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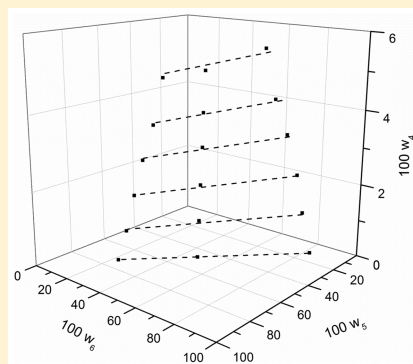
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# Liquid–Liquid Equilibrium Data for Fatty Systems Containing Monoacylglycerols and Diacylglycerols

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**ABSTRACT:** Edible oils can be deacidified by solvent extraction, and the comprehension of liquid–liquid equilibrium is essential to the design process. Thus, this study aims to determine the data of liquid–liquid equilibrium for the fatty systems containing triacylglycerols (TAG) of refined oils (soybean, cottonseed, and rice bran) + commercial fatty acid (linoleic and oleic) + diacylglycerols (DAG) of commercial mixture of mono- and diacylglycerols + monoacylglycerols (MAG) of commercial mixture of mono- and diacylglycerols + anhydrous ethanol at different temperatures (303.15 K and 318.15 K). The high performance size exclusion chromatography (HPSEC) method was used for quantification of all components: TAG, DAG, MAG, fatty acids, and ethanol in both phases in equilibrium. The preference of fatty acids to solvent phase is consistent to previously reported data in literature. The mass fraction of MAG was more than 2 times greater in the solvent phase, and the DAG concentration is higher in the oil phase. The average deviation between experimental and calculated compositions, using NRTL model, was less than 1 %. The obtained parameter set enables the simulation of liquid–liquid extractors for edible soybean, cottonseed, and rice bran oil deacidification, considering the complex multicomponent mixtures composed of tri-, di-, and monoacylglycerols and fatty acids.



## INTRODUCTION

Cottonseed and soybean are some of the most important cultivated oilseeds in the world, with cottonseed oil being the fifth most produced and the soybean oil the second most produced and consumed oil in the world. Moreover, the rice bran oil has been used only to a small extent of its potential as edible oil because of problems with the stability and storage of rice bran. Brazil is the largest producer and exporter of oilseeds and one of 10th largest producer and exporter of vegetable oil in the world.<sup>1,2</sup>

Crude vegetable oils are composed mainly by triacylglycerols and free fatty acids, and in smaller amounts by mono- and diacylglycerols, besides 2% of nonglyceride compounds like tocopherols, phospholipids, pigments, and other minority and undesirable compounds.<sup>3</sup> The removal of free fatty acids is performed during the deacidification step which is the most important step on vegetable oil processing, due to its relation with losses of a significant part of the oil and other desirable compounds. Liquid–liquid extraction (refining with solvent) is a good alternative for the traditional refining processes,<sup>4</sup> and it is based on the difference of solubility of fatty acids and triacylglycerols in the solvent and in the difference of solvent, triacylglycerols, and fatty acids' boiling points.<sup>5</sup> Several authors have been studying the deacidification of vegetable oils by liquid–liquid extraction with different oils, like corn,<sup>6,7</sup> canola, olive,<sup>6</sup> grape seed,<sup>8,9</sup> garlic, sesame,<sup>9</sup> soybean,<sup>10</sup> palm,<sup>11</sup> and others, analyzing besides the free fatty acid extraction, minority components, and the influence of water and temperature, for example,

in the distribution of these components. Literature data showed excellent results in the employment of short chain alcohols as solvent, such as anhydrous or hydrated ethanol, which present low toxicity, easy recovery, good values of selectivity, and distribution coefficients of free fatty acid.<sup>12–14</sup>

The correct choice of analysis method of fatty compounds depends of what will be determined and the information to be obtained.<sup>15,16</sup> The chromatographic techniques are commonly used to separate the acylglycerols, and the high performance size exclusion chromatography (HPSEC) has been used. The HPSEC technique is based on molar mass separation of compounds and well-applied in crude and refined oil quality evaluation, in quantification and separation of mono-, di-, and triacylglycerols and free fatty acids.<sup>15</sup> Arzamendi et al.<sup>17</sup> and Kittirattanapiboon and Krisnangkura<sup>18</sup> used the HPSEC technique to monitor the biodiesel production where the partial acylglycerols (DAG, MAG, and fatty acids) are formed during the transesterification reaction, and Aryusuk et al.<sup>19</sup> used the HPSEC technique to quantify the wax in crude rice bran oil, including the determination of mono-, di-, and triacylglycerols and fatty acids.

These data involving triacylglycerols and fatty acids are important for vegetable oil deacidification comprehension by liquid–liquid extraction, but there is no information in literature

Received: March 23, 2015

Accepted: July 8, 2015

Published: July 24, 2015



**Table 1. Fatty Acid Compositions of Vegetable Oils, Commercial Fatty Acids, and Commercial Mixture of Mono- and Diacylglycerols**

fatty acids	symbol	Cx:y <sup>b</sup>	M <sup>c</sup> g·mol <sup>-1</sup>	oils			commercial fatty acids		commercial mixture of mono- and diacylglycerols
				refined soybean	refined cottonseed	refined rice bran	linoleic acid	oleic acid	
				100 w	100 w	100 w	100 w	100 w	
decanoic	C	C10:0	172.26				0.64		
dodecanoic	L	C12:0	200.32	0.19	0.21				0.02
tetradecanoic	M	C14:0	228.38	0.06	0.67	0.28	0.22		0.72
hexadecanoic	P	C16:0	256.43	10.82	22.75	19.79	5.07	1.00	22.17
cis-hexadec-9-enoic	Po	C16:1	254.42	0.06	0.43	0.15	0.12		0.47
heptadecanoic	Ma	C17:0	270.45				0.03	0.22	
cis-heptadec-9-enoic	Mg	C17:1	268.43				0.03	0.04	
octadecanoic	S	C18:0	284.49	3.93	2.26	1.83	1.68	2.25	2.37
cis-octadec-9-enoic	O	C18:1	282.47	24.38	17.18	39.73	25.49	90.76	16.50
cis,cis-octadeca-9,12-dienoic	Li	C18:2	280.45	52.81	55.90	34.66	66.46	5.42	57.17
trans,trans-octadeca-9,12-dienoic <sup>a</sup>		C18:2T	280.45	0.44				0.22	
all-cis-octadeca-9,12,15-trienoic	Le	C18:3	278.44	6.43	0.15	1.95		0.08	0.25
all-trans-octadeca-9,12,15-trienoic <sup>a</sup>		C18:3	278.44		0.17				
icosanoic	A	C20:0	312.54	0.33	0.24	0.77	0.08		0.21
cis-icos-9-enoic	Ga	C20:1	310.52	0.19	0.06	0.53	0.12		
henecoisanoic	He	C21:0	326.56		0.06		0.06		
docosanoic	Be	C22:0	340.59	0.36	0.09	0.31			0.12

