Liquid−Liquid Equilibrium for Systems Composed of Grape Seed Oil + Oleic Acid + Ethanol + Water at (283.2, 290.7, and 298.2) K

Guilherme Sanaiotti, Jane Sélia R. Coimbra,* José Carlos Gomes, and Luis Antônio Minim

LPS, Separation Process Laboratory, Department of Food Technology, University of Viçosa (UFV), P. H. Rolfs Av., sn, 36570-000, Viçosa, MG, Brazil

This work presents experimental data of systems composed of grape seed oil + oleic acid + ethanol + water from (283.2 to 298.2) K. The solvent selectivity and oleic acid distribution coefficient were more affected by water content in the alcoholic solvent than by temperature. The enhancement of the water content in the solvent and the reduction of temperature within the studied ranges led to greater values of solvent selectivity. Nevertheless, greater oleic acid distribution coefficients were found as a result of the reductions in temperature and water content in the solvent.

Introduction

Grape seed oil has several applications in diverse industrial segments, ranging from use in salad dressings to cosmetics, aside from the most frequent utilizations. Although known to Europeans for centuries, this oil was not produced in considerable amounts until the twentieth century, largely due to the low oil content of the seeds as compared to other oleaginous raw materials. In many other countries, such as Brazil, the production of this oil is still insignificant, and grape seeds are considered a disposable coproduct by the majority of wineries.

The high content of linoleic acid commonly found in the grape seed oil is evidence of its potential as an edible oil in controlled diets, due to the fact that consumption of this fatty acid is associated with the reduction of cholesterol levels and prevention of cardiovascular and inflammatory diseases.[1]

A representative knowledge of crude grape seed oil acidity remains a subject of debate to this day. Böchzelt et al.[2] verified free fatty acid contents ranging from 0.14 % to 1.05 %, in mass, expressed as oleic acid, in mechanically extracted oils from seeds of seven distinct varieties of grapes. Despite the low acidity contents determined, higher values could be found depending on the storage conditions and extraction methods. Oils obtained from residual pressed cakes or by solvent extraction can have higher acidic values. There are reports of free fatty acid contents close to 3.00 %.[3]

The removal of free fatty acids, also known as deacidification, can be considered the most important operation in vegetable oil refining because the effect of the neutral oil losses in this procedure is significant on the process costs.[4] The presence of free fatty acids in the final product can also adversely affect oxidation stability, especially when encountered in high compositions of unsaturated free fatty acids typically found in grape seed oil.[5]

Deacidification is usually performed by chemical or physical refining in almost all vegetable oil industries. During chemical refining, losses are largely due to the formation of long chain carboxylates, which act as anionic surfactants, decreasing the interfacial tension at the oil−water interface,[6] consequently causing greater mass transfer of triacylglycerols to the water bulk. This effect is even more amplified when the degumming operation is skipped.

Physical refining requires high temperatures of (493 to 543) K and low pressures of (5 to 10) mmHg, demanding high initial and operating costs.[4] Once these high temperatures are reached, decomposition of compounds such as vitamins and antioxidants is favored, which is undesirable in the current market trend of edible vegetable oils.

Deacidification by countercurrent liquid−liquid extraction seems to be an attractive alternative to physical or chemical refining to achieve Codex Alimentarius quality specifications,[7] once it can be performed at mild temperature conditions and atmospheric pressure. Several studies suggest that hydrated ethanol is more appropriate for the deacidification of vegetable oils when compared to other short chain alcohols and various selective solvents such as acetone, furfural, ethyl acetate, and ethyl−methyl−ketone.[8–14] Results showed good solvent selectivity and free fatty acid distribution coefficients greater than unity.[8–11]

Rodrigues et al.[8] determined liquid−liquid equilibrium data for systems composed of refined grape seed oil + linoleic acid + ethanol + water at 298.2 K; however, equilibrium data at lower temperatures for systems containing crude grape seed oil are not available in the literature. Information about the effect of different temperatures on solvent selectivity and distribution coefficients of free fatty acids for such systems is not very well elucidated as well. Thus, this work presents experimental data of systems composed of grape seed oil + oleic acid + ethanol + water at (283.2, 290.7, and 298.2) K.

