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1 Phase equilibria of mixtures involving fatty acid ethyl esters and 2 fat alcohols between 4 and 27 kPa for bioproduct production

3
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12 **Abstract**

13 The aim of this paper is to bring valuable phase equilibria information for the design
14 and operation of biolubricant and related biofuel product processes. As a result, Vapor-Liquid
15 Equilibrium (VLE) measurements, at different temperatures, pressures and global
16 compositions, for the ternary systems [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol] and
17 [Ethanol + 1-Octanol + 1-Dodecanol], as well as a multicomponent system containing these
18 alcohols together with *Balanites aegyptiaca* fatty acid ethyl esters are reported for the first
19 time (data pressure and temperature ranges: 4394-26790 Pa, 306-423 K). The Dortmund
20 modified UNIFAC model showed very high accuracy in the prediction of these VLE, with
21 overall average absolute deviations on the liquid and vapor molar compositions of 0.007 and
22 0.0003 for the ternary systems, 0.003 and 0.006 for the multicomponent system.

23
24 **Keywords:** Vapor-liquid equilibria; Multicomponent systems; Ebulliometry; Dortmund
25 modified UNIFAC; Biodiesel; Biolubricants

26 **1. Introduction**

27 Biomass harnessing in accordance with the biorefinery and green circular economy
28 concepts to generate energy carriers and high value-added products from conversion
29 technologies satisfying the eco-design, eco-energy and eco-materials criteria is an essential
30 environmental, economic and social issue [1,2]. Production of biodiesel and biolubricants
31 from non-edible oilseed plants by reactive distillation using transesterification as conversion
32 route is such an illustration [2,3]. Indeed, first, this class of biomass does not bring about
33 indirect land use change and even often contributes to soil improvement (erosion prevention
34 or biofumigation). It also offers a wide range of applications beneficial for human and his
35 environment by using all the biomass (pharmaceuticals, feed, biopesticides...) [1,2,4].
36 Second, the other possible oil conversion routes into biolubricants (through estolide formation
37 or epoxidation followed by acetylation) are economically less favorable than
38 transesterification that can be used to produce both bioproducts successively (with biodiesel
39 being a precursor of biolubricants) [3,5,6]. Third, thanks to its intensification, reactive
40 distillation offers significant savings in terms of material and energy consumed and effluents
41 produced [2,7]. Lastly, besides reducing dependence on fossil resources and environmental
42 footprint thanks to their biodegradability, biodiesel and biolubricants also improve the
43 economic and social development of a country through employment opportunities and the
44 required education upstream [2,7,8].

45 Compared to the commonly commercialized methyl biodiesel, ethyl biodiesel has
46 better biodegradability, higher flash point, improved cold-flow properties and oxidation
47 stability, and lower emissions of NO_x, CO, and ultrafine particles [9,10]; not to mention the
48 possibility of integrating the ethanol fermentation industry into the production process of
49 biodiesel and biolubricants (by using ethanol and fusel oil respectively) [3,8]. Moreover,
50 biolubricants whose fatty acid group is esterified with long-chain alcohol such as 2-ethyl-1-

51 hexanol, 1-octanol, or even 1-dodecanol exhibit excellent lubricating characteristics,
52 especially for metalworking applications [2,3,5]. Non-edible oils with high amounts of oleic
53 and linoleic acids (30-40% each) and much lower level of linolenic acid, such as oils from
54 *Balanites aegyptiaca* (BA), cottonseeds, or Indian mustard seeds, are considered optimal for
55 producing biofuel and biolubricants exhibiting a good balance between thermal-oxidative
56 stability, viscosity and cold-flow properties [2,6,11].

57 Robust process simulation of biolubricants production from biodiesel requires
58 quantitative and reliable information about the vapor-liquid equilibria (VLE) of mixtures
59 containing alcohols and fatty acid esters, as well as the liquid-liquid and vapor-liquid-liquid
60 equilibria with the presence of glycerol, and eventually water, when dealing with the
61 preliminary biodiesel production step [7,12,13]. Nevertheless, despite the recently published
62 extensive work on phase equilibria involved in biodiesel production [7,13,14], VLE
63 information for the biolubricant production operating under low pressure is still lacking. As
64 an illustration, **Table 1** [12,15-20] gives an overview of the low-pressure VLE related to
65 biodiesel components that were published over the past 10 years. No similar information was
66 found for biolubricants.

67 Accordingly, this paper aims to provide complete experimental VLE data for mixtures
68 of relevance for the biolubricant and related biofuel industries. Besides, the predictive
69 capabilities of a thermodynamic model implemented in most commercial process simulators
70 have been evaluated over the investigated ternary and multicomponent mixtures, containing
71 BA oil ethyl esters (BAEEs) and/or fat alcohols, such as 2-ethyl-1-hexanol, 1-octanol, or 1-
72 dodecanol. It is shown that the phase equilibria behavior of the reaction mixture at the start of
73 the BAEE transesterification, leading to the BA oil biolubricant, can be accurately described.

74

75

76 **2. Material and Methods**

77

78 *2.1 Chemicals and BAEs production*

79 The description of the chemicals used in this study as internal standards, solvent, or
80 ternary system formulation is given in **Table 2**. The BAEs were produced in a batch stirred
81 tank reactor according to Nitièma-Yefanova et al. procedure ((i) two-stage transesterification
82 with intermediary addition of glycerol after 30 min of reaction, the whole carried out for 50
83 min at 35 °C and 1 atm, with 1.0 wt% potassium hydroxide as the catalyst and ethanol to oil
84 molar ratio equal to 8; (ii) dry-purification using 4 wt% of rice husk ash as adsorbent under 35
85 °C, for 20 min) [21,22]). Lastly, a vacuum distillation (180-200 °C; 10 mbar) was carried out
86 to obtain a high-grade BAE mixture (composition and details of the analysis given in
87 [Supplementary Material](#), respectively [SM1](#) and [SM2](#) [23]).