<sup>a</sup>Trans isomers. <sup>b</sup>Cx:y; x = number of carbon and y = number of double bonds. <sup>c</sup>M = molar mass.

about the behavior of partial acylglycerols in these kind of systems. Regarding mono- and diacylglycerol distribution in alcoholic and oil phases, the development of a methodology which relates, equates, and elucidates the composition in each phase is necessary.

Thus, the aim of this work was to investigate the liquid–liquid equilibrium of refined oil (soybean, cottonseed, and rice bran) + commercial fatty acid (linoleic and oleic) + commercial mixture of mono- and diacylglycerols + anhydrous ethanol at different temperatures (303.15 K and 318.15 K) using high performance size exclusion chromatography (HPSEC) for the quantification of the components in each phase. The measured liquid–liquid equilibrium data set was used for adjusting parameters of the NRTL (nonrandom two-liquid) model.

## EXPERIMENTAL SECTION

**Materials.** The solvents used in this work were anhydrous ethanol and anhydrous acetic acid (glacial) both from Merck (Germany) and with purity greater than 99.5 % by mass and toluene CHROMASOLV Plus for HPLC from Sigma-Aldrich (USA) and purity greater than 99.5 % by mass. Commercial oleic and linoleic acids were acquired from Sigma-Aldrich (USA) with purity 90.76 % and 66.46 % by mass, respectively. A commercial mixture of mono- and diacylglycerols was used as a partial acylglycerols source in this work. Refined soybean and cottonseed oils were kindly supplied by Cargill (Mairinque, Brazil), and refined rice bran oil was kindly supplied by Irgovel (Pelotas, Brazil).

**Experimental Methods.** Refined oils and fatty acids used in this work were analyzed by gas chromatography of the fatty acid methyl esters, according to the official method Ce 1–62 of the American Oil Chemists' Society (AOCS)<sup>20</sup> to determine their fatty acid composition. Prior to the chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters according to Hartman and Lago.<sup>21</sup> The chromatographic analysis was carried out using a capillary gas chromatography system under the same experimental conditions shown in

Lanza et al.<sup>22</sup> The fatty acid compositions of the commercial oleic and linoleic acids, commercial mixture of mono- and diacylglycerols, refined soybean, cottonseed, and rice bran oils are presented in Table 1.

The composition expressed in terms of mono-, di-, and triacylglycerols of the commercial mixture of mono- and diacylglycerols was taken using gas chromatography, according to the standard test method ASTM D6584 of the American Society for Testing and Materials (ASTM International). The diacylglycerol compositions of the oils (soybean, cottonseed, rice bran oils) were determined by HPSEC chromatography according to a published method,<sup>18</sup> using the calibration curve of commercial mixture of mono- and diacylglycerols. The HPLC system was equipped with an automatic injector (Shimadzu, model SIL-20A, Japan), with a 5  $\mu$ m Phenogel 300  $\times$  7.8 mm ID size exclusion column (Phenomenex, Torrance, CA, USA) and a RI detector. The column temperature was set at 313 K, and the injection volume was 0.20  $\mu$ L. A mobile phase of 0.25 % (v/v) acetic acid in toluene, at a flow rate of 1.0 mL·min<sup>-1</sup> was used during the 17 min run time. The concentrations of the samples were 10 mg·mL<sup>-1</sup>, each prepared in toluene. The triacylglycerol compositions were calculated by difference, since it was not detected monoacylglycerols in these oils. Table 2 presents the composition of oils and commercial mixture of mono- and diacylglycerols expressed in tri-, di-, and monoacylglycerols.

**Table 2. Composition of Fatty Compounds in Tri-(TAG), Di-(DAG), and Monoacylglycerols (MAG)**

component	TAG	DAG	MAG
	100 w	100 w	100 w
soybean oil	99.18	0.82	0.00
cottonseed oil	98.35	1.65	0.00
rice bran oil	95.96	4.04	0.00
commercial mixture of mono- and diacylglycerols	6.49	32.35	61.16

Table 3. Probable Tri-, Di-, and Monoacylglycerol Composition of Vegetable Oils and Commercial Mixture of Mono- and Diacylglycerols

main TAG <sup>a</sup>	group <sup>b</sup>	M <sup>c</sup>	refined soybean	refined cottonseed	refined rice bran	commercial mixture of mono- and diacylglycerols
		g·mol <sup>-1</sup>	100 w	100 w	100 w	100 w
PPP	48:0	807.33			1.00	
MLiP	48:2	803.30		0.74		2.87
POP	50:1	833.37	0.95	3.20	5.48	0.55
PLiP	50:2	831.35	2.12	10.62	5.05	0.73
MLiO	50:3	829.34		0.96		10.16
PPLe	50:3	829.34			0.62	3.99
LiLiM	50:4	827.32		0.83		
POS	52:1	861.42	0.63	0.58	0.98	1.03
OOP	52:2	859.41	3.66	4.20	10.78	
POLi	52:3	857.39	10.27	15.34	17.63	14.53
LiLiP	52:4	855.38	12.36	25.28	8.81	
PLiLe	52:5	853.36	2.76		0.94	1.78
LiLiPo	52:5	853.36		0.52		
OOS	54:2	887.46	1.11		1.42	0.93
OOO	54:3	885.44			7.74	25.53
SLiO	54:3	885.44	4.80	1.85		6.49
OOLi	54:4	883.43	13.19	6.51	16.67	
LiLiO	54:5	881.41	22.12	14.01	14.97	
LiLiLi	54:6	879.40	19.70	15.35	5.69	0.67
LiLiLe	54:7	877.38	5.68		0.74	14.17
LeLeLi	54:8	875.37	0.65			16.57
OLiA	56:3	913.50			0.81	
LiLiA	56:4	911.48			0.66	
		$\bar{M}_{TAG}$	872.37	861.47	866.87	861.90
DAG						
MP	30:0	540.86		0.25		0.24
PP	32:0	568.91	1.02	4.61	4.72	4.34
MO	32:1	566.90		0.32		0.34
MLi	32:2	564.88		1.12		1.21
PS	34:0	596.96	0.21	0.19	0.33	0.18
PO	34:1	594.95	6.71	10.24	17.04	9.60
PLi	34:2	592.93	14.00	29.30	15.43	28.88
PLe	34:3	590.91	0.92		0.73	
PoLi	34:3	590.91		0.35		0.45
SO	36:1	623.00	2.55	0.81	1.27	0.78
SLi	36:2	620.99	1.60	0.62		0.59
OO	36:2	620.99	5.99	3.57	17.36	3.49
OLi	36:3	618.97	28.56	19.73	27.24	19.56
LiLi	36:4	616.95	33.09		14.09	
LiLe	36:5	614.94	5.14		0.81	
LeLe	36:6	612.92	0.22	28.90		30.33
OA	38:1	651.05			0.27	
LiA	38:2	649.04			0.71	
		$\bar{M}_{DAG}$	618.00	605.17	608.62	605.29
MAG						
M	14:0	302.45				0.90
P	16:0	330.50				23.80
Po	16:1	328.49				0.22
S	18:0	358.56				0.78
O	18:1	356.54				18.63
Li	18:2	354.52				55.67
		$\bar{M}_{MAG}$				348.69

