Full Length Article

Phase equilibrium data and modeling of ethylic biodiesel, with application to a non-edible vegetable oil

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ABSTRACT

Contributing to extending the knowledge for the design and operation of biodiesel production processes, isobaric *PTxy* vapor-liquid equilibria data of ethanol + ethyl hexanoate, 1-pentanol + ethyl hexanoate and 1-pentanol + ethyl octanoate at two different pressures are reported for the first time. Consistency tests were applied to attest the quality of the collected data, for these especially complex measurements. Besides that, vapor pressures of the pure ethyl esters have also been measured. For modeling purposes, the Lyngby and Dortmund UNIFAC variants were used to predict the VLE phase diagrams. Generally, the predictions are of very good quality, being the UNIFAC-Do (Dortmund) better, as the deviations in temperature and vapor compositions are always lower to 1.0 K and 0.020, respectively. Checking for the viability for extrapolations in pressure, CPA EoS was also applied to the modeling of the experimental data with very good results. Finally, aiming at examining the model capabilities to describe multicomponent systems, VLE measurements involving two alcohols and the fatty acid ethyl ester mixture obtained from non-edible vegetable oil have been carried out showing the good performance of the predictive models.

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1. Introduction

The ever increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources have led to the development of fatty acid esters as diesel substitutes, known as biodiesel [1]. For a rational design and operation of biodiesel production processes, it is essential to have quantitative and reliable information about the vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium of mixtures containing alcohols, fatty acid esters or glycerol. However, experimental data for many of theses systems is still missing [2]. In 2014 the extended review by Coniglio et al. [2] highlighted the great lack of data, while in the work by Cunico et al. [3], from the same year, a comprehensive application of thermodynamic consistency tests for VLE over systems containing the main classes of compounds present in the biodiesel production, showed that only 3% of the data sets had quality factors higher than 0.5 (maximum is 1.0) [3].

These works [2,3] strongly suggested the need of more precise and consistent measurements that can be used to test and develop models for the design and operation of the biodiesel production processes. Among those, conventional excess Gibbs energy models such as Wilson, NRTL, and UNIQUAC equations, group-contribution approaches of the UNIFAC family, but also equations of state (EoS) like CPA, Peng-Robinson, SAFT have been applied [2,4,5], but further developments are still needed. In particular, due to the real competition of edible oils for human nutrition, non-edible vegetable oils (NEVO) are becoming one of the leading raw materials for biodiesel production, for which fundamental and application studies are extremely necessary. The oil based on *Balanites aegyptiaca* (BA) [6,7] is well characterized, containing mostly the fatty acids C16 and C18, with a well-known impact on fuel properties. Moreover, the BA oil quality parameters are quite similar to those of soy oil, which is one of the most used for biodiesel production. In addition, ethyl esters of BA oil showed cleaner combustion than petrodiesel [8]. This suggests that BA can be an attractive alternative for sustainable biodiesel production.

Therefore, the aim of this work is to deliver a large body of consistent and complete experimental VLE data for compounds, and mixtures, of relevance in the biofuel industry. Besides that,

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group-contribution approaches and Cubic-Plus-Association (CPA) equation of state (EoS) are evaluated for their predictive capabilities, not only in binary mixtures, but perhaps more importantly over a multicomponent mixture containing alcohols and ethyl esters synthesized from BA oil.

2. Material and methods

2.1. Chemicals

The list of chemicals used in this work is given in Table 1 along with supplier and purity. These chemicals were used as received without any further purification.

2.2. Production of BAEEs

Balanites aegyptiaca oil was obtained by extraction, i.e. simultaneous cold pressing and filtration of the seed kernels collected from trees growing in arid and semi-arid regions of Burkina Faso [6,7]. The BA ethyl esters (BAEEs) were synthesized via alkali catalysis (KOH), under a two-stage procedure based on intermediate addition of glycerol. Alkali catalysis was operated at 35 °C, with an ethanol to oil molar ratio equal to 8:1, a catalyst concentration of 1 wt% based on the initial mass of oil, and a reaction time of 50 min, while the addition of glycerol marking the start of the second step was carried out after 30 min of reaction. The ester content of the BAEEs yielded 97% on weigh basis. The resulting ethyl esters are later purified by the dry-washing method conducted in batch mode, using 4 wt% of rice husk ash, which were mixed and stirred continuously for 20 min and heated at 35 °C. A vacuum distillation (180–200 °C; 10 mbar) was finally carried out in order to insure a high grade level of the BAEE mixture used afterwards for VLE study. The BAEE final composition and details of the analytical method [9] used to obtain it are presented in Supplementary Material, SM1 and SM2, respectively.