88

89 *2.2 VLE experiments and procedure*

90 The VLE experiments were carried out in an all-glass ebulliometer, operating between
91 1 and 100 kPa, with dynamic recirculation of the vapor and liquid phases helping to reach
92 more quickly the equilibrium conditions in addition to the Cottrell pump (model EEA 3000,
93 Pignat, France) [24]. Similar devices have proven to be performant for yielding VLE
94 measurements of high level [25,26]. A detailed description of the ebulliometer of which a
95 schematic diagram is provided in **Figure 1** is available in the paper by Muhammad et al. [12].
96 The uncertainties on the measured temperature and pressure are, respectively, ± 0.01 K and \pm
97 0.013 kPa (± 0.1 mmHg). These were determined, prior to any VLE experiment series, by
98 checking the calibration of the ebulliometer sensors using an external reference thermometer
99 and measuring the vapor pressure of ethanol, selected as a reference compound, over a wide
100 temperature range. The composition of the vapor and liquid phases were determined by gas-
101 chromatography coupled with a flame ionization detector (GC-FID 7820, Agilent

102 Technology, USA). Details of the equipment, operating conditions, and calibration are given
103 in **Supplementary Material (SM2) [23]**. All compositional analyzes were performed by
104 using three internal standards (one specific for the BAEs, one different for short, and another
105 for fat alcohols; **SM2**). Thus, for the GC-FID calibration, standard solutions of well-known
106 composition were prepared by weighing the components of the studied system (with ethyl
107 oleate as a surrogate of the BAEs), and the required IS(s). Performance of the GC-FID
108 calibration was then checked by analyzing the composition of supplementary standard
109 solutions and was used to estimate the mole fraction uncertainty: ± 0.002 for the ternary
110 systems, ± 0.004 for the multicomponent system.

111 Regarding the procedure for generating the VLE measurements, the liquid mixture of
112 well-known composition (prepared by weighing the required amounts of pure alcohols and/or
113 BAEs) was loaded into the ebulliometer until complete filling the reboiler (total liquid
114 volume poured: around 120 mL). After reaching the selected set-point pressure under
115 vigorous mixing, the heating power was adjusted to observe a satisfactory boiling: 1 drop per
116 second for the condensed vapor phase, a semi-continuous flowrate for the liquid phase. When
117 the equilibrium state was reached (commonly after 1 to 1.5 h of recirculating for the ternary
118 mixtures, 3 to 3.5 h for the multicomponent mixtures), the temperature and pressure were
119 noted down, and samples were collected for quantification, starting first with the global
120 mixture (via the mixing cell septum) and then dealing with simultaneously the liquid and
121 condensed vapor phases (via the tubes placed in the sampling ports). The equilibrium state
122 was identified when steady temperature and pressure were observed for the selected set-point
123 pressure, leading then to assume that the composition of both the liquid and vapor phases
124 were also constant. After withdrawing for GC-FID analysis the required amount of liquid
125 from the collected samples, these were re-introduced into the ebulliometer (via the mixing cell
126 septum) to keep approximatively the same mixture global composition. Subsequently, this

127 procedure was repeated for higher set-point pressures by adjusting both the heating power and
128 the total amount of liquid inside the ebulliometer to maintain a satisfactory boiling. While the
129 heating power required to be increased, a supplementary volume of liquid needed to be
130 introduced in the ebulliometer (allowing thus operating at nearly constant volume during
131 subsequent experiments). This additional liquid (introduced via the loading funnel) was: (i)
132 for the ternary systems, the mixture initially loaded in the ebulliometer (or the C8-alcohol for
133 the highest pressures); (ii) for the multicomponent system, the ternary mixture [Ethanol + 2-
134 Ethyl-1-hexanol + 1-Dodecanol] of well-known composition (in order to induce a significant
135 change in the global composition of the investigated system, without nonetheless perturbing
136 the equilibrium state of the ebulliometer radically).

137

138 *2.3 VLE modeling*

139 Given the large number of components present in the reaction mixture during the
140 transesterification of biodiesel into biolubricant (over 10 typically), the resulting lack of
141 information regarding the VLE data for each of the binaries involved, the highly non-ideal
142 thermodynamic behavior of these mixtures, and the operating conditions of the production
143 process (low pressure), the excess Gibbs energy (G^E) models based on the group contribution
144 (GC) concept are the most appropriate. Indeed, cubic equations of state with GC-estimated
145 binary interaction parameters were applied successfully to systems involving molecules similar
146 to biodiesel or biolubricants, but under moderate to high-pressures with supercritical carbon
147 dioxide [27-29]. Among the G^E -GC approaches, namely original UNIFAC [30] and its
148 variants (Lyngby modified UNIFAC [31], Dortmund modified UNIFAC [32-34], linear
149 UNIFAC [35]), the regularly updated Dortmund modified UNIFAC model [32-34] was
150 selected as it has yielded excellent VLE predictions for complex mixtures involving ethyl

151 esters and alcohols [12,14,36]. Accordingly, the implicit γ - ϕ approach leads to express the
 152 vapor-liquid equilibrium condition by:

$$153 \quad x_i \cdot \gamma_i(T, x) \cdot P_i^s(T) = P \cdot y_i \cdot \mathfrak{S}_i(T, P, y) \quad (1a)$$

$$154 \quad \text{with } \mathfrak{S}_i(T, P, y) = \frac{\phi_i^V(T, P, y)}{\phi_i^*(T, P_i^s)} \cdot \exp\left(\frac{1}{RT} \cdot \int_P^{P_i^s} v_{i,L}^*(T, P) dP\right). \quad (1b)$$