<sup>a</sup>Groups with a total triacylglycerol (TAG) composition lower than 0.5 % were ignored. <sup>b</sup>*x*:*y*, *x* = number of carbons (except carbons of glycerol); *y* = number of double bonds. <sup>c</sup>*M* = molar mass.

From fatty acid compositions presented in Table 1, the probable triacylglycerol compositions of refined oils and commercial mixture of mono- and diacylglycerols could be

determined, using the algorithm suggested by Antoniosi Filho et al.,<sup>23</sup> ignoring the triacylglycerol sets with a total concentration less than 0.5 %. Table 3 presents the probable triacylglycerol

**Table 4.** Experimental Liquid–Liquid Equilibrium Data for the System TAG Soybean Oil (1) + DAG (2) + MAG (3) + Commercial Linoleic Acid (4) + Anhydrous Ethanol (5) in Mass Percentage at 303.15 K and 318.15 K<sup>a</sup>

T/K	overall composition					oil phase					solvent phase				
	100 w <sub>1</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>	100 w <sub>1</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>	100 w <sub>1</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>
303.15	47.95	2.00	3.04	0.00	47.01	74.58	1.95	2.19	0.00	21.28	9.29	1.40	5.30	0.00	84.00
	47.29	1.96	2.97	0.68	47.11	75.98	1.88	1.86	0.54	19.74	10.87	1.34	4.41	0.78	82.60
	46.57	2.03	3.12	1.51	46.76	74.82	1.93	2.03	1.28	19.93	11.03	1.43	4.82	1.79	80.94
	45.77	1.97	3.01	2.11	47.14	74.62	1.93	1.96	1.80	19.69	12.20	1.39	4.87	2.47	79.07
	44.81	1.97	3.02	3.06	47.14	72.20	1.94	2.08	2.67	21.12	14.41	1.50	4.85	3.61	75.63
	43.32	1.97	3.06	4.66	46.98	63.60	1.83	2.21	4.34	28.01	19.29	1.43	4.16	5.27	69.85
318.15	47.84	2.02	3.08	0.00	47.06	78.26	1.81	1.95	0.00	17.98	11.44	1.47	4.98	0.00	82.11
	46.90	2.00	3.06	1.00	47.04	75.07	1.80	1.96	0.83	20.34	12.25	1.41	4.91	1.19	80.24
	45.85	2.02	3.12	1.99	47.02	73.61	1.87	1.89	1.64	20.99	14.84	1.56	5.04	2.48	76.07
	44.95	2.02	3.12	2.93	46.97	72.34	1.95	2.32	2.59	20.79	15.36	1.44	4.68	3.34	75.18
	42.98	1.98	3.08	5.03	46.94	65.87	1.88	2.01	4.69	25.55	20.43	1.54	3.98	5.65	68.40

<sup>a</sup>The standard uncertainty for the temperature  $u(T)$  is 0.1 K, and the standard uncertainty for the mass fractions  $u(w)$  is 0.15 %.

compositions and the average molar masses of these fatty compounds. These compositions were also used to determine the probable mono- and diacylglycerol compositions. Starting from triacylglycerol compositions, all possible combinations of mono- and diacylglycerols were made. In Table 3, the probable diacylglycerol compositions of soybean, cottonseed, rice bran oils, the probable mono- and diacylglycerol compositions of commercial mixture and all average molar masses are shown.

The free fatty acid contents of refined oils were determined according to the official method 2201 of the International Union of Pure and Applied Chemistry (IUPAC)<sup>24</sup> using the automatic titrator Titrand 808 (Metrohm, Switzerland). Refined soybean and cottonseed oils presented a free fatty acid content of 0.11 % and 0.09 % by mass expressed in linoleic acid, respectively, and the free fatty acid of refined rice bran oil was 0.21 % by mass expressed in oleic acid.

**Experimental Procedures.** Each liquid–liquid equilibrium experiment was prepared by the addition of commercial mixture of mono- and diacylglycerols, fatty acid (oleic or linoleic) anhydrous ethanol, and a different refined oil in a sealed glass tubes (10 mL) (PerkinElmer). These components were weighted in the tubes on an analytical balance (Precisa, model XT220A, Sweden) accurate to  $\pm 0.0001$  g. The tubes were sealed and vigorously stirred during 20 min using a vortex (Scientific Industries, model Vortex Genie 2, USA). All systems were left at rest for a minimum of 36 h at constant temperature in a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA) accurate to  $\pm 0.1$  K. This led to the liquid–liquid equilibrium through the formation of two clear and transparent phases with a well-defined interface. Equilibrium data for the systems containing refined soybean and cottonseed oil were measured at 303.15 K and 318.15 K using commercial linoleic acid as the major source of free fatty acid, and the commercial mixture of mono- and diacylglycerols. The system containing refined rice bran oil was measured at the same temperatures above using commercial oleic acid as the major source of free fatty acid, and the commercial mixture of mono- and diacylglycerols. In both cases the uncertainty of the equilibrium temperature was not greater than 0.1 K. After equilibrium was attained, samples of both liquid phases were collected and analyzed by HPSEC chromatography according to the method described by Kittirattanapiboon and Krisnangkura,<sup>18</sup> previously cited. Each component in liquid–liquid equilibrium phases was quantified by a different calibration curve (external calibration), using six concentration levels of the same components used in the equilibrium systems. To verify the

quality of the results, the procedure developed by Marcilla et al.<sup>25</sup> was used, where the values of the deviations of the global mass balances less than 0.5 % ensure the good quality of the experimental data. The global mass balance deviation is the difference between the sums of the calculated masses of both liquid phases with the actual value for total mass used in the experiment.