2.3. VLE apparatus and measurements

The VLE experiments were performed by using an all-glass dynamic recirculating ebulliometer, model EEA 3000 manufactured by Pignat Company (France), represented in Fig. S1 of SM3 [10]. This device is equipped with a Cottrell circulation pump that promotes a vigorously mixing of liquid and vapor phases. The adiabaticity of the equilibrium chamber (1) is attained by vacuum with a silver wall having an outlet temperature (TI/02) from the vapor-liquid outlet of the Cottrell pump. The vapor phase is condensed (3) and sent by gravity into the buffer cell (6) equipped with a magnetic stirrer, while the liquid phase is fed directly by gravity in the same buffer cell. The two mixed phases are then recycled to the boiler (2). The samples are taken from the two sampling outlets by collecting them in a test tube fitted on the return

circuits of condensed vapor and liquid phases, upstream of the buffer cell. The vacuum circuit (4) consists of two solenoid valve pressure control systems (EV1 and EV2). A dry ice trap (7) is also available at the top of the equipment to protect the pressure sensor (PIC/01) from contact with the fluids being studied, but is also needed for precise measurements under atmospheric pressure. The uncertainty of the temperature sensor is ±0.01 K, while pressure sensor presents an uncertainty of ±0.013 kPa (±0.1 mmHg).

Initially, the sensors accuracy was analyzed calibrating the temperature sensor in the ebulliometer using a reference thermometer, and measuring the vapor pressure at different temperatures for ethanol selected as reference compound (green species with well-known properties in a large temperature range). After, the vapor pressures of some pure ethyl esters to be studied in binary and multicomponent mixtures are determined using the dynamic ebulliometer. The measurement of vapor pressure serves two guiding purposes: to check the calibration of the equipment and to extend considerably the available vapor pressure data for the studied compounds.

For the isobaric VLE measurements the more volatile compound is initially introduced into the boiler (2) via the funnel (5). A portion of the liquid is evaporated in the boiler by means of an electrical resistance of 500 W, and the system let to equilibrate. The equilibrium state, commonly reached in 0.5 to 1 h of recirculating, is identified when steady temperature is observed for the selected set-point pressure, leading then to assume that composition of both the liquid and vapor phases is also constant. Then, the equilibrium temperature is noted down and samples are collected simultaneously from the liquid and vapor phases for quantification. The less volatile component (esters) are after introduced through funnel (5) in amounts equivalent to the quantity removed from the ebulliometer in the form of vapor and liquid samples. This procedure is continued until the samples in both the liquid and vapor phases finally result in pure ester, signifying the end of the equilibrium diagram. This is perceptible as the temperature of the ebulliometer reaches a constant value, and the addition of more esters has an insignificant effect on the equilibrium temperature and the composition of both phases. For each binary system two different set-point pressures are studied.

2.4. Analytical method

All collected samples were analyzed in an Agilent Technology gas chromatograph coupled with a flame ionization detector (GC-FID). Details of the equipment, operating conditions and calibration are given in SM2. The temperature programs selected for the GC-column and the internal standard (IS) selected for calibration were adapted to the analyzed mixture. For all investigated systems, two ISs were used to determine the collected sample composition (one for the alcohol(s) and the other one for the ester(s)). Preliminary GC-FID calibration was carried out with standard solutions of well-known composition in the two ISs and components of the studied system, prepared over the full range of composition. Calibration performance was then checked by preparing supplementary standard solutions with intermediary compositions in the system components. This last stage allowed for estimating the composition uncertainty ranging from ±0.001 for the binary systems to ±0.004 for the mixtures involving BAEEs.

3. Results and discussion

3.1. Pure component vapor pressure

After the calibration procedure, the equipment was tested to measure the vapor pressure of ethanol. The experimental values

Table 1
Source and purity of compounds used in this study.

Chemical name	CAS	Source	Purity/mol %
Ethanol	64-17-5	Sigma Aldrich	≥99.8
1-Butanol	71-36-3	Fluka	≥99.5
1-Pentanol	71-41-0	Sigma Aldrich	≥99
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 hexanoate	123-66-0	Sigma Aldrich	≥99
Ethyl octanoate	106-32-1	Sigma Aldrich	≥99
Ethyl oleate	111-62-6	Sigma Aldrich	≥98
Methyl heptadecanoate	1731-92-6	Fluka	≥99
Potassium hydroxide	1710-58-3	Fluka	≥85

are presented in Table S3, and a comparison with those calculated from the DIPPR database [11] is given in Fig. S2 of SM4. In this plot the percentage relative deviation is shown for each experimental point, varying from −0.2% up to 0.2%, exhibiting also a random distribution, while the average relative deviation is about 0.1%, which is lower than the values usually found [12,13] and gives a good indication about the quality of the vapor pressure measured in this work. The equation applied in the vapor pressure calculation is:

$$\ln(P_i^S/Pa) = A_i + \frac{B_i}{(T/K)} + C_i \ln(T/K) + D_i(T/K)^{E_i} \tag{1}$$

where T is the absolute temperature, and P_i^S the vapor pressure of compound i. Table S4 of SM4 presents the coefficients (A_i to E_i) found in the DIPPR database [11].