155 In this expression, x_i (y_i) refers to the mole fraction of component i in the liquid (vapor)
 156 phase; γ_i (ϕ_i^V) denotes the activity (fugacity) coefficient of component i in the liquid (vapor)
 157 phase of composition x (y), temperature T and pressure P ; P_i^s , ϕ_i^* and $v_{i,L}^*$ are specific to the
 158 pure component i and refer respectively to its vapor pressure, fugacity coefficient, and liquid
 159 molar volume. Being concerned with low pressure VLEs of mixtures with no molecular
 160 association in the vapor phase, the latter was assumed perfect (so $\phi_i^*(T, P_i^s) = 1$ and
 161 $\phi_i^V(T, P, y) = 1$), leading to set $\mathfrak{S}_i(T, P, y) = 1$. While the activity coefficients γ_i were
 162 estimated by the Dortmund modified UNIFAC model (UNIFAC-Do), the vapor pressures P_i^s
 163 were evaluated according to the following equation:

$$164 \quad \ln(P_i^s / Pa) = A_i + \frac{B_i}{(T / K)} + C_i \cdot \ln(T / K) + D_i \cdot (T / K)^{E_i} \quad (2)$$

165 of which values of coefficients A_i to E_i , were taken from the DIPPR database [37] for all the
 166 pure components investigated. Values of these coefficient together with the component
 167 decomposition into UNIFAC structural groups are given in **Supplementary Material (SM3**
 168 **and SM4**, respectively; [30,32-34,38,39]). Thus, it was possible to calculate the compositions
 169 of the liquid and vapor phases at a given temperature, pressure, and global composition for
 170 each investigated mixture.

171

172

173 3. Results and Discussion

174

175 The comparisons between the experimental and estimated values of the vapor and
176 liquid phase compositions (at a given temperature, pressure, and global composition of the
177 considered mixture) were performed in terms of various deviations described in **Table 3**.

178

179 3.1 Ternary systems

180 For each of the two ternary systems investigated, five VLE data sets were measured
181 for pressure and temperature ranging respectively: (i) from 13574 to 26790 Pa and 317 to 332
182 K regarding system [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol]; (ii) from 7051 to 23657 Pa
183 and 306 to 332 K regarding system [Ethanol + 1-Octanol + 1-Dodecanol]. This information,
184 as well as the relating predictions obtained with the UNIFAC-Do model, were gathered in
185 **Tables 4 and 5**, and **Figure 2**, the last displaying additionally the deviations per component (AAD_i)
186 and per data set (AAD_k).

187 Not surprisingly, on the basis of the accuracy depicted by the UNIFAC-Do model for
188 the binaries [Ethanol + 2-Ethyl-1-hexanol] and [Ethanol + 1-Octanol] (**Supplementary**
189 **Material, SM4 [30,32-34,38,39]**), predictions obtained for both ternary systems are in very
190 good agreement with the experimental data ($AAD_k(x) \leq 0.012$; **Figure 2**); even excellent
191 regarding the vapor phase for which the observed deviations are much lower than the
192 experimental uncertainty (i.e., 0.001). **Figure 2** also shows that the deviations on the liquid
193 phase composition are somewhat randomly distributed, although the poorest results are
194 obtained for ethanol while remaining acceptable ($AAD_i(x) \leq 0.015$). Globally, the deviations
195 obtained for the two ternary systems are $AAD_{overall}(x) = 0.007$ and $AAD_{overall}(y) = 0.0003$,
196 which is remarkable considering the structural specificities of these mixtures, both on the

197 entropic and enthalpic aspects (molecules different in shape and size, with additionally cross-
198 associations).

199

200 3.2. Multicomponent systems

201 The investigated system contains 10 components, i.e., the BAEEs with ethanol, 2-
202 ethyl-1-hexanol, 1-octanol, and 1-dodecanol. In total, 15 VLE data sets were measured for
203 this system at various global compositions, for pressures and temperatures ranging from 4394
204 to 10270 Pa and 360 to 423 K, respectively. These measurements, together with the
205 corresponding predictions obtained with the UNIFAC-Do model, were gathered in **Table 6**,
206 and **Figure 3** displays additionally the deviations per component (AAD_i) and per data set (AAD_k).
207 More pronounced deviations are observed compared to the ternary systems,
208 particularly for the vapor phase compositions, which are now predicted by the UNIFAC-Do
209 model with much less accuracy than the liquid phase compositions. Nonetheless, the overall
210 deviations remain very acceptable for both phases: $AAD_{overall}(x) = 0.003$ and
211 $AAD_{overall}(y) = 0.006$. These results are likely due to the large amounts of alcohols in the
212 vapor phase for these multicomponent mixtures, particularly ethanol, which was already the
213 poorest represented among the substances studied in the ternary systems previously
214 investigated (here for ethanol: $AAD_i(y) = 0.05 \max$). Furthermore, in the liquid phase, the
215 cross-association involved by the alcohols might be mitigated by the presence of the BAEEs,
216 although the mixture studied here also contains a structural complexity on the entropic aspect
217 with molecules differing in size and shape. These two aspects can be realized looking at the
218 activity coefficients in the **SM5** section (**Supplementary Material**) [32-34]. Moreover, the
219 deviations on the liquid and vapor phase compositions are rather randomly distributed,
220 particularly at the lowest pressure (4394 Pa), for which the very good prediction results are
221 worthy of being stressed ($AAD_k(x) \leq 0.002$ and $AAD_k(y) \leq 0.005$, for all data sets measured at

222 4394 Pa). Lastly, let mention that, in that case, the assumption of the ideal liquid solution
223 yields rougher predictions of the liquid and vapor phase compositions ($AAD_k(x)$ and
224 $AAD_k(y)$ up to 0.004 and 0.008, respectively), with a deviation on the vapor mole fraction
225 $AAD_i(y)$ up to four times larger for ethanol (which agrees with the bad results obtained when
226 assuming the ideal liquid solution for the investigated ternaries involving alcohols;
227 [Supplementary Material, SM5](#)). At higher temperatures, the activity coefficients are closer
228 to one, and consequently, for the system [Alcohols + BAEs], better predictions are found
229 assuming ideality.