**Thermodynamic Modeling.** The experimental data measured for the systems were used to adjust the parameters of the NRTL model. The parameter adjustments were made by treating the systems as pseudoquinary composed by triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG), fatty acids, and ethanol. In the NRTL model, the activity coefficient is represented in eq 1:

$$\ln \gamma_i = \frac{\sum_{j=1}^K \tau_{ji} G_{ji} w_j / \bar{M}_j}{\sum_{j=1}^K G_{ji} w_j / \bar{M}_j} + \sum_{j=1}^K \left[ \frac{w_j G_{ij}}{\bar{M}_j \sum_{l=1}^K G_{lj} w_l / \bar{M}_l} \times \left( \tau_{ij} - \frac{\sum_{l=1}^K \tau_{li} G_{li} w_l / \bar{M}_l}{\sum_{l=1}^K G_{li} w_l / \bar{M}_l} \right) \right] \quad (1)$$

where:

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (2)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \quad (3)$$

$$\alpha_{ij} = \alpha_{ji} \quad (4)$$

$A_{ij}$  and  $\alpha_{ij}$  are the adjustable binary parameters between the pair of components  $i$  and  $j$ ,  $K$  is the number of components,  $T$  is the equilibrium temperature (K), and  $\bar{M}$  represents the average molar mass of the pseudocomponent.

Estimation of the NRTL parameters was performed by minimizing the objective function of compositions, eq 5 below, according to the procedure suggested by Stragevitch and d'Avila.<sup>26</sup>

$$\text{OF}(w) = \sum_{m=1}^D \sum_{n=1}^N \sum_{i=1}^{K-1} \left[ \left( \frac{w_{i,n,m}^{\text{SP,exp}} - w_{i,n,m}^{\text{SP,calc}}}{\sigma_{w_{i,n,m}}^{\text{SP}}} \right)^2 + \left( \frac{w_{i,n,m}^{\text{OP,exp}} - w_{i,n,m}^{\text{OP,calc}}}{\sigma_{w_{i,n,m}}^{\text{OP}}} \right)^2 \right] \quad (5)$$



**Table 5. Experimental Liquid–Liquid Equilibrium Data for the System TAG Cottonseed Oil (6) + DAG (2) + MAG (3) + Commercial Linoleic Acid (4) + Anhydrous Ethanol (5) in Mass Percentage at 303.15 K and 318.15 K<sup>a</sup>**

T/K	overall composition					oil phase					solvent phase				
	100 w <sub>6</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>	100 w <sub>6</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>	100 w <sub>6</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>4</sub>	100 w <sub>5</sub>
303.15	47.60	2.38	3.00	0.00	47.02	72.63	2.89	1.91	0.00	22.56	11.14	2.11	4.22	0.00	82.52
	46.46	2.45	3.17	1.01	46.92	69.48	2.95	1.93	0.80	24.85	13.09	2.21	4.58	1.13	78.99
	45.60	2.37	3.04	1.99	47.01	66.49	2.88	1.90	1.76	26.98	14.87	2.19	4.09	2.18	76.67
	44.50	2.36	3.06	3.00	47.07	63.04	2.88	2.25	2.69	29.14	17.78	2.20	3.98	3.28	72.76
	43.64	2.40	3.16	3.91	46.88	59.24	2.83	2.29	3.61	32.02	21.18	2.34	3.89	4.22	68.37
	42.58	2.36	3.12	4.99	46.94	55.60	2.48	2.66	4.82	34.44	23.90	2.29	3.55	5.53	64.74
318.15	47.63	2.42	3.08	0.00	46.87	72.37	2.91	1.93	0.00	22.78	14.24	2.17	4.21	0.00	79.39
	46.66	2.35	2.97	1.02	47.00	69.84	2.78	1.91	0.80	24.67	16.42	2.17	4.21	1.11	76.09
	45.61	2.35	3.00	2.01	47.03	65.95	2.79	2.22	1.79	27.25	18.41	2.10	4.28	2.36	72.85
	44.45	2.38	3.11	3.04	47.02	63.10	2.75	2.01	2.69	29.44	21.00	2.37	3.84	3.41	69.37
	43.76	2.34	3.03	3.93	46.95	61.23	2.74	2.23	3.68	30.12	23.97	2.31	3.78	4.43	65.51

<sup>a</sup>The standard uncertainty for the temperature  $u(T)$  is 0.1 K, and the standard uncertainty for the mass fractions  $u(w)$  is 0.22 %.

**Table 6. Experimental Liquid–Liquid Equilibrium Data for the System TAG Rice Bran Oil (7) + DAG (2) + MAG (3) + Commercial Oleic Acid (8) + Anhydrous Ethanol (5) in Mass Percentage at 303.15 K and 318.15 K<sup>a</sup>**