The measured pure component vapor pressures of two fatty acid ethyl esters (FAEEs), ethyl hexanoate and ethyl octanoate, are also presented in Table S3. It must be mentioned that for some substances the number of data available in the open literature is really small, like for ethyl octanoate for which only 48 data points are registered in the Dortmund databank [14].

Available data for FAEEs are insufficient to check their validity as done for ethanol. Alternatively, the data discrimination method of Wilsak and Thodos [15,16] is here applied. As briefly presented in the SM5, the data can be considered of good quality if the δ values are placed on a smooth concave curve as can be seen for both compounds in Fig. 1. Moreover, the difference between the δ values

at the same temperature, gives the relative deviation between two sets of data, which is generally lower than 4%.

3.2. Binary systems

The isobaric VLE data measured for ethanol + ethyl hexanoate binary system at 40 and 53.33 kPa are presented in Table 2, where besides temperature, the liquid (x) and vapor (y) equilibrium mole fraction compositions are given. The two substances present very different boiling points, which makes the VLE measurements pretty demanding. On the contrary, 1-pentanol and ethyl hexanoate have very close boiling points, and the VLE behavior for this system was studied at 14.65 and 40 kPa as indicated in Table 3. Finally, Table 4 compiles the VLE data for the system 1-pentanol + ethyl octanoate at 15 and 40 kPa. All mixtures studied are zeotropic.

For sub-atmospheric conditions, the activity coefficients of each compound i (γ_i) in the mixture at the equilibrium pressure P can be calculated by:

$$\gamma_i = \frac{y_i P}{x_i P_i^S} \tag{2}$$

A moderate positive deviation from ideal behavior was observed for all systems, as previously found for similar alcohol + ester binary systems [13,20], more evident as the difference between the carbon number in the alcohol and ester increases. Though esters are not able to self-associate, cross association
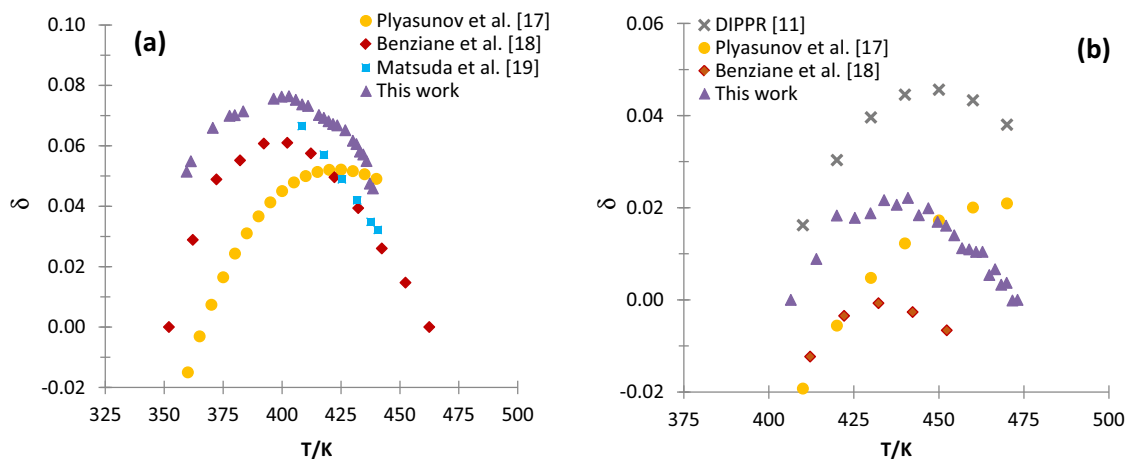

Fig. 1. Vapor pressure analysis for ethyl hexanoate (a) and ethyl octanoate (b) by the Wilsak and Thodos method [11,15–19].

Table 2
Isobaric VLE data for ethanol (1) + ethyl hexanoate (2) system.[a]

40.00 kPa			53.33 kPa		
T (K)	x_1	y_1	T (K)	x_1	y_1
329.58	1.0000	1.0000	335.98	1.0000	1.0000
331.08	0.9091	0.9892	337.68	0.9014	0.9889
332.48	0.8115	0.9819	338.88	0.8218	0.9823
334.18	0.6874	0.9743	340.58	0.7144	0.9755
336.58	0.5223	0.9663	343.08	0.5653	0.9669
338.98	0.4317	0.9588	346.48	0.4283	0.9553
341.68	0.3439	0.9487	350.19	0.3130	0.9408
348.29	0.2284	0.9210	356.49	0.2421	0.9164
357.49	0.1423	0.8723	362.79	0.1624	0.8816
373.29	0.0710	0.7334	369.39	0.1179	0.8408
384.60	0.0402	0.5740	388.70	0.0586	0.6535
400.10	0.0166	0.2011	402.81	0.0323	0.3806
408.02	0.0000	0.0000	417.31	0.0000	0.0000

[a] Experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_1) = u(y_1) = 0.001$.