Experimental Section

Materials. In the present work, the components utilized in the experiment were given the following notations: crude grape seed oil (1), refined grape seed oil (2), oleic acid (3), ethanol (4), and water (5).

Crude and refined grape seed oils were used in this study as sources of triacylglycerols. Refined grape seed oil was purchased from Campestre (Brazil), and crude grape seed oil was extracted from a mixture of three different red seed varieties (Cabernet

---

* To whom correspondence should be addressed. E-mail: jcoimbra@ufv.br. Fax: +55-31-3899-2208. Phone: +55-31-3899-1618.

10.1021/je800034c CCC: $40.75

Sauvignon, Merlot, and Pinot Noir) with an expeller press (Ecirtec, model MPE-40).

Gas chromatography was used to determine fatty acid composition in commercial oleic acid (Synth, Brazil), refined, and crude grape seed oils. Prior to quantification, the samples were converted to methyl esters according to the IUPAC 2301 method.[15] A Shimadzu 17-A chromatograph equipped with a 0.20 μm, 100 m × 0.25 mm i.d. fused silica cyanopropylsiloxane column (Sigma, model SP-2560) and a flame ionization detector were used for the determination of the fatty acid compositions. The equipment was utilized under the following experimental conditions: hydrogen as the carrier gas at a rate of 0.65 $\text{mL}\cdot\text{min}^{-1}$, injection and detection temperature of 493.15 K, and column temperature of (465.15 to 478.15) K increasing at a rate of 1.5 $\text{K}\cdot\text{min}^{-1}$.

The methyl esters were identified by comparison with the retention times of external standards purchased from Sigma (USA), and the quantification was accomplished by area normalization. All measurements were performed in triplicate.

Anhydrous ethanol was purchased from Merck (Germany), with purity greater than 99.9 %. The hydrated ethanol solvents with water mass fractions of (4.00 and 5.58) % were then prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol. Water compositions in the oils and solvents were quantified by Karl Fischer titration (Schott, model Tritoline KF). The Karl Fischer reagent was purchased from Merck (Germany), which was regularly standardized with the Riedel de Haën Hydranal volumetric standard (Germany).

The free fatty acid mass fractions of crude and refined grape seed oils were used in the calculation of the overall composition of all tie lines, and water mass fractions were considered in data involving hydrated ethanol.

Experimental Procedure. Equilibrium cells, such those described by Silva et al.,[16] were used for determination of the liquid–liquid equilibrium. The components were weighted on an analytic balance (Denver instruments, model M310), accurate to ± 0.0001 g. The mixture was then vigorously agitated for 15 min with a magnetic stirrer (Fisatom, model 752A), and temperature was controlled by a thermostatic bath (Tecnal, model TE184), accurate to ± 0.1 K. After a clear and well-defined interface was formed (approximately 4 h later), samples of each phase were collected, and the oleic acid composition was determined by potentiometric titration (modified AOCS Ca 5a-40 method[17]) using a digital burette (Witeg, model Titerx 2000), accurate to ± 0.01 mL, and a pH meter (Marte, model MB10), accurate to ± 0.01.

According to prior results obtained from titration curves of 12 samples, with oleic acid mass fractions ranging from (0.03 to 4.82) %, the confidence interval for the mean pH corresponding to the equivalence point was found to be (10.62 ± 0.12). Therefore, titrations were carried out until pH 10.50 was reached to avoid possible overestimated responses and due to the fact that the determination of potentiometric titration curves, as exemplified in Figure 1, for all equilibrium samples would be an arduous and time demanding task.

Water content was determined by Karl Fischer titration (Schott, model Tritoline KF), accurate to ± 0.001 mL. The solvent was evaporated in an oven (Fanen, model 320SE) at atmospheric pressure and 383.2 K for 3 h, sufficient conditions for the remaining mixture to achieve a constant mass. The quantity of triacylglycerols was then found by calculating the difference.