T/K	overall composition					oil phase					solvent phase				
	100 w <sub>7</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>8</sub>	100 w <sub>5</sub>	100 w <sub>7</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>8</sub>	100 w <sub>5</sub>	100 w <sub>7</sub>	100 w <sub>2</sub>	100 w <sub>3</sub>	100 w <sub>8</sub>	100 w <sub>5</sub>
303.15	46.29	3.55	3.06	0.00	47.09	73.53	4.71	2.03	0.00	19.74	9.84	2.52	4.52	0.00	83.11
	45.42	3.55	3.13	0.91	46.99	70.98	4.62	1.81	0.81	21.78	11.39	2.54	4.84	1.04	80.19
	44.62	3.47	3.04	1.86	47.00	69.10	4.68	2.02	1.53	22.66	12.41	2.44	4.47	2.10	78.58
	43.33	3.43	3.07	3.12	47.05	64.67	4.39	2.24	2.80	25.90	15.01	2.62	4.18	3.46	74.74
	42.43	3.38	3.04	4.19	46.95	61.35	4.32	2.22	3.91	28.20	18.41	2.79	4.11	4.66	70.03
	41.49	3.35	3.06	5.18	46.96	55.98	4.16	2.21	4.82	32.83	21.97	2.95	3.83	5.52	65.74
318.15	46.40	3.57	3.08	0.00	46.95	72.60	4.77	1.88	0.00	20.74	11.42	2.48	4.80	0.00	81.30
	45.45	3.51	3.04	1.11	46.89	68.66	4.95	1.94	0.81	23.52	12.53	2.49	4.16	1.17	79.65
	43.97	3.46	3.06	2.34	47.18	67.01	4.28	1.99	2.03	24.69	13.79	2.63	4.03	2.48	77.07
	43.38	3.46	3.11	2.96	47.10	63.27	4.69	2.21	2.64	27.19	15.45	2.71	4.14	3.21	74.48
	42.53	3.40	3.07	4.07	46.94	59.75	4.46	2.28	3.68	29.83	17.77	2.77	4.24	4.48	70.74
	42.03	3.34	2.99	4.54	47.11	59.86	4.46	2.14	4.13	29.40	18.65	2.69	4.09	5.00	69.57

<sup>a</sup>The standard uncertainty for the temperature  $u(T)$  is 0.1 K, and the standard uncertainty for the mass fractions  $u(w)$  is 0.20 %.

**Table 7. NRTL Parameters for the Binary Interactions between TAG Soybean Oil (1), DAG (2), MAG (3), Commercial Linoleic Acid (4), Anhydrous Ethanol (5), TAG Cottonseed Oil (6), TAG Rice Bran Oil (7), and Commercial Oleic Acid (8)**

T = 303.15 K					T = 318.15 K				
pair ij	A <sub>ij</sub> /K	A <sub>ji</sub> /K	α <sub>ij</sub>		pair ij	A <sub>ij</sub> /K	A <sub>ji</sub> /K	α <sub>ij</sub>	
12	−1420.7	−277.31	0.48797		12	−1405.3	−288.34	0.51377	
13	291.75	1520.7	0.54133		13	320.29	1361.6	0.54637	
14	129.21	−33.23	0.54448		14	120.48	−34.952	0.56932	
15	14.508	1333.5	0.53501		15	13.748	1373.4	0.52147	
23	29855	5139.2	0.13635		23	29463	6381.7	0.18275	
24	−1059.7	−2010.2	0.57000		24	−1279.7	−2273.3	0.56288	
25	−1042.5	−271.58	0.34317		25	−1063.1	−266.14	0.35485	
26	1148.2	−5099.8	0.10496		26	995.63	−4459.3	0.13112	
27	−99.458	−2341.6	0.54055		27	−69.648	−2329.7	0.54504	
28	−3528.3	−3538.6	0.16350		28	−3728.3	−4125.9	0.19489	
34	−1351.3	6811	0.16511		34	−1912.3	6002.4	0.13849	
35	453.88	881.16	0.21665		35	401.25	830.69	0.27044	
36	1007.8	20.148	0.10000		36	999.74	23.326	0.10402	
37	5043.4	−318.02	0.12947		37	3561.6	−325.91	0.16169	
38	502.48	3143.8	0.16991		38	400.8	3365	0.18817	
45	3616.2	−177.92	0.43197		45	4126.9	−198.9	0.42975	
46	−138.67	1112.2	0.10121		46	−121.96	1115.6	0.11333	
56	1648	−409.63	0.39324		56	1688.4	−414.56	0.38529	
57	2579.6	−851.79	0.19737		57	2575.5	−844.06	0.21312	
58	−1785.3	−1401.8	0.10355		58	−2092.8	−1007.7	0.10088	
78	48.479	−714.43	0.15896		78	50.568	−629.19	0.11529	

**Table 8.** Average Deviations between Experimental and NRTL Calculated Phase Compositions

system	T/K	$\Delta w/\%$
TAG soybean oil (1) + DAG (2) + MAG (3) + anhydrous ethanol (5)	303.15	0.97
	318.15	0.12
TAG cottonseed oil (6) + DAG (2) + MAG (3) + anhydrous ethanol (5)	303.15	0.54
	318.15	0.23
TAG rice bran oil (7) + DAG (2) + MAG (3) + anhydrous ethanol (5)	303.15	0.28
	318.15	0.20
TAG soybean oil (1) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5)	303.15	0.95
	318.15	0.41
TAG cottonseed oil (6) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5)	303.15	0.51
	318.15	0.31
TAG rice bran oil (7) + DAG (2) + MAG (3) + commercial oleic acid (8) + anhydrous ethanol (5)	303.15	0.33
	318.15	0.21
global	303.15	0.65
	318.15	0.30

where  $D$  is the total number of data groups,  $N$  is the total number of tie lines in the data group,  $K$  is the total number of components in the data group,  $w$  is the mass fraction, subscripts  $i$ ,  $n$  and  $m$ , are the component, tie line, and group number, respectively, and the superscripts SP and OP stand for the solvent and oil phases, respectively; exp and calc refer to experimental and calculated compositions.  $\sigma_{w_{i,n,m}}^{SP}$  and  $\sigma_{w_{i,n,m}}^{OP}$  are the standard deviations observed in the compositions of the two liquid phases.

The average deviations between experimental and calculated compositions in both phases were calculated according to eq 6:

$$\Delta w = 100 \sqrt{\frac{\sum_{n=1}^N \sum_{i=1}^K [(w_{i,n}^{SP,exp} - w_{i,n}^{SP,calc})^2 + (w_{i,n}^{OP,exp} - w_{i,n}^{OP,calc})^2]}{2NK}} \quad (6)$$