Table 3
Isobaric VLE data for 1-pentanol (1) + ethyl hexanoate (2) system.[a]

14.65 kPa			40.00 kPa		
T (K)	x_1	y_1	T (K)	x_1	y_1
361.83	1.0000	1.0000	385.15	1.0000	1.0000
362.23	0.9051	0.9215	386.05	0.8620	0.9124
362.23	0.8829	0.9059	386.95	0.7845	0.8554
362.73	0.8226	0.8616	388.05	0.6845	0.7953
362.83	0.8019	0.8497	389.55	0.5784	0.7306
363.43	0.7081	0.7906	390.65	0.4987	0.6846
363.53	0.6826	0.7786	393.35	0.3923	0.5889
364.43	0.5869	0.7237	395.56	0.3041	0.5042
364.43	0.5819	0.7199	397.86	0.2390	0.4160
365.43	0.5081	0.6677	401.06	0.1463	0.2971
365.43	0.4918	0.6675	403.26	0.0938	0.2068
366.53	0.4122	0.6122	404.36	0.0708	0.1580
366.63	0.4026	0.6045	408.07	0.0000	0.0000
368.23	0.3121	0.5330			
369.34	0.2660	0.4876			
371.13	0.1963	0.3999			
371.34	0.1944	0.3931			
374.14	0.1204	0.2683			
374.63	0.1033	0.2426			
375.64	0.0785	0.1967			
379.14	0.0000	0.000			

[a] Experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_1) = u(y_1) = 0.001$.

Table 4
Isobaric VLE data for 1-pentanol (1) + ethyl octanoate (2) system.[a]

15.00 kPa			40.00 kPa		
T (K)	x_1	y_1	T (K)	x_1	y_1
362.33	1.0000	1.0000	385.05	1.0000	1.0000
363.73	0.9247	0.9853	387.05	0.8827	0.9792
364.93	0.8574	0.9737	389.75	0.7835	0.9609
365.63	0.8203	0.9676	389.85	0.7904	0.9611
366.63	0.7672	0.9584	391.45	0.7180	0.9482
367.63	0.7126	0.9495	392.15	0.6858	0.9436
368.43	0.6667	0.9421	394.15	0.6149	0.9276
369.74	0.6124	0.9335	394.45	0.5996	0.9258
369.94	0.5976	0.9298	396.46	0.5327	0.9087
373.14	0.4832	0.9028	397.06	0.4947	0.9002
373.44	0.4768	0.9002	400.46	0.4340	0.8773
376.84	0.3741	0.8704	401.16	0.4125	0.8700
377.74	0.3561	0.8613	407.06	0.3139	0.8140
380.44	0.2948	0.8300	407.56	0.2973	0.8144
384.15	0.2380	0.7893	414.37	0.2214	0.7300
384.95	0.2235	0.7782	415.28	0.2043	0.7232
396.26	0.1138	0.5917	425.28	0.1192	0.5652
397.26	0.1058	0.5745	426.68	0.1119	0.5552
404.76	0.0553	0.3885	437.79	0.0479	0.2791
405.96	0.0509	0.3590	438.69	0.0404	0.2505
416.27	0.0000	0.0000	446.39	0.0000	0.0000

[a] Experimental uncertainties u are: $u(T) = 0.01$ K, $u(P) = 0.013$ kPa, $u(x_1) = u(y_1) = 0.001$.

between the ester and the hydroxyl groups exists, that somehow brings some light to the fact that the alcohol activity coefficient at infinite dilution is close to 1 (Table S5, SM6).

3.2.1. Thermodynamic consistency

For the system ethanol + ethyl hexanoate, VLE data have been measured by Matsuda et al. [19] at the same pressures, which will be briefly compared in the next section. More adequately, the quality of the experimental data was analyzed by applying a quality assessment algorithm for VLE data proposed by Kang et al. [21,22]. Four consistency tests were combined: the Herington test, the Van Ness test, the infinite dilution test, and the pure component test [21–26]. For each test, a quality factor F_{test} was calculated. The maximum value is 1.0 for the pure component test and 0.25 for the remaining three tests. Then, for each VLE data set, an overall quality factor (Q_{VLE}) can be calculated as follows [12,21]:

$$Q_{VLE} = F_{purecomponent} \cdot (F_{Herington} + F_{vanNess} + F_{Infinitedilution})/0.75 \quad (3)$$

The quality factors are shown in Table 5, attaining the maximum value for the ethanol + ethyl hexanoate binary mixture. For the remaining systems, the overall quality factors are between 0.27 and 0.61, which are very satisfactory as Cunico et al. [3] reports that for systems with fatty esters, fatty acids, among other components relevant in the biofuel industry, only 3% of the data sets presents an overall quality factor higher than 0.5, with an average of 0.23 among 92 VLE data sets, while in this work the average is 0.56.

