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

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ABSTRACT

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

1. Introduction

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

Compared to the commonly commercialized methyl biodiesel, ethyl biodiesel has better biodegradability, higher flash point, improved cold-flow properties and oxidation stability, and lower emissions of NOx, CO, and ultrafine particles [9,10]; not to mention the possibility of integrating the ethanol fermentation industry into the production process of biodiesel and biolubricants (by using ethanol and fusel oil respectively) [3,8]. Moreover, biolubricants whose fatty acid group is esterified with long-chain alcohol such as 2-ethyl-1-hexanol, 1-octanol, or even 1-dodecanol exhibit excellent lubricating characteristics, especially for metalworking applications [2,3,5]. Non-edible oils with high amounts of oleic and linoleic acids (30–40% each) and much lower level of linolenic acid, such as oils from *Balanites aegyptiaca* (BA), cottonseeds, or Indian mustard seeds, are considered optimal for producing biofuel and biolubricants exhibiting a good balance between thermal-oxidative stability, viscosity and cold-flow properties [2,6,11].

Robust process simulation of biolubricants production from biodiesel requires quantitative and reliable information about the vapor–liquid equilibria (VLE) of mixtures containing alcohols and fatty acid esters, as well as the liquid–liquid and vapor–liquid–liquid equilibria with the presence of glycerol, and eventually water, when dealing with the

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Table 1
Overview of the low-pressure VLE information related to biodiesel components 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 of only the vapor phase)	NRTL, UNIQUAC and UNIFAC-Do	[15]
Ethanol + Ethyl palmitate	309–422	0.0150–9.300			
Ethyl palmitate + Ethyl stearate	502–520	0.0053	Differential scanning calorimetry	Wilson, NRTL and UNIQUAC	[16]
Ethyl palmitate + Ethyl oleate	502–537	0.0053; 0.0093			
Ethyl palmitate + Ethyl linoleate	514–537	0.0093			
Ethyl myristate + Ethyl palmitate	420–443	0.0005;	Dynamic ebulliometry (recirculation of both the vapor and liquid phases)	NRTL, original UNIFAC, UNIFAC-Do	[17]
	435–458	0.0010;			
	444–468	0.0015			
Methyl myristate + Methyl linoleate	467–511	0.00533;	Differential scanning calorimetry	NRTL, UNIQUAC	[18]
Methyl palmitate + Methyl linoleate	491–511	0.00533			
Jatropha ethyl esters [a] + Ethanol + Water	296–342	0.0067–0.0667;	Dynamic ebulliometry (recirculation of only the vapor phase)	UNIQUAC	[19]
Jatropha ethyl esters[a] + Ethanol + Water	283–329	0.0067–0.0667			
Soybean methyl esters [a] + Methanol	283–365	0.0067–0.0667;	Dynamic ebulliometry (recirculation of only the vapor phase)	UNIQUAC	[20]
Soybean ethyl esters [a] + Ethanol	295–386	0.0067–0.0667;			
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 + *Balanites aegyptiaca* ethyl esters (Ethyl-palmitate + Ethyl stearate + Ethyl oleate + Ethyl *cis*-vaccenate + Ethyl linoleate + Ethyl arachidate)	448–471	0.0080–0.0120	Dynamic ebulliometry (recirculation of both the vapor and liquid phases)	CPA, NRTL, UNIFAC-Do	[12]

[a] The mixture of fatty acid ethyl esters was considered as a pseudo-pure component, both for the experimental study and modeling.

Table 2
Description of the chemicals used in this study (as internal standards, solvent or for 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

preliminary biodiesel production step [7,12,13]. Nevertheless, despite the recently published extensive work on phase equilibria involved in biodiesel production [7,13,14], VLE information for the biolubricant production operating under low pressure is still lacking. As an illustration, Table 1 [12,15–20] gives an overview of the low-pressure VLE related to biodiesel components that were published over the past 10 years. No similar information was found for biolubricants.

