prediction at 101.3 kPa for the system mC5 + EA (see Figure 6 and Table 12) whereas slightly less accurate predictions are observed when the pressure decreases. The average deviation between the predicted and the experimental equilibrium temperatures does not exceed 0.16 K at 101.3 kPa but reaches 0.34 K at 25 kPa.

## 5. Conclusion

This study contains new experimental densities (from 288.15 K to 308.15 K at 0.1 MPa) and VLE data (from 25 to 101.3 kPa) for the binary system mC5 + EA. New experimental vapor pressures and densities for the pure components involved in this study (mC5, mC6 and EA) are also reported.

This study reveals that, similarly to the behavior of the system EA + mC6, interactions between mC5 and EA generate positive and marked excess molar volumes. The VLE experiments performed in this work highlight that the phase behavior of the mixture mC5 + EA is characterized by positive deviations from ideality and the existence of an azeotrope. The experimentally determined azeotropic composition moves from 0.679 at 25 kPa to 0.621 at 101.3 kPa. This shifting of the azeotrope is a consequence of a Bancroft point at a higher pressure.

The reported VLE data were found to be consistent and temperature-dependent NRTL parameters are given in the document, allowing a precise correlation of the experimental data.

The predictive UNIFAC (Dortmund) model was also tested. It gives satisfactory results at atmospheric pressure whereas discrepancies appear between experimental and predicted isobaric VLE data at 25 and 50 kPa.

## **Supporting Information**

Coefficients of the polynomial functions density (at 298.15 K) – composition; calibration curve analysis of the binary systems; Redlich-Kister parameters for the correlation of the excess molar volumes; Density values of the liquid and condensed vapor phases obtained for each isobaric VLE measurements; Experimental data additional plots (relative and absolute volatilities) related to the binary system mC5 + EA; Example of density uncertainty calculation.

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## **Notes**

The authors declare no competing financial interest.

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