Also interesting to note is that in some systems such as 1-pentanol + ethyl octanoate, the alcohol activity coefficient calculated from the experimental data shows a maximum for alcohol mole fraction close to 0.20 (Fig. S3 of SM6). This strongly contributes for the small quality factor for the infinite dilution test. In this test, the infinite dilution activity coefficients are estimated

Table 5
Consistency test results for all the binary systems.

Pressure	Herington	van Ness	Infinite Dilution	Pure	Overall
Ethanol-Ethyl hexanoate					
40 kPa	0.20	0.25	0.14	1.00	0.79
53.33 kPa	0.16	0.25	0.25	1.00	0.88
1-Pentanol-Ethyl hexanoate					
14.65 kPa	0.07	0.25	0.14	1.00	0.61
40 kPa	0.04	0.25	0.04	0.61	0.27
1-Pentanol-Ethyl octanoate					
15 kPa	0.25	0.25	0.05	0.55	0.40
40 kPa	0.25	0.25	0.05	0.55	0.40

from experimental data either using the excess Gibbs energy function or the natural logarithm of activity coefficient ratio and compared, which can give very different results in the case of the alcohol (see Table S5 of SM6), and makes the quality factor much lower when the alcohol activity coefficient at infinite dilution estimated from $\ln(\gamma_1/\gamma_2)$ is close to one. It is also relevant to mention that for the system 1-pentanol + ethyl octanoate, the quality factor F_{pure} reduces considerably the overall quality factor, most probably because the vapor pressure of pure ethyl octanoate is not so well established in the literature.

3.2.2. Thermodynamic modeling

The experimental data were correlated using the NRTL activity coefficient model [27] with a temperature dependence given in SM7. The binary interaction parameters were estimated by the least-squares method, by minimizing the following objective function F_{obj}:

$$F_{obj} = \sum_{i=1}^{N} \left(\frac{P_i^{calc} - P_i^{exp}}{P_i^{exp}} \right)^2 \tag{4}$$

where N is the number of experimental points, and the superscripts "calc" and "exp" represent calculated and experimental values, respectively. Table S6 (SM7) presents the obtained binary interaction parameters.

Predictive group-contribution activity coefficient methods, namely Lyngby modified UNIFAC [28] and Dortmund modified UNIFAC [29–33] were also evaluated. The identification and number of groups considered in each component are given in Table S7 (SM7).

Model performance is evaluated in terms of average deviations in temperature and vapor phase composition (of the alcohol) for each isobaric VLE data set as given in Table 6. The deviations show that all systems are very satisfactorily described by the different models but, due to its correlative nature, NRTL performs much bet-

ter than others. Observing Fig. 2a, in the system ethanol + ethyl hexanoate the pure predictive Dortmund modified UNIFAC (UNIFAC-Do) model performs as good as the NRTL correlative model, as can be inferred by the correspondent overlapping curves, while in the system 1-pentanol + ethyl hexanoate, both predictive approaches show higher deviations than NRTL, in particular concerning the boiling curve (Fig. 2b). In fact, in all systems studied higher deviations are observed when the liquid phase is rich in the ester, as can be easily understood comparing the calculated and experimental activity coefficients (Fig. S3, SM6). Nevertheless, UNIFAC-Do gives always better results than Lyngby modified UNIFAC (UNIFAC-Ly), and can be used as a predictive tool.

Like mentioned in section 3.2.1 a comparison between the data measured in this work, for the binary system ethanol + ethyl hexanoate, and from Matsuda et al. [19] is given in Figs. 2a and 3. These authors did not measure the vapor phase composition, but Figs. 2a and 3 clearly show an evident deviation in the boiling temperatures when the liquid phase is richer in ethyl hexanoate if compared to results collected in this work, a deviation which is also observed when comparing Matsuda et al. [19] experimental data to all predicted results.

The use of high pressures for the synthesis of biodiesel is envisaged for real plants. Therefore, testing the features of an equation of state like CPA in the calculation of the VLE diagram is of enormous relevance. The compounds of the ester family are non-self-associating (only three pure compound parameters) while alcohols are considered as having two association sites and species for which the 2B association scheme applies (five pure compound parameters). The set of parameters for the selected compounds for this work were already previously established in the open literature [34–36] and are presented at Table S8 (SM7).

The cross-association between the ester group and the hydroxyl group for the systems here selected needs to be explicitly taken accounted for, as previously done when studying and describing the VLE of several ester + methanol/ethanol systems [37], by using

Table 6
Average temperature and vapor composition deviations[*] using NRTL, UNIFAC-Ly, UNIFAC-Do, and CPA EoS.