230

231 **4. Conclusions**

232

233 VLE measurements, at different temperatures, pressures, and global compositions, for
234 the ternary systems [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol] and [Ethanol + 1-Octanol +
235 1-Dodecanol], as well a multicomponent system containing these alcohols together with
236 *Balanites aegyptiaca* fatty acid ethyl esters are reported for the first time. The Dortmund
237 modified UNIFAC model showed very high accuracy in the prediction of these VLE, with
238 overall average absolute deviations on the liquid and vapor molar compositions of 0.007 and
239 0.0003, respectively, for the ternary systems, and 0.003 and 0.006 for the multicomponent
240 systems. The VLE experiments and modelling carried out in this work bring valuable
241 information for the design and operation of bioproduct production processes under low
242 pressures.

243

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249

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- 389

390

TABLES

391

392 **Table 1.** Overview of the low-pressure VLE information related to biodiesel components

393 published over the past 10 years (no similar information was found for biolubricants).

System	T/K range	P/MPa range	Experimental technique	Modeling information	Ref.
Ethanol + Ethyl stearate	313-419	0.017-0.098	Dynamic ebulliometry (recirculation	NRTL, UNIQUAC	[15]
Ethanol + Ethyl palmitate	309-422	0.0150-9.300	of only the vapor phase)	and UNIFAC-Do	
Ethyl palmitate + Ethyl stearate	502-520	0.0053	Differential scanning calorimetry	Wilson, NRTL	[16]
Ethyl palmitate + Ethyl oleate	502-537	0.0053; 0.0093		and UNIQUAC	
Ethyl palmitate + Ethyl linoleate	514-537	0.0093			
Ethyl myristate + Ethyl palmitate	420-443	0.0005;	Dynamic ebulliometry (recirculation	NRTL, original	[17]
	435-458	0.0010;	of both the vapor and liquid phases)	UNIFAC,	
	444-468	0.0015		UNIFAC-Do	
Methyl myristate + Methyl linoleate	467-511	0.00533;	Differential scanning calorimetry	NRTL, UNIQUAC	[18]
Methyl palmitate + Methyl linoleate	491-511	0.00533			
<i>Jatropha</i> ethyl esters ^a + Ethanol + Water	296-342	0.0067-0.0667;	Dynamic ebulliometry (recirculation	UNIQUAC	[19]
<i>Jatropha</i> ethyl esters ^a + Ethanol + Water	283-329	0.0067-0.0667;	of only the vapor phase)		
Soybean methyl esters ^a + Methanol	283-365	0.0067-0.0667;	Dynamic ebulliometry (recirculation	UNIQUAC	[20]
Soybean ethyl esters ^a + Ethanol	295-386	0.0067-0.0667;	of only the vapor phase)		
Soybean methyl esters ^a + Methanol + Glycerol	283-328	0.0067-0.0667;			
Soybean ethyl esters ^a + Ethanol + Glycerol	296-341	0.0067-0.0667			
1-Octanol + 1-Dodecanol + <i>Balanites</i>	448-471	0.0080-0.0120	Dynamic ebulliometry (recirculation	CPA, NRTL,	[12]
<i>aegyptiaca</i> ethyl esters (Ethyl- palmitate +			of both the vapor and liquid phases)	UNIFAC-Do	
Ethyl stearate + Ethyl oleate + Ethyl cis-					
vaccenate + Ethyl linoleate + Ethyl arachidate)					

394 ^a The mixture of fatty acid ethyl esters was considered as a pseudo-pure component, both for

395 the experimental study and modeling.

396

397 **Table 2.** Description of the chemicals used in this study (as internal standards, solvent or for
 398 ternary systems synthesis).

Chemical name	CAS	Source	Purity/mass %
Ethanol	64-17-5	Sigma Aldrich	≥ 99.8
1-Butanol	71-36-3	Fluka	≥ 99.5
2-Ethyl-1-hexanol	104-76-7	Sigma Aldrich	≥ 99.0
1-Octanol	111-87-5	Sigma Aldrich	≥ 99
1-Decanol	112-30-1	Fluka	≥ 99.5
1-Dodecanol	112-53-8	Sigma Aldrich	≥ 98
Ethyl oleate	111-62-6	Sigma Aldrich	≥ 98
Methyl heptadecanoate	1731-92-6	Fluka	≥ 99
n-Heptane	142-82-5	Sigma Aldrich	≥ 99

399

400 **Table 3.** Expressions of the deviations used in this work.

Definition	Expression	
<ul style="list-style-type: none"> • Deviation between the experimental and calculated liquid (vapor) mole fractions of component i for the data set k 	$\Delta x_i = x_i^{k,exp} - x_i^{k,cal}$	1a
	$(\Delta y_i = y_i^{k,exp} - y_i^{k,cal})$	1b
<ul style="list-style-type: none"> • Average absolute deviation between the experimental and calculated liquid (vapor) mole fractions for component i over all the N_{sets} data sets 	$AAD_i(x) = \sum_{k=1}^{N_{sets}} \Delta x_i / N_{sets}$	2a
	$(AAD_i(y) = \sum_{k=1}^{N_{sets}} \Delta y_i / N_{sets})$	2b
<ul style="list-style-type: none"> • Average absolute deviation between the experimental and calculated liquid (vapor) mole fractions for the data set k over all the N_C components of the mixture 	$AAD_k(x) = \sum_{i=1}^{N_C} \Delta x_i / N_C$	3a
	$(AAD_k(y) = \sum_{i=1}^{N_C} \Delta y_i / N_C)$	3b
<ul style="list-style-type: none"> • Overall average absolute deviation between the experimental and calculated liquid (vapor) mole fractions over all the mixture N_C components and all the N_{sets} data sets 	$AAD_{overall}(x) = \sum_{k=1}^{N_{sets}} \left(\sum_{i=1}^{N_C} \Delta x_i / N_C \right) / N_{sets}$	4a
	$(AAD_{overall}(y) = \sum_{k=1}^{N_{sets}} \left(\sum_{i=1}^{N_C} \Delta y_i / N_C \right) / N_{sets})$	4b

401

402 **Table 4.** Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 2-Ethyl-1-hexanol (2) +
403 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and
404 vapor (y) phases in equilibrium, as well as the deviations between the experimental and predicted mole fractions of each component in the liquid
405 (vapor) phase Δx_i (Δy_i) as defined in **Table 3**; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.002$).