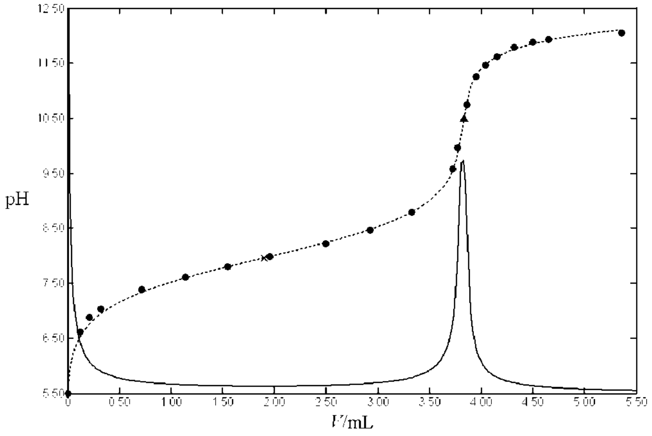

Figure 1. Potentiometric titration curve of crude grape seed oil utilizing 0.100 M $NaOH_{(aq)}$: ▲, equivalence point; ×, pK; ●, experimental data; ---, titration curve; —, first derivate.

Table 1. Fatty Acid Composition of Crude and Refined Grape Seed Oils

fatty acid		crude grape seed oil 100 w	refined grape seed oil 100 w
tetradecanoic	$C_{14:0}$[a]	0.05	0.10
hexadecanoic	$C_{16:0}$	6.62	6.80
cis-hexadec-9-enoic	$C_{16:1}$	0.10	0.10
heptadecanoic	$C_{17:0}$	0.05	0.05
cis-heptadec-9-enoic	$C_{17:1}$	0.05	1.10
octadecanoic	$C_{18:0}$	3.91	3.60
cis-octadec-9-enoic	$C_{18:1}$	14.75	26.89
cis,*cis*-octadeca-9,12-dienoic	$C_{18:2}$	73.76	59.97
all-*cis*-octadeca-9,12,15-trienoic	$C_{18:3}$	0.30	0.40
icosanoic	$C_{20:0}$	0.20	0.20
cis-icos-9-enoic	$C_{20:1}$	0.10	0.20
docosanoic	$C_{22:0}$	0.05	0.40
tetracosanoic	$C_{24:0}$	0.05	0.20

[a] $C_{x:y}$: x, number of carbons; y, number of double bonds.

Table 2. Fatty Acid Composition of Commercial Oleic Acid

fatty acid		molar mass $\text{g}\cdot\text{mol}^{-1}$	100x	100 w
decanoic	$C_{10:0}$[a]	172.26	0.16	0.10
dodecanoic	$C_{12:0}$	200.32	0.26	0.18
tetradecanoic	$C_{14:0}$	228.37	3.61	2.98
hexadecanoic	$C_{16:0}$	256.42	7.31	6.78
cis-hexadec-9-enoic	$C_{16:1}$	254.41	6.23	5.73
heptadecanoic	$C_{17:0}$	270.45	0.31	0.31
cis-heptadec-9-enoic	$C_{17:1}$	268.43	0.85	0.82
octadecanoic	$C_{18:0}$	284.48	2.86	2.95
cis-octadec-9-enoic	$C_{18:1}$	282.46	59.79	61.12
trans-octadec-9-enoic	$C_{18:1}$	282.46	4.55	4.66
cis,*cis*-octadeca-9,12-dienoic	$C_{18:2}$	280.45	11.12	11.28
trans,*trans*-octadeca-9,12-dienoic	$C_{18:2}$	280.45	0.72	0.73
all-*cis*-octadeca-9,12,15-trienoic	$C_{18:3}$	278.43	1.12	1.13
all-*trans*-octadeca-9,12,15-trienoic	$C_{18:3}$	278.43	0.39	0.39
icosanoic	$C_{20:0}$	312.53	0.10	0.11
cis-icos-9-enoic	$C_{20:1}$	310.51	0.31	0.35
cis,*cis*-icos-11,14-dienoic	$C_{20:2}$	308.50	0.09	0.10
all-*cis*-icosa-5,8,11,14-tetraenoic	$C_{20:4}$	304.47	0.09	0.10
docosanoic	$C_{22:0}$	340.58	0.08	0.10
tetracosanoic	$C_{24:0}$	368.64	0.04	0.05

[a] $C_{x:y}$: x, number of carbons; y, number of double bonds.