Pressure (kPa)	Model							
	NRTL		UNIFAC-Ly		UNIFAC-Do		CPA	
	ΔT (K)	Δy_1	ΔT (K)	Δy_1	ΔT (K)	Δy_1	ΔT (K)	Δy_1
Ethanol (1) + Ethyl hexanoate (2)								
40.00	0.41	0.007	2.20	0.020	0.39	0.010	2.31	0.030
53.33	0.34	0.004	2.50	0.020	0.94	0.010	2.58	0.024
1-Pentanol (1) + Ethyl hexanoate (2)								
14.65	0.19	0.007	0.84	0.010	0.64	0.010	0.84	0.012
40.00	0.14	0.020	0.61	0.020	0.68	0.020	0.72	0.022
1-Pentanol (1) + Ethyl octanoate (2)								
15.00	0.32	0.003	1.50	0.008	0.96	0.004	1.54	0.009
40.00	0.59	0.008	1.00	0.004	0.94	0.004	1.13	0.010

[*] $\Delta T/K = \sum_{k=1}^{N} |T_k^{exp} - T_k^{cal}|/N$; $\Delta y_1 = \sum_{k=1}^{N} |y_{ik}^{exp} - y_{ik}^{cal}|/N$.
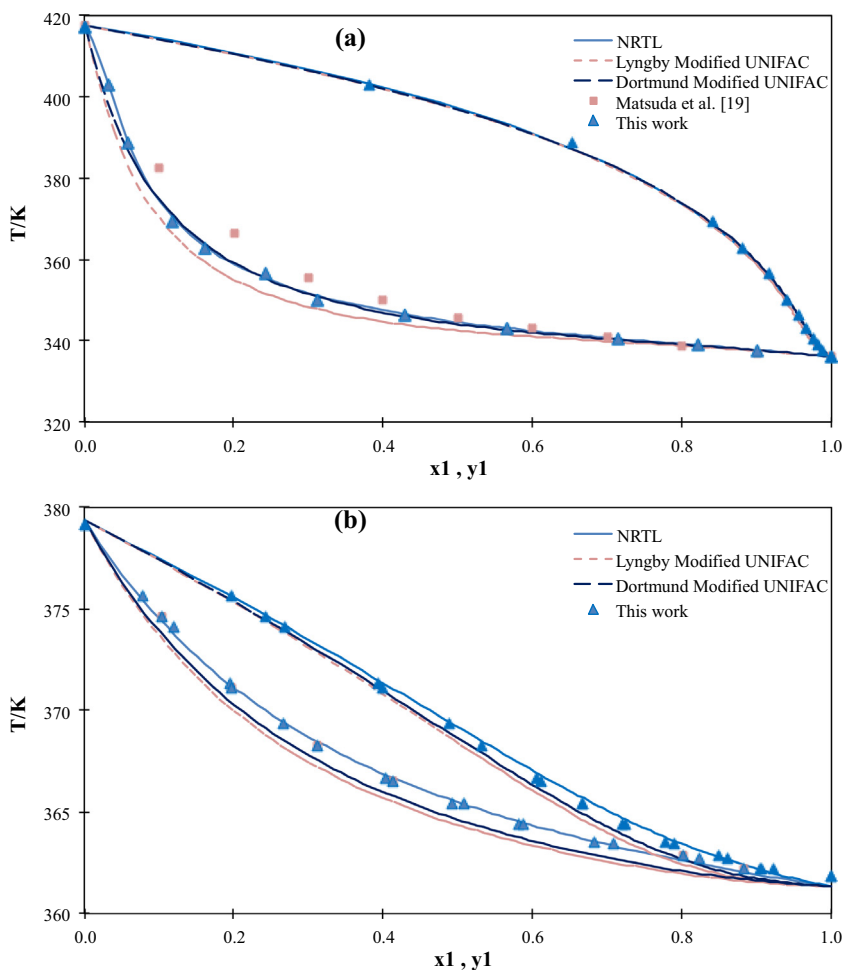
Fig. 2. Vapor-liquid equilibrium diagrams of (a) ethanol (1) + ethyl hexanoate (2) at 53.33 kPa and (b) 1-pentanol (1) + ethyl hexanoate (2) at 14.65 kPa: Comparison with Matsuda et al. [19] and modeling performances.

a solvation scheme involving combining rules for the cross-association energy and leaving the cross-association volume (β_{ij}), along with the binary interaction parameter (k_{ij}), as an adjustable parameter. In that work it was possible to infer that the cross-association volume parameter can be kept constant, around 0.1, while the binary interaction parameter is regressed from experimental data. For ethanol systems it is also possible to establish a linear correlation for the binary interaction parameter with the ester carbon number. The same approach is followed in this work: a cross-association volume of 0.1 was applied for all the systems, for the ethanol + ethyl hexanoate system the binary interaction parameter was computed from the linear correlation established in a previous work [37], and for the remaining systems, the binary interaction parameters were regressed from the experimental VLE data at both pressures. The corresponding parameter values are presented at Table S9 (SM7), while the model performance can also be seen in Table 6.

Fig. 3 compares the performance of the three predictive approaches used. In fact, as CPA EoS is concerned, the only binary system for which the results are pure prediction is the system ethanol + ethyl hexanoate. While the dew curve is the same between different models, UNIFAC-Do predicts much better the boiling curve as can be confirmed by the deviations presented in Table 6.