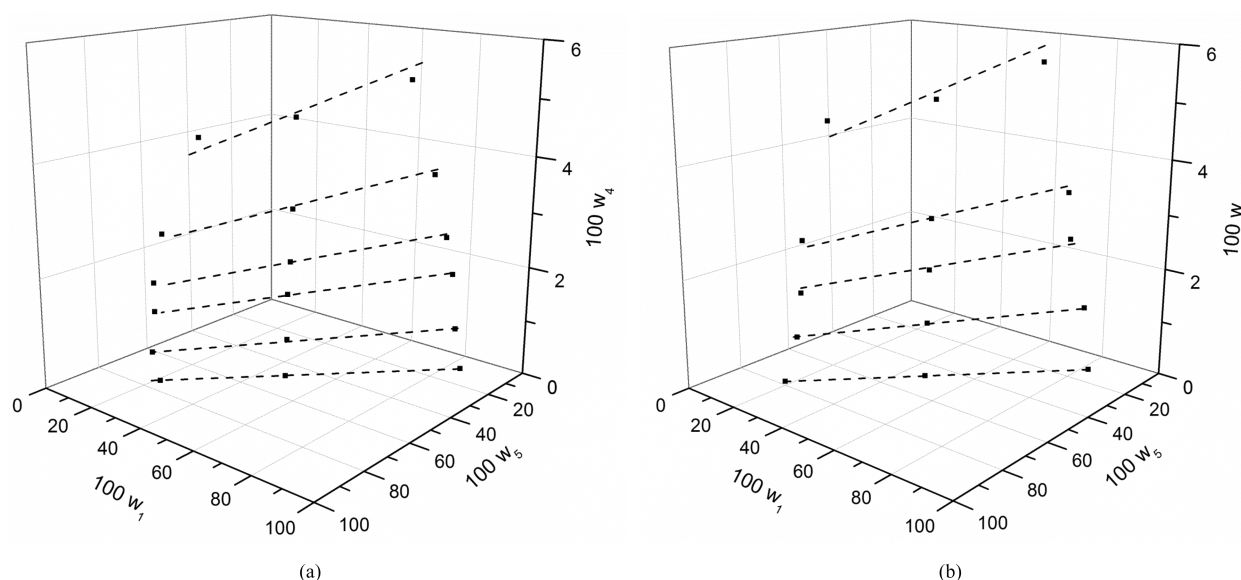
## RESULTS AND DISCUSSION

The following notations were used to represent the components of the systems: TAG soybean oil (1), DAG (2), MAG (3), commercial linoleic acid (4), anhydrous ethanol (5), TAG cottonseed

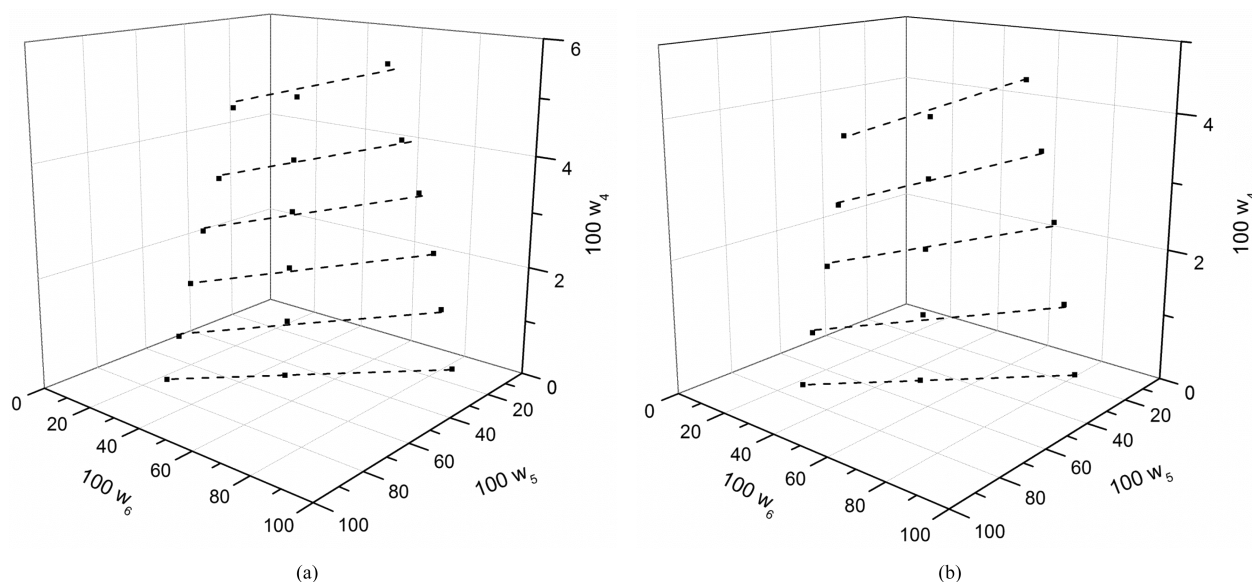
oil (6), TAG rice bran oil (7), and commercial oleic acid (8), with TAG corresponding to the triacylglycerols, DAG to the diacylglycerols from commercial mixture of mono- and diacylglycerols and MAG to the monoacylglycerols from commercial mixture of mono- and diacylglycerols.

The overall and the corresponding liquid–liquid phase compositions, in mass percentage for pseudoquinary systems, at 303.15 K and 318.15 K, are presented in Tables 4, 5, and 6. The global mass balance deviations for all systems studied varied within the range from 0.494 % to 0.002 %, ensuring the quality of experimental data.<sup>25</sup>