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

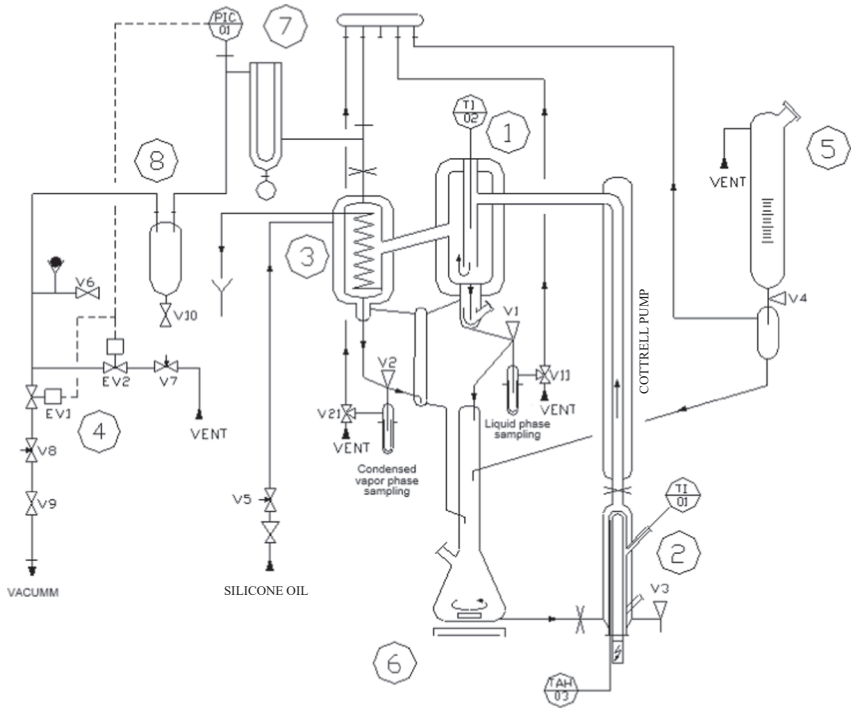
2. Material and methods

2.1. Chemicals and BAEEs production

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

2.2. VLE experiments and procedure

The VLE experiments were carried out in an all-glass ebulliometer, operating between 1 and 100 kPa, with dynamic recirculation of the vapor and liquid phases helping to reach more quickly the equilibrium conditions in addition to the Cottrell pump (model EEA 3000, Pignat, France) [24]. Similar devices have proven to be performant for yielding VLE measurements of high level [25,26]. A detailed description of the ebulliometer of which a schematic diagram is provided in Fig. 1 is available in the paper by Muhammad et al. [12]. The uncertainties on the measured temperature and pressure are, respectively, ±0.01 K and ± 0.013 kPa (±0.1 mmHg). These were determined, prior to any VLE experiment series, by checking the calibration of the ebulliometer sensors using an external reference thermometer and measuring the vapor pressure of ethanol, selected as a reference compound, over a wide temperature range. The composition of the vapor and liquid phases were determined by gas-chromatography coupled with a flame ionization detector (GC-FID 7820, Agilent Technology, USA). Details of the equipment, operating conditions, and calibration are given in Supplementary Material (SM2) [23]. All compositional analyzes were performed by using three internal standards (one specific for the BAEEs, one different for short, and another for fat alcohols; SM2). Thus, for the GC-FID calibration, standard solutions of well-known composition were prepared by weighing the components of the studied system (with ethyl oleate as a surrogate of the BAEEs), and the required IS(s). Performance of the GC-FID calibration was then checked by analyzing the composition of supplementary standard solutions and was used to estimate the mole fraction uncertainty: ±0.002 for the ternary systems, ±0.004 for the multicomponent system.



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

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

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

Table 3
Expressions of the deviations used in this work.

Definition	Expression	
• 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
•Average absolute deviation between the experimental and calculated liquid (vapor) mole fractions for component i over all the N_{sets} data sets	$AAD_i(x) = \sum_{k=1}^{N_{sets}} \lvert\Delta x_i\rvert / N_{sets}$	2a
	$(AAD_i(y) = \sum_{k=1}^{N_{sets}} \lvert\Delta y_i\rvert / N_{sets})$	2b
•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	$AAD_k(x) = \sum_{i=1}^{N_C} \lvert\Delta x_i\rvert / N_C$	3a
	$(AAD_k(y) = \sum_{i=1}^{N_C} \lvert\Delta y_i\rvert / N_C)$	3b
•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	$AAD_{overall}(x) = \sum_{k=1}^{N_{sets}} \left(\sum_{i=1}^{N_C} \lvert\Delta x_i\rvert / N_C\right) \Big/ N_{sets}$	4a
	$(AAD_{overall}(y) = \sum_{k=1}^{N_{sets}} \left(\sum_{i=1}^{N_C} \lvert\Delta y_i\rvert / N_C\right) \Big/ N_{sets})$	4b

thus operating at nearly constant volume during subsequent experiments). This additional liquid (introduced via the loading funnel) was: *(i)* for the ternary systems, the mixture initially loaded in the ebulliometer (or the C8-alcohol for the highest pressures); *(ii)* for the multicomponent system, the ternary mixture [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol] of well-known composition (in order to induce a significant change in the global composition of the investigated system, without nonetheless perturbing the equilibrium state of the ebulliometer radically).