Component	Set 1 P (Pa) = 13574; T (K) = 317.48					Set 2 P (Pa) = 16878; T (K) = 321.98				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.5917	0.5579	0.9972	0.0088	-0.0003	0.5895	0.5627	0.9969	0.0147	-0.0002
2-Ethyl-1-hexanol	0.2727	0.2901	0.0028	-0.0109	0.0003	0.2749	0.2927	0.0031	-0.0099	0.0002
1-Dodecanol	0.1356	0.1520	0.0000	0.0022	0.0000	0.1356	0.1446	0.0000	-0.0048	0.0000
Component	Set 3 P (Pa) = 20182; T (K) = 325.67					Set 4 P (Pa) = 23486; T (K) = 328.97				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.5847	0.5450	0.9965	-0.0056	-0.0003	0.5843	0.5452	0.9962	-0.0050	-0.0002
2-Ethyl-1-hexanol	0.2783	0.3047	0.0035	0.0037	0.0003	0.2786	0.3046	0.0038	0.0033	0.0003
1-Dodecanol	0.1370	0.1503	0.0000	0.0019	0.0000	0.1371	0.1502	0.0000	0.0018	0.0000
Component	Set 5 P (Pa) = 26790; T (K) = 332.06									
	z_i	x_i	y_i	Δx_i	Δy_i					
Ethanol	0.5753	0.5415	0.9960	-0.0039	0.0000					
2-Ethyl-1-hexanol	0.2845	0.3070	0.0040	0.0026	0.0001					
1-Dodecanol	0.1401	0.1515	0.0000	0.0014	0.0000					

406

407

408 **Table 5.** Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 1-Octanol (2) +
409 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and
410 vapor (y) phases in equilibrium, as well as the deviations between the experimental and predicted mole fractions of each component in the liquid
411 (vapor) phase Δx_i (Δy_i) as defined in **Table 3**; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.002$).

Component	Set 1 P (Pa) = 7051; T (K) = 306.44					Set 2 P (Pa) = 10372; T (K) = 313.74				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.5488	0.4881	0.9989	-0.0096	-0.0001	0.5478	0.5091	0.9988	0.0097	0.0002
1-Octanol	0.2777	0.3152	0.0011	0.0062	0.0001	0.2780	0.3006	0.0012	-0.0071	-0.0001
1-Dodecanol	0.1736	0.1967	0.0000	0.0034	0.0000	0.1742	0.1903	0.0000	-0.0026	0.0000
Component	Set 3 P (Pa) = 13693; T (K) = 319.34					Set 4 P (Pa) = 17014; T (K) = 323.64				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.5437	0.4797	0.9988	-0.0187	0.0004	0.5374	0.4889	0.9989	-0.0154	0.0008
1-Octanol	0.2804	0.3198	0.0012	0.0116	-0.0004	0.2843	0.3101	0.0011	0.0055	-0.0007
1-Dodecanol	0.1759	0.2005	0.0000	0.0071	0.0000	0.1783	0.2010	0.0000	0.0099	0.0000
Component	Set 5 P (Pa) = 23657; T (K) = 332.04									
	z_i	x_i	y_i	Δx_i	Δy_i					
Ethanol	0.5043	0.4552	0.9985	-0.0187	0.0012					
1-Octanol	0.3049	0.3350	0.0015	0.0115	-0.0012					
1-Dodecanol	0.1908	0.2098	0.0000	0.0072	0.0000					

412

413

414 **Table 6.** Experimental VLE data and predictions by the UNIFAC-Do model for the multicomponent systems [Alcohols + BAEs] (are given at
415 different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and vapor (y) phases in equilibrium,
416 as well as the deviations between the experimental and predicted mole fractions of each component in the liquid (vapor) phase Δx_i (Δy_i) as
417 defined in **Table 3**; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.004$).

Component	Set 1 P (Pa) = 10270; T (K) = 416.93					Set 2 P (Pa) = 10270; T (K) = 418.73				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0178	0.0058	0.2164	0.0038	0.0414	0.0167	0.0000	0.1987	-0.0017	0.0463
2-Ethyl-1-hexanol	0.2624	0.2381	0.6174	0.0138	-0.0238	0.2570	0.2281	0.6324	0.0146	-0.0175
1-Octanol	0.0535	0.0505	0.0947	0.0014	-0.0026	0.0530	0.0492	0.0951	0.0015	-0.0060
1-Dodecanol	0.4211	0.4390	0.0710	-0.0159	-0.0132	0.4310	0.4475	0.0733	-0.0208	-0.0208
Ethyl Palmitate	0.0397	0.0419	0.0004	-0.0017	-0.0001	0.0409	0.0428	0.0005	-0.0025	-0.0002
Ethyl Stearate	0.0297	0.0313	0.0000	-0.0013	-0.0002	0.0305	0.0320	0.0000	-0.0018	-0.0002
Ethyl Oleate	0.0786	0.0834	0.0000	-0.0031	-0.0008	0.0802	0.0853	0.0000	-0.0037	-0.0009
Ethyl Cis-Vaccenate	0.0019	0.0020	0.0000	-0.0001	0.0000	0.0019	0.0020	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0946	0.1071	0.0000	0.0031	-0.0007	0.0880	0.1121	0.0000	0.0144	-0.0008
Ethyl Arachidate	0.0008	0.0008	0.0000	-0.0001	0.0000	0.0008	0.0008	0.0000	-0.0001	0.0000