Fig. 4 compares the results from UNIFAC-Do and CPA for systems (a) 1-pentanol + ethyl hexanoate at 40.00 kPa, and (b) 1-pentanol + ethyl octanoate at 15 kPa. Both approaches present very

similar and satisfactory results. In Fig. 4b is evident the difference in the boiling temperature of ethyl octanoate, which is related to the type of model used. Applying CPA EoS, the vapor pressure is calculated within the model, while with UNIFAC vapor pressure is calculated in accordance to Eq. (1) with coefficients of Table S4 (SM4), giving rise to such differences.

3.3. Multicomponent systems: Data and modeling

The multicomponent system here studied is a mixture of BAEEs with 1-octanol and 1-dodecanol, and the VLE measurements were conducted at 8, 10 and 12 kPa. In total 12 runs were carried out within a temperature range between 447 K and 472 K. Technical limitations to attain equilibrium in such complex mixtures imposed the selection of the composition of the charge to the ebulliometer as well as pressure and temperature ranges. Table S10 (SM8) compiles the collected data.

In order to test the performance of the predictive approaches, UNIFAC-Do and CPA were used to calculate the compositions of both phases at given pressure and temperature. In that regard, within CPA, data were difficult to find and so assumptions had to be made in order to establish binary interaction parameters: no binary interaction parameters were assigned for alcohol-alcohol and ester-ester binaries. For alcohol-ester, since the previous calculations with ethyl hexanoate and 1-pentanol, or ethanol, the regressed k_{ij} was almost the same it suggests that for longer alcohols this value might become constant. So the value of k_{ij} for
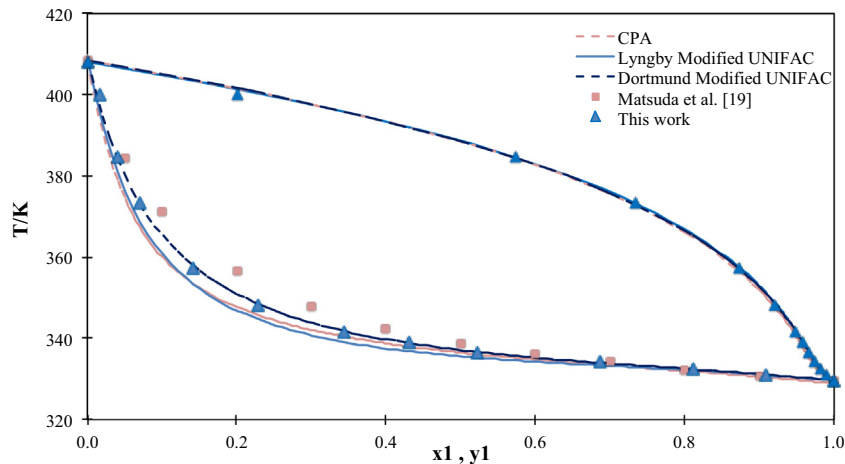
Fig. 3. Vapor-liquid equilibrium diagrams of ethanol (1) + ethyl hexanoate (2) at 40.00 kPa: Comparison with Matsuda et al. [19] and between predictive models.
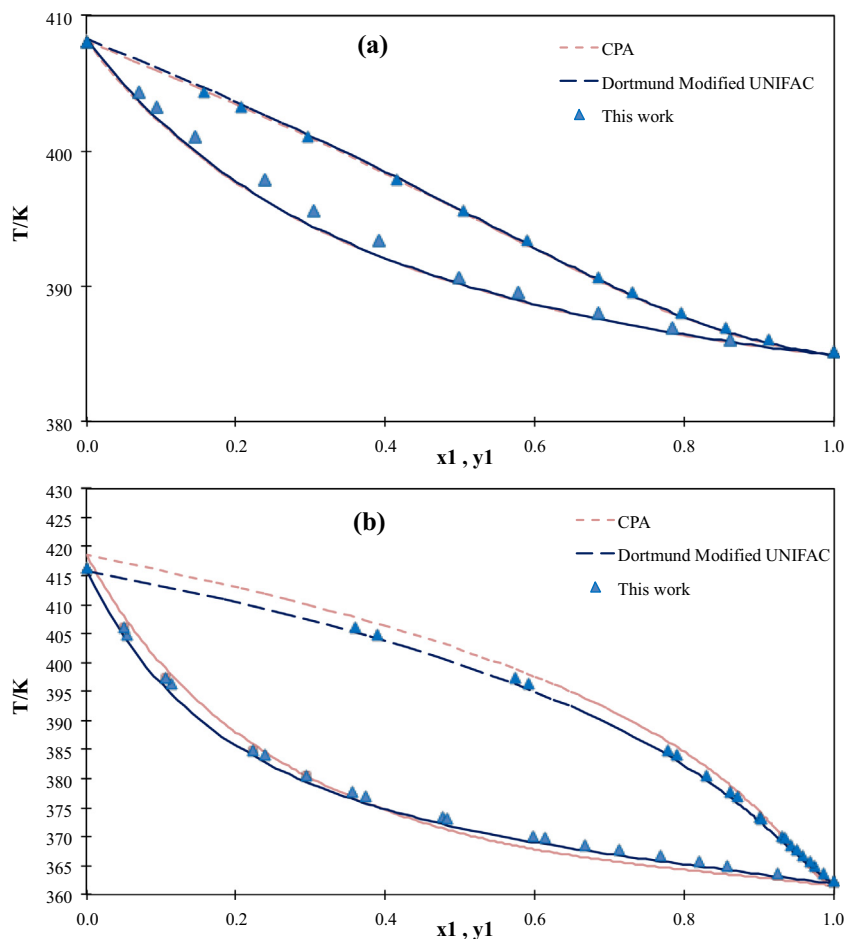