2.3. VLE modeling

Given the large number of components present in the reaction mixture during the transesterification of biodiesel into biolubricant (over 10 typically), the resulting lack of information regarding the VLE data for each of the binaries involved, the highly non-ideal thermodynamic behavior of these mixtures, and the operating conditions of the production process (low pressure), the excess Gibbs energy (G^E) models based on the group contribution (GC) concept are the most appropriate. Indeed, cubic equations of state with GC-estimated binary iteraction parameters were applied successfully to systems involving molecules similar to biodiesel or biolubricants, but under moderate to high-pressures with supercritical carbon dioxide [27–29]. Among the G^E-GC approaches, namely original UNIFAC [30] and its variants (Lyngby modified UNIFAC [31], Dortmund modified UNIFAC [32–34], linear UNIFAC [35]), the regularly updated Dortmund modified UNIFAC model [32–34] was selected as it has yielded excellent VLE predictions for complex mixtures involving ethyl esters and alcohols [12,14,36]. Accordingly, the implicit γ-φ approach leads to express the vapor–liquid equilibrium condition by:

$$x_i \cdot \gamma_i(T,x) \cdot P_i^s(T) = P \cdot y_i \cdot \Im_i(T,P,y) \tag{1a}$$

$$with\ \Im_i(T,P,y) = \frac{\varphi_i^V(T,P,y)}{\varphi_i^*(T,P_i^s)} \cdot exp\left(\frac{1}{RT} \cdot \int_P^{P_i^s} v_{i,L}^*(T,P)\, dP\right)$$

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

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

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

Table 4
Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 2-Ethyl-1-hexanol (2) + 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and vapor (y) phases in equilibrium, 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 defined in Table 3; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.002$).

	Set 1					Set 2				
	P (Pa) = 13574; T (K) = 317.48					P (Pa) = 16878; T (K) = 321.98				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 3					Set 4				
	P (Pa) = 20182; T (K) = 325.67					P (Pa) = 23486; T (K) = 328.97				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 5									
	P (Pa) = 26790; T (K) = 332.06									
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$					
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					

Table 5
Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 1-Octanol (2) + 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and vapor (y) phases in equilibrium, 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 defined in Table 3; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.002$).

	Set 1 P (Pa) = 7051; T (K) = 306.44					Set 2 P (Pa) = 10372; T (K) = 313.74				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 3 P (Pa) = 13693; T (K) = 319.34					Set 4 P (Pa) = 17014; T (K) = 323.64				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 5 P (Pa) = 23657; T (K) = 332.04									
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$					
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					

3. Results and discussion

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

3.1. Ternary systems

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

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

3.2. Multicomponent systems

The investigated system contains 10 components, i.e., the BAEEs with ethanol, 2-ethyl-1-hexanol, 1-octanol, and 1-dodecanol. In total, 15 VLE data sets were measured for this system at various global compositions, for pressures and temperatures ranging from 4394 to 10270 Pa and 360 to 423 K, respectively. These measurements, together with the corresponding predictions obtained with the UNIFAC-Do model, were gathered in Table 6, and Fig. 3 displays additionally the deviations per component (AAD_i) and per data set (AAD_k). More pronounced