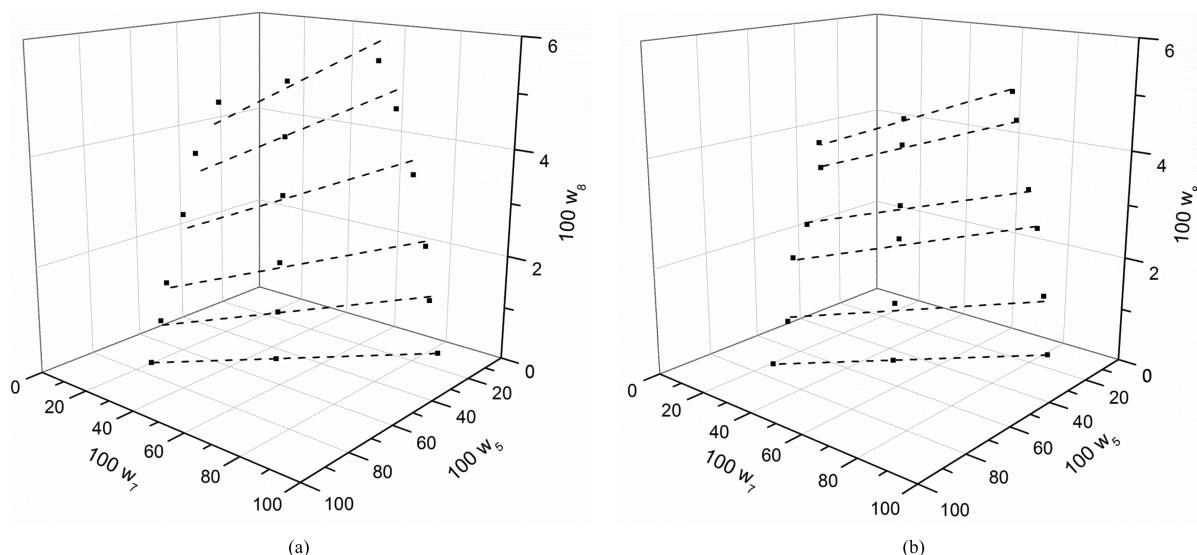
As aforementioned for the thermodynamic modeling, it is necessary to calculate the average molar masses of the pseudocomponents. In each system studied, some pseudocomponents, such as TAG and DAG are derived from oil and commercial mixture of mono- and diacylglycerols (Table 2). In the case of the system with soybean oil, TAG is derived from soybean oil and from commercial mixture. Based on Table 3, the average molar masses of TAG from soybean oil and commercial mixture are 872.37 g·mol<sup>-1</sup> and 861.90 g·mol<sup>-1</sup>, respectively. As the values are not exactly the same, it was calculated the average molar masses of TAG for each overall experimental composition, considering TAG derived from both sources. The values of the average molar masses of TAG in the overall composition were very close to the respectively average molar mass of TAG from soybean oil. DAG is also derived from soybean oil and from commercial mixture, and the average molar masses of DAG from soybean oil and commercial mixture are 618.00 g·mol<sup>-1</sup> and 605.29 g·mol<sup>-1</sup>, respectively. As the values are not so close, it was calculated the average molar masses of DAG for each overall experimental composition, considering DAG derived from both sources. The values of the average molar masses of DAG in the overall composition were very close to the respectively average molar mass of DAG from commercial mixture. Starting from these conclusions, the average molar mass of TAGs used in the thermodynamic modeling were the respective average molar masses of TAG from oils. The same procedure was used for DAGs. As MAG comes from only the commercial mixture, its average molar mass is presented in Table 3. The average molar



**Figure 1.** TAG soybean oil (1) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5). (a) at 303.15 K; (b) at 318.15 K; ■, experimental; ---, NRTL model.



**Figure 2.** TAG cottonseed oil (6) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5). (a) at 303.15 K; (b) at 318.15 K; ■, experimental; ---, NRTL model.



**Figure 3.** TAG rice bran oil (7) + DAG (2) + MAG (3) + commercial oleic acid (8) + anhydrous ethanol (5). (a) at 303.15 K; (b) at 318.15 K; ■, experimental; ---, NRTL model.

masses of commercial linoleic acid and commercial oleic acid were calculated from their respectively fatty acid compositions presented in Table 1, and the values were  $279.07 \text{ g}\cdot\text{mol}^{-1}$  and  $282.11 \text{ g}\cdot\text{mol}^{-1}$ , respectively. These results were used in the thermodynamic modeling for commercial fatty acids since the oils used in the systems are refined.

Table 7 presents the adjusted NRTL parameters, and the average deviations between the experimental and the calculated compositions (eq 6) for each investigated system are shown in Table 8.

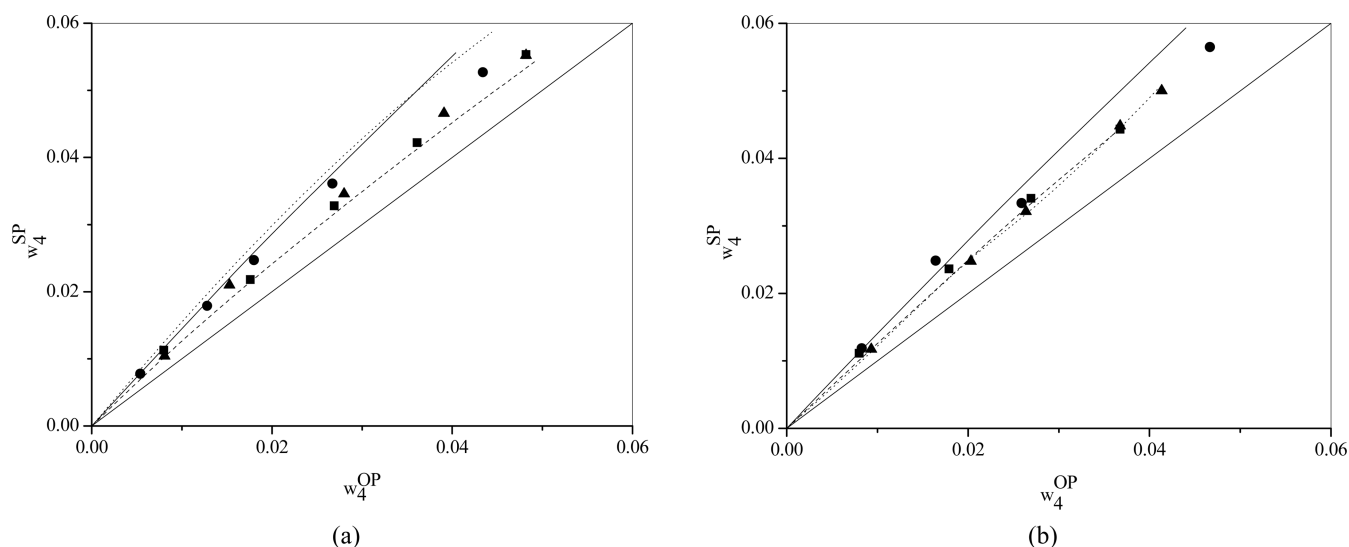
Figure 1 shows the experimental tie lines and those calculated using the NRTL model for the system containing TAG soybean oil (1) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5) at 303.15 K (a) and 318.15 K (b), respectively. Figure 2 shows the experimental data and those calculated by the NRTL model for system containing TAG cottonseed oil (6) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5) at 303.15 K (a) and 318.15 K

(b), respectively. Finally, Figure 3 shows the experimental tie lines and those calculated using the NRTL model for systems containing TAG rice bran oil (7) + DAG (2) + MAG (3) + commercial oleic acid (8) + anhydrous ethanol (5) at 303.15 K (a) and 318.15 K (b), respectively. A good alignment can be observed among phase compositions and overall composition in all figures. Apart from that, the corresponding low average deviations between the experimental and the calculated compositions for all systems, which range from 0.12 % to 0.97 % (Table 8), prove that the selected thermodynamic model was able to accurately describe the phase compositions for the systems studied in this work.