Component	Set 3 P (Pa) = 10270; T (K) = 420.93					Set 4 P (Pa) = 10270; T (K) = 421.93				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0167	0.0000	0.1601	-0.0014	0.0281	0.0149	0.0000	0.1586	-0.0013	0.0331
2-Ethyl-1-hexanol	0.2523	0.2156	0.6578	0.0168	0.0142	0.2424	0.2020	0.6419	0.0102	-0.0116
1-Octanol	0.0524	0.0473	0.0993	0.0018	-0.0054	0.0510	0.0453	0.1047	0.0010	-0.0011
1-Dodecanol	0.4368	0.4576	0.0823	-0.0232	-0.0245	0.4410	0.4655	0.0942	-0.0160	-0.0178
Ethyl Palmitate	0.0415	0.0441	0.0005	-0.0029	-0.0003	0.0420	0.0451	0.0006	-0.0020	-0.0002
Ethyl Stearate	0.0310	0.0330	0.0000	-0.0021	-0.0002	0.0314	0.0337	0.0000	-0.0015	-0.0003
Ethyl Oleate	0.0813	0.0877	0.0000	-0.0043	-0.0010	0.0826	0.0897	0.0000	-0.0029	-0.0011
Ethyl Cis-Vaccenate	0.0019	0.0021	0.0000	-0.0001	0.0000	0.0020	0.0021	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0851	0.1117	0.0000	0.0153	-0.0008	0.0919	0.1157	0.0000	0.0126	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	-0.0001	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

Component	Set 5 P (Pa) = 10270; T (K) = 423.02					Set 6 P (Pa) = 6966; T (K) = 360.02				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0140	0.0000	0.1303	-0.0012	0.0151	0.0728	0.0524	0.9429	0.0191	0.0521
2-Ethyl-1-hexanol	0.2381	0.1944	0.6514	0.0092	-0.0035	0.2781	0.2830	0.0509	-0.0041	-0.0412
1-Octanol	0.0504	0.0441	0.1088	0.0009	0.0014	0.0544	0.0559	0.0054	-0.0006	-0.0064
1-Dodecanol	0.4458	0.4711	0.1087	-0.0161	-0.0103	0.3854	0.3986	0.0008	-0.0051	-0.0045
Ethyl Palmitate	0.0426	0.0459	0.0007	-0.0020	-0.0001	0.0360	0.0372	0.0000	-0.0005	0.0000
Ethyl Stearate	0.0318	0.0343	0.0000	-0.0015	-0.0003	0.0268	0.0278	0.0000	-0.0003	0.0000
Ethyl Oleate	0.0836	0.0912	0.0000	-0.0028	-0.0011	0.0703	0.0724	0.0000	-0.0013	0.0000
Ethyl Cis-Vaccenate	0.0020	0.0022	0.0000	-0.0001	0.0000	0.0017	0.0017	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0909	0.1159	0.0000	0.0136	-0.0010	0.0738	0.0702	0.0000	-0.0071	0.0000
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0007	0.0007	0.0000	0.0000	0.0000

Component	Set 7 P (Pa) = 6966; T (K) = 377.29					Set 8 P (Pa) = 6966; T (K) = 404.65				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0509	0.0223	0.7739	0.0068	0.0490	0.0158	0.0000	0.2244	-0.0019	0.0401
2-Ethyl-1-hexanol	0.2860	0.2890	0.2002	0.0001	-0.0302	0.2759	0.2463	0.6252	0.0014	-0.0260
1-Octanol	0.0560	0.0569	0.0206	-0.0005	-0.0087	0.0557	0.0518	0.0921	-0.0007	-0.0020
1-Dodecanol	0.3975	0.3989	0.0053	-0.0187	-0.0098	0.4220	0.4374	0.0579	-0.0138	-0.0108
Ethyl Palmitate	0.0371	0.0371	0.0000	-0.0020	-0.0001	0.0398	0.0415	0.0003	-0.0015	-0.0001
Ethyl Stearate	0.0277	0.0276	0.0000	-0.0015	0.0000	0.0300	0.0310	0.0000	-0.0014	-0.0001
Ethyl Oleate	0.0721	0.0735	0.0000	-0.0024	-0.0001	0.0777	0.0826	0.0000	-0.0015	-0.0006
Ethyl Cis-Vaccenate	0.0017	0.0018	0.0000	0.0000	0.0000	0.0018	0.0020	0.0000	0.0000	0.0000
Ethyl Linoleate	0.0703	0.0922	0.0000	0.0183	-0.0001	0.0805	0.1066	0.0000	0.0195	-0.0004
Ethyl Arachidate	0.0007	0.0007	0.0000	0.0000	0.0000	0.0008	0.0008	0.0000	-0.0001	0.0000

419

420

421 **Table 6.** Continued.

Component	Set 9 P (Pa) = 6966; T (K) = 404.85					Set 10 P (Pa) = 6966; T (K) = 405.95				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0160	0.0078	0.2191	0.0061	0.0421	0.0171	0.0000	0.1996	-0.0018	0.0216
2-Ethyl-1-hexanol	0.2787	0.2511	0.6321	0.0060	-0.0262	0.2683	0.2382	0.6404	0.0062	-0.0091
1-Octanol	0.0557	0.0523	0.0924	0.0001	-0.0022	0.0546	0.0508	0.0965	0.0002	0.0006
1-Dodecanol	0.4141	0.4308	0.0560	-0.0137	-0.0124	0.4274	0.4447	0.0631	-0.0161	-0.0117
Ethyl Palmitate	0.0390	0.0408	0.0003	-0.0016	-0.0001	0.0404	0.0424	0.0004	-0.0018	-0.0001
Ethyl Stearate	0.0296	0.0305	0.0000	-0.0017	-0.0001	0.0302	0.0317	0.0000	-0.0014	-0.0001
Ethyl Oleate	0.0768	0.0810	0.0000	-0.0025	-0.0006	0.0789	0.0841	0.0000	-0.0022	-0.0006
Ethyl Cis-Vaccenate	0.0018	0.0019	0.0000	0.0000	0.0000	0.0019	0.0020	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0876	0.1029	0.0000	0.0076	-0.0005	0.0806	0.1053	0.0000	0.0170	-0.0005
Ethyl Arachidate	0.0008	0.0008	0.0000	-0.0001	0.0000	0.0008	0.0008	0.0000	0.0000	0.0000