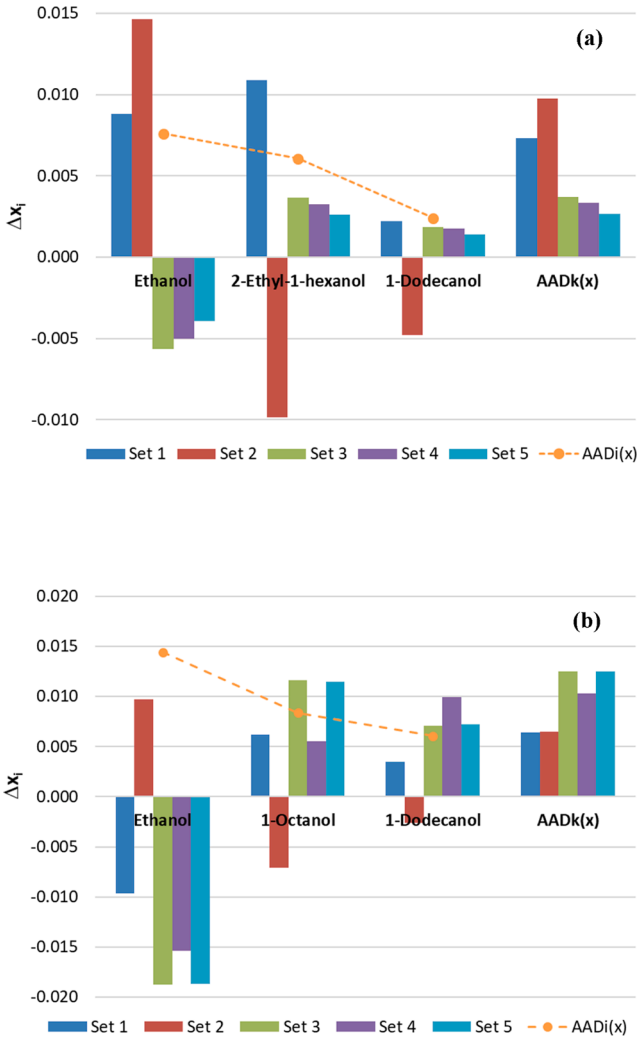


Fig. 2. Deviations between the experimental and predicted liquid mole fractions for the ternary systems [Ethanol (1) + 2-Ethyl-1-hexanol (2) + 1-Dodecanol (3)] **(a)** and [Ethanol (1) + 1-Octanol (2) + 1-Dodecanol (3)] **(b)** (the deviations observed for the vapor mole fractions are all below the experimental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

Table 6
Experimental VLE data and predictions by the UNIFAC-Do model for the multicomponent systems [Alcohols + BAEEs] (are given at different pressures and temperatures: the molar compositions of the global mixture (z) and of the liquid (x) and vapor (y) phases in equilibrium, 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 defined in Table 3; the experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_i) = u(y_i) = 0.004$).

	Set 1					Set 2				
	P (Pa) = 10270; T (K) = 416.93					P (Pa) = 10270; T (K) = 418.73				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 3					Set 4				
	P (Pa) = 10270; T (K) = 420.93					P (Pa) = 10270; T (K) = 421.93				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 5					Set 6				
	P (Pa) = 10270; T (K) = 423.02					P (Pa) = 6966; T (K) =360.02				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 7					Set 8				
	P (Pa) = 6966; T (K) = 377.29					P (Pa) = 6966; T (K) =404.65				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
Eth$\triangle$yl 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
	Set 9					Set 10				
	P (Pa) = 6966; T (K) = 404.85					P (Pa) = 6966; T (K) =405.95				
Component	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
	Set 11					Set 12				
	P (Pa) = 4394; T (K) = 400.12					P (Pa) = 4394; T (K) =402.92				
Component	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

(*continued on next page*)

Table 6 (*continued*)

	Set 1 P (Pa) = 10270; T (K) = 416.93					Set 2 P (Pa) = 10270; T (K) = 418.73				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 13 P (Pa) = 4394; T (K) = 403.12					Set 14 P (Pa) = 4394; T (K) =403.12				
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$
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
	Set 15 P (Pa) = 4394; T (K) = 404.52									
Component	z_i	x_i	y_i	$\triangle x_i$	$\triangle y_i$					
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					

deviations are observed compared to the ternary systems, particularly for the vapor phase compositions, which are now predicted by the UNIFAC-Do model with much less accuracy than the liquid phase compositions. Nonetheless, the overall deviations remain very acceptable for both phases: $AAD_{overall}(x) = 0.003$ and $AAD_{overall}(y) = 0.006$. These results are likely due to the large amounts of alcohols in the vapor phase for these multicomponent mixtures, particularly ethanol, which was already the poorest represented among the substances studied in the ternary systems previously investigated (here for ethanol: $AAD_i(y) =$ 0.05 max). Furthermore, in the liquid phase, the cross-association involved by the alcohols might be mitigated by the presence of the BAEEs, although the mixture studied here also contains a structural complexity on the entropic aspect with molecules differing in size and shape. These two aspects can be realized looking at the activity coefficients in the SM5 section (Supplementary Material) [32–34]. Moreover, the deviations on the liquid and vapor phase compositions are rather randomly distributed, particularly at the lowest pressure (4394 Pa), for which the very good prediction results are worthy of being stressed ($AAD_k(x) \leqslant 0.002$ and $AAD_k(y) \leqslant 0.005$, for all data sets measured at 4394 Pa). Lastly, let mention that, in that case, the assumption of the ideal liquid solution yields rougher predictions of the liquid and vapor phase compositions ($AAD_k(x)$ and $AAD_k(y)$ up to 0.004 and 0.008, respectively), with a deviation on the vapor mole fraction $AAD_i(y)$ up to four times larger for ethanol (which agrees with the bad results obtained when assuming the ideal liquid solution for the investigated ternaries involving alcohols; Supplementary Material, SM5). At higher temperatures, the activity coefficients are closer to one, and consequently, for the system [Alcohols + BAEEs], better predictions are found assuming ideality.