It can be noted and confirmed by several authors in the literature that, in liquid–liquid equilibrium of fatty systems, the increase in temperature and free fatty acid concentration lead to the increase in solubility between both phases.<sup>11,27–29</sup>

Figure 4 presents the distribution diagrams for the three systems at 303.15 K (a) and 318.15 K (b). In Figure 4a, it is





**Figure 4.** Distribution diagram at (a) 303.15 K and (b) 318.15 K for systems of TAG soybean oil (1) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5): ●, experimental; —, NRTL model; TAG cottonseed oil (6) + DAG (2) + MAG (3) + commercial linoleic acid (4) + anhydrous ethanol (5): ■, experimental; ---, NRTL model; TAG rice bran oil (7) + DAG (2) + MAG (3) + commercial oleic acid (8) + anhydrous ethanol (5): ▲, experimental; ···, NRTL model.

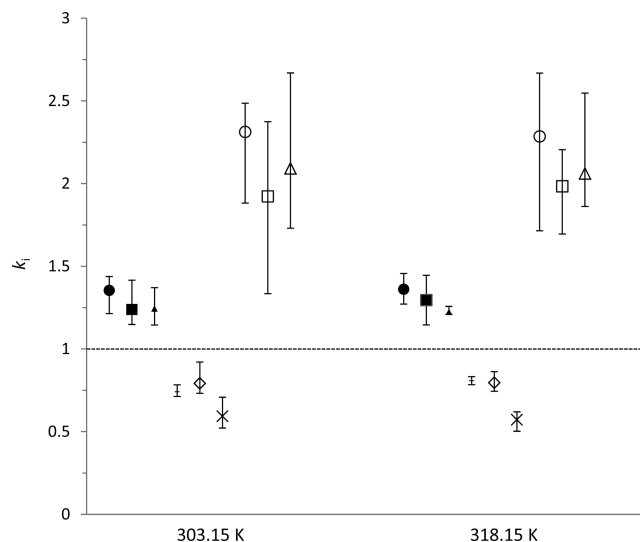
possible to observe that the commercial linoleic acid in cottonseed oil system and commercial oleic acid in rice bran oil system distribute in a similar way in both phases. The commercial linoleic acid in soybean oil system has a slightly preference to the solvent phase when compared to the fatty acid behavior in the other two systems. In Figure 4b, despite the small difference among the distribution of fatty acids in the different systems, it is possible to note a slightly preference for solvent phase as the following sequence: commercial linoleic acid in soybean oil system, commercial linoleic acid in cottonseed oil system and commercial oleic acid in rice bran oil system.

Another result that can be observed is the behavior of minority compounds in phases. This is represented by distribution coefficient calculated by eq 7:

$$k_i = \frac{w_i^{\text{SP}}}{w_i^{\text{OP}}} \quad (7)$$

where  $w_i^{\text{SP}}$  corresponds to the content of each commercial fatty acid, DAG, or MAG in the solvent phase and  $w_i^{\text{OP}}$  corresponds to the content of each commercial fatty acid, DAG, or MAG in the oil phase.

The distribution coefficients of DAG (Figure 5) were smaller than the unity, indicating the preference of DAG for the oil phase, besides, it was possible to observe in Figure 5 and Tables 4 and 5 that DAG concentration is slightly higher in the oil phase for the systems with refined soybean oil and cottonseed oil. In the case of system with refined rice bran oil, the DAG concentration is almost twice higher in the oil phase (Table 6), with distribution coefficient values close to 0.5. MAG prefers the solvent phase, being about two times more concentrated in that phase, as shown in Figure 5, with distribution coefficient values close to or higher than 2. The free fatty acid distribution coefficients, assumed to be commercial linoleic acid for refined soybean and cottonseed oils, and to be commercial oleic acid for rice bran oil, were higher than the unity showing that free fatty acids prefer the solvent phase, which is an important information to the liquid–liquid deacidification, as reported previously by some authors.<sup>7,30,31</sup> Based on Figure 5, at 303.15 K, it is possible to observe that the distribution coefficient of commercial linoleic acid in soybean oil system is slightly higher than the distribution coefficients of



**Figure 5.** Average distribution coefficient ( $k_i$ ) at 303.15 K and 318.15 K of: ●, linoleic acid; —, DAG, and ○, MAG in the system composed of TAG soybean oil + DAG + MAG + linoleic acid + ethanol; ■, linoleic acid; ◇, DAG, and □, MAG in the system composed of TAG cottonseed oil + DAG + MAG + linoleic acid + ethanol; ▲, oleic acid; ×, DAG, and △, MAG in the system composed of TAG rice bran oil + DAG + MAG + oleic acid + ethanol.

commercial linoleic acid in cottonseed oil system and of commercial oleic acid in rice bran oil system. At 318.15 K, as noted in Figure 4, the values of distribution coefficient of commercial fatty acids decreased as the following sequence: commercial linoleic acid in soybean oil system, commercial linoleic acid in cottonseed oil system and commercial oleic acid in rice bran oil system.

## CONCLUSIONS

Phase equilibrium data for liquid–liquid systems containing TAG of refined oils (soybean, cottonseed, and rice bran) + DAG + MAG + commercial fatty acids (linoleic and oleic) + anhydrous ethanol were measured in two temperatures (303.15 K and 318.15 K). The low deviations obtained in the global mass

balance indicate the good quality of the experimental data. The adjustment of the binary parameters of the NRTL model was representative to describe the liquid–liquid equilibrium of the systems studied, proven by the average deviation between the experimental and calculated values. The increase in temperature decreases the heterogeneous areas, and the free fatty acid concentrations increase the solubility of both liquid phases. The distribution coefficients of DAG were smaller than the unity, showing that DAG prefers the oil phase, besides the distribution coefficients of MAG and fatty acids were greater than the unity, showing that these components prefer the solvent phase.

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### Funding

The authors wish to acknowledge Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (process number 1089097), Fundação de Amparo a Pesquisa do Estado de São Paulo (process number 2008/56258-8) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (process numbers 483340/2012-0; 406856/2013-3; 305870/2014-9; 309780/2014-4) for the financial support.

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