Component	Set 11 P (Pa) = 4394; T (K) = 400.12					Set 12 P (Pa) = 4394; T (K) = 402.92				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0216	0.0050	0.1477	0.0039	-0.0137	0.0040	0.0000	0.0416	-0.0003	-0.0056
2-Ethyl-1-hexanol	0.2473	0.1767	0.6839	-0.0093	0.0182	0.2268	0.1880	0.7500	0.0050	0.0155
1-Octanol	0.0378	0.0309	0.0841	-0.0012	0.0074	0.0468	0.0419	0.1161	0.0006	0.0049
1-Dodecanol	0.4317	0.4876	0.0840	0.0064	-0.0101	0.4357	0.4624	0.0917	-0.0019	-0.0128
Ethyl Palmitate	0.0398	0.0457	0.0004	0.0001	-0.0001	0.0436	0.0467	0.0005	-0.0006	-0.0001
Ethyl Stearate	0.0298	0.0342	0.0000	0.0000	-0.0002	0.0326	0.0350	0.0000	-0.0004	-0.0002
Ethyl Oleate	0.0796	0.0913	0.0000	0.0002	-0.0007	0.0871	0.0936	0.0000	-0.0010	-0.0009
Ethyl Cis-Vaccenate	0.0019	0.0022	0.0000	0.0000	0.0000	0.0021	0.0022	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1097	0.1256	0.0000	-0.0001	-0.0007	0.1203	0.1292	0.0000	-0.0014	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

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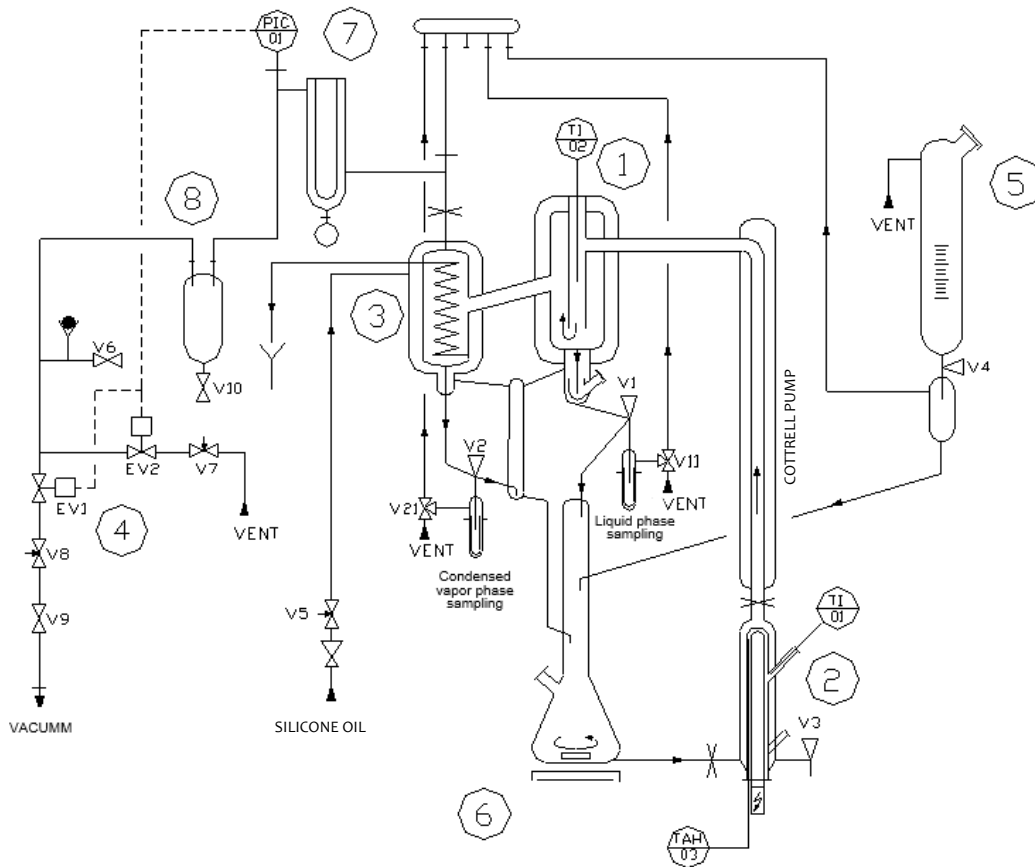
423

Component	Set 13 P (Pa) = 4394; T (K) = 403.12					Set 14 P (Pa) = 4394; T (K) = 403.12				
	z_i	x_i	y_i	Δx_i	Δy_i	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0122	0.0000	0.1073	-0.0007	-0.0036	0.0234	0.0037	0.1293	0.0028	0.0013
2-Ethyl-1-hexanol	0.2217	0.1718	0.6930	0.0036	0.0120	0.2594	0.1665	0.6886	-0.0019	0.0082
1-Octanol	0.0417	0.0355	0.1009	0.0001	0.0047	0.0367	0.0278	0.0808	-0.0004	0.0044
1-Dodecanol	0.4415	0.4792	0.0982	-0.0010	-0.0110	0.4271	0.4989	0.1007	0.0038	-0.0118
Ethyl Palmitate	0.0430	0.0477	0.0006	-0.0003	-0.0001	0.0385	0.0461	0.0005	-0.0006	-0.0001
Ethyl Stearate	0.0322	0.0357	0.0000	-0.0002	-0.0002	0.0289	0.0346	0.0000	-0.0005	-0.0002
Ethyl Oleate	0.0861	0.0955	0.0000	-0.0005	-0.0009	0.0771	0.0923	0.0000	-0.0012	-0.0009
Ethyl Cis-Vaccenate	0.0021	0.0023	0.0000	0.0000	0.0000	0.0018	0.0022	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1187	0.1314	0.0000	-0.0011	-0.0009	0.1063	0.1271	0.0000	-0.0020	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