Fig. 4. Vapor-liquid equilibrium diagrams of (a) 1-pentanol (1) + ethyl hexanoate (2) at 40.00 kPa and (b) 1-pentanol (1) + ethyl octanoate (2) at 15.00 kPa: Comparison UNIFAC-Do and CPA.

the 1-pentanol-ethyl hexanoate system was selected for the binaries 1-octanol-ester and 1-dodecanol-ester. The parameter β_{ij} was kept equal to 0.1 as typically done for alcohol-ester systems.

Fig. 5 makes a global comparison between the UNIFAC-Do and CPA predictions concerning the deviations in the liquid ($\Delta x = x^{exp} - x^{calc}$) and vapor phase mole fraction ($\Delta y = y^{exp} - y^{calc}$), neglecting ethyl *cis*-vaccenate and ethyl arachidate, which are

infinitely diluted in the charge. Generally, the deviations with CPA are smaller than with UNIFAC-Do, what can be related to the fact that CPA itself represents the vapor pressure of the pure compounds. However, while for liquid compositions the deviations are very small for all compounds, those are much more pronounced for the alcohol vapor phase composition. Curiously, UNIFAC-Do underestimates the composition of 1-octanol in the vapor phase, while
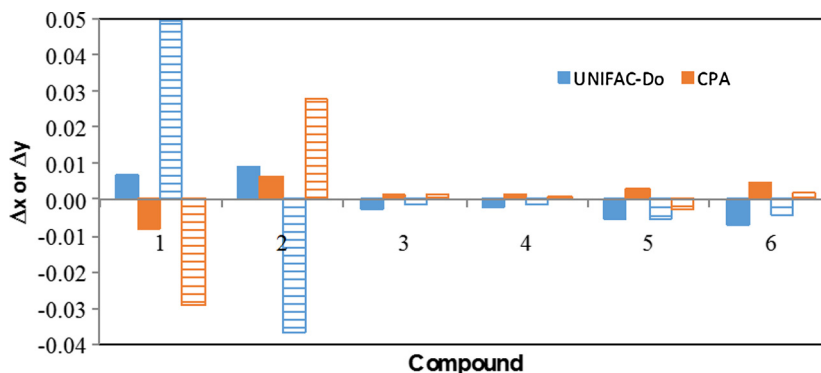
Fig. 5. Liquid (solid bar) and vapor (horizontal line bar) mole fraction deviations in the 1-octanol + 1-dodecanol + BAEE system: Comparison between UNIFAC-Do and CPA. (1) 1-octanol, (2) 1-dodecanol, (3) ethyl palmitate, (4) ethyl stearate, (5) ethyl oleate and (6) ethyl linoleate.

the CPA EoS overestimates it, occurring the opposite situation with1-dodecanol.

In more detail Table S11 (SM8) presents the global deviations for each set. Globally, both methods predict quite well the mole fraction composition in the liquid phase, while for the vapor phase deviations are more pronounced. Within UNIFAC-Do deviations are very uniform, while with CPA deviations in the vapor phase mole fraction increases with the concentration of BAEEs in the charge increases.

4. Conclusions

The vapor pressures of ethyl hexanoate and ethyl octanoate have been measured in the temperature range between 359.5 and 473.1 K. The quality of the data was checked and new data increases considerably the information available for the two pure compounds. The complete *PTxy* phase diagram for binary systems ethanol + ethyl hexanoate, 1-pentanol + ethyl hexanoate and 1-pentanol + ethyl octanoate at two different pressures are reported for the first time. Consistency tests showed quality factors much higher than those usually found for the same class of systems.

Concerning modeling, NRTL with temperature dependent interaction parameters showed a very good performance for correlating the data, but the very satisfactory accuracy of the modified UNIFAC (Dortmund) in the prediction of the phase diagrams must be stressed, where average deviations in temperature and vapor compositions were 0.76 K and 0.010, respectively. Finally, the CPA EoS with a unique estimated parameter showed also very high precision in the description of these particular complex systems. The two methods proved also to be very satisfactory in the prediction of the phase composition in a multicomponent system containing *Balanites aegyptiaca* fatty acid ethyl esters, 1-octanol and 1-dodecanol.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.05.007.

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