4. Conclusions

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

CRediT authorship contribution statement

Frédéric Roze: Investigation, Data curation. **Patrice Pignat:** Conceptualization. **Olga Ferreira:** Conceptualization, Formal analysis, Methodology. **Simão P. Pinho:** Conceptualization, Formal analysis, Writing - review & editing. **Jean-Noël Jaubert:** Resources, Funding acquisition, Review & editing. **Lucie Coniglio:** Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

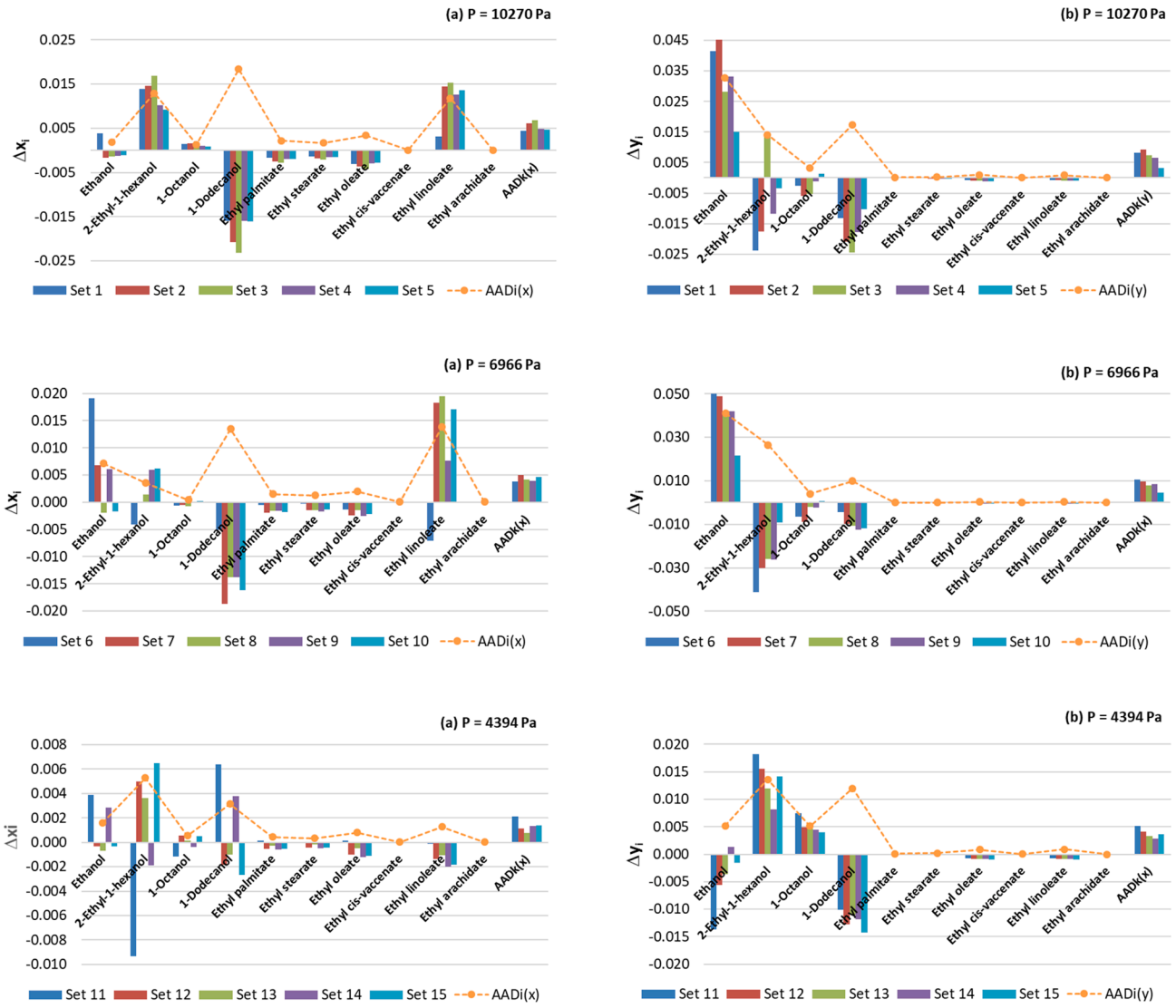


Fig. 3. Deviations between the experimental and predicted mole fractions in the liquid **(a)** or in the vapor **(b)** phase in equilibrium for the multicomponent system [Alcohols + BAEEs] at different temperatures and pressures (predictions obtained with UNIFAC-Do model [32–34]; see Table 3 for the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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.121304.

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