Component	Set 15 P (Pa) = 4394; T (K) = 404.52				
	z_i	x_i	y_i	Δx_i	Δy_i
Ethanol	0.0054	0.0000	0.0473	-0.0003	-0.0016
2-Ethyl-1-hexanol	0.2287	0.1764	0.7410	0.0065	0.0142
1-Octanol	0.0437	0.0369	0.1090	0.0005	0.0040
1-Dodecanol	0.4394	0.4749	0.1021	-0.0027	-0.0142
Ethyl Palmitate	0.0430	0.0474	0.0006	-0.0006	-0.0001
Ethyl Stearate	0.0322	0.0355	0.0000	-0.0004	-0.0002
Ethyl Oleate	0.0860	0.0949	0.0000	-0.0011	-0.0010
Ethyl Cis-Vaccenate	0.0020	0.0023	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1186	0.1307	0.0000	-0.0018	-0.0010
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000

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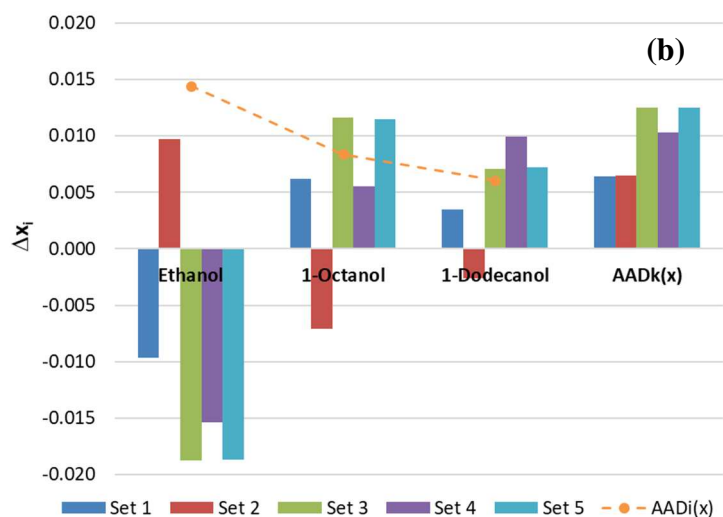
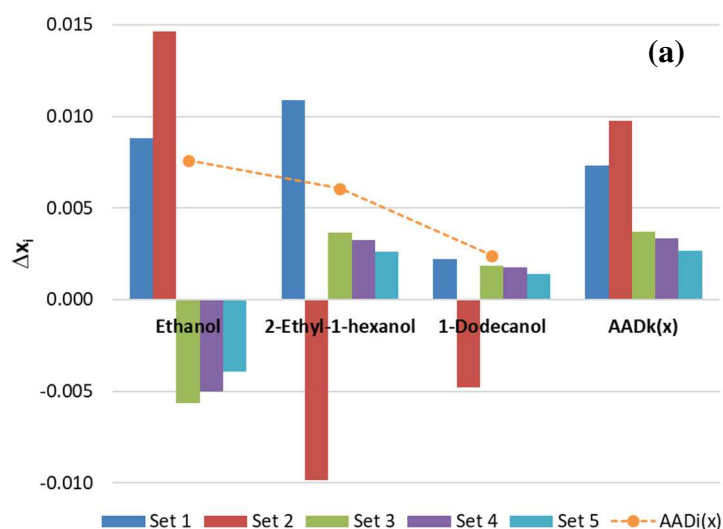


428

Number	Description
1	Double envelope adiabatic equilibrium chamber - An optional plug for sampling a potential second liquid phase is also provided
2	Reboiler: electrical resistance placed in a quartz sleeve (maximum power 500 W)
3	Glass condenser (comprising a pipe coil arranged inside a double envelope cell with cooling by circulating silicone oil operating from -40°C up to 205°C)
4	Vacuum circuit (comprising pump valves, vent valves, control solenoid valves)
5	Funnel for loading the liquid fluid to be studied (maximum volume 150 cm^3)
6	Mixing cell equipped with a magnetic stirrer - A plug with septum allows for potential sampling
7	Dry ice trap
8	Glass buffer reserve (capacity: 8 L) used for vacuum balancing in order to stabilize the pressure of the device after sampling
V1 (V2)	Valve for sampling the liquid (condensed vapor) phase
V11 (V21)	3-Way valve of vacuum setting the sampling tube of the liquid (condensed vapor) phase
V3; V10	Drain valves of the ebulliometer and of the vacuum buffer reserve 8
V4; V6	Valves of pouring and vent
V5; V7; V8	Condenser cooling oil flow control valve; vent flow control valve; vacuum flow control valve
EV1; EV2	Vacuum control solenoid valve; air inlet regulation solenoid valve

429

430 **Figure 1.** Schematic diagram of the dynamic ebulliometer (Pignat Company, France, EEA
 431 model 3000) [24].



432

433

434

435 **Figure 2.** Deviations between the experimental and predicted liquid mole fractions for the
 436 ternary systems [Ethanol (1) + 2-Ethyl-1-hexanol (2) + 1-Dodecanol (3)] (a) and [Ethanol (1)
 437 + 1-Octanol (2) + 1-Dodecanol (3)] (b) (the deviations observed for the vapor mole fractions
 438 are all below the experimental uncertainty, i.e. 0.001; the predictions are obtained with the
 439 UNIFAC-Do model [32-34]; the analytical expressions of the deviations are given in **Table**
 440 **3**).

441



442 **Figure 3.** Deviations between the experimental and predicted mole fractions in the liquid (a)
 443 or in the vapor (b) phase in equilibrium for the multicomponent system [Alcohols + BAEEs]
 444 at different temperatures and pressures (predictions obtained with UNIFAC-Do model [32-
 445 34]; see **Table 3** for the analytical expressions of the deviations).

446

Phase equilibria of mixtures involving fatty acid ethyl esters and fat alcohols between 4 and 27 kPa for bioproduct production

Graphical abstract

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