All experiments were repeated three times, aiming to obtain a better representation of the average phase compositions. The type A standard uncertainties[18] of the equilibrium data ranged from (0.01 to 0.16) % for triacylglycerols, (0.01 to 0.04) % for oleic acid, (0.01 to 0.16) % for ethanol, and (0.01 to 0.08) % for water, being that the lowest figures were attained for the lowest compositions. Results indicated good precision and repeatability of the equilibrium data.

Table 3. Liquid−Liquid Equilibrium Data for Systems of Crude Grape Seed Oil (1) + Oleic Acid (3) + Ethanol (4) + Water (5) at 283.2 K

	overall composition				alcoholic phase				oil phase			
100 w_{5s}[a]	100 w_1	100 w_3	100 w_4	100 w_5	100 w_1	100 w_3	100 w_4	100 w_5	100 w_1	100 w_3	100 w_4	100 w_5
0.00	45.01	4.99	50.00		7.18	5.91	86.91		80.15	4.12	15.73	
	46.02	3.99	49.99		6.36	4.74	88.90		81.97	3.28	14.75	
	47.00	3.00	50.00		5.80	3.59	90.61		83.63	2.44	13.93	
	47.99	2.00	50.01		5.27	2.42	92.31		85.32	1.65	13.03	
	49.03	0.98	49.99		4.77	1.21	94.02		87.10	0.82	12.08	
	12.97	0.05	86.98		4.01	0.05	95.94		88.97	0.05	10.98	
4.00	44.96	5.00	47.99	2.05	2.25	5.47	88.23	4.05	85.38	4.49	9.89	0.24
	45.94	4.00	48.00	2.06	1.97	4.37	89.52	4.14	86.88	3.58	9.32	0.22
	46.94	3.01	47.99	2.06	1.81	3.31	90.68	4.20	88.28	2.68	8.83	0.21
	47.93	1.99	48.02	2.06	1.65	2.26	91.87	4.22	89.92	1.75	8.14	0.19
	48.94	1.00	48.00	2.06	1.49	1.15	93.12	4.24	91.23	0.89	7.71	0.17
	12.93	0.05	83.52	3.50	1.20	0.05	94.76	3.99	92.76	0.05	7.04	0.15
5.58	44.96	5.00	47.20	2.84	1.41	5.26	87.73	5.60	85.95	4.74	9.02	0.29
	45.93	4.01	47.21	2.85	1.31	4.23	88.78	5.68	87.51	3.80	8.42	0.27
	46.95	3.00	47.20	2.85	1.17	3.16	89.95	5.72	89.13	2.84	7.78	0.25
	47.94	2.00	47.21	2.85	1.06	2.14	90.88	5.92	90.59	1.86	7.32	0.23
	48.94	0.98	47.23	2.85	1.00	1.08	91.98	5.94	92.00	0.93	6.88	0.19
	12.92	0.05	82.16	4.87	0.90	0.05	93.42	5.63	93.44	0.05	6.34	0.17

[a] w_{5s}: water mass fraction in the alcoholic solvent.

Table 4. Liquid−Liquid Equilibrium Data for Systems of Crude Grape Seed Oil (1) + Oleic Acid (3) + Ethanol (4) + Water (5) at 290.7 K

	overall composition				alcoholic phase				oil phase			
100 w_{5s}[a]	100 w_1	100 w_3	100 w_4	100 w_5	100 w_1	100 w_3	100 w_4	100 w_5	100 w_1	100 w_3	100 w_4	100 w_5
0.00	44.99	5.01	50.00		8.83	5.86	85.31		78.06	4.22	17.72	
	45.96	4.01	50.03		7.72	4.68	87.60		79.84	3.37	16.79	
	47.00	3.01	49.99		7.06	3.58	89.36		81.60	2.53	15.87	
	48.00	2.03	49.97		6.35	2.43	91.22		83.38	1.68	14.94	
	49.01	1.02	49.97		5.70	1.24	93.06		85.30	0.85	13.85	
	12.99	0.05	86.96		4.71	0.05	95.24		87.37	0.05	12.58	
4.00	44.92	5.01	48.02	2.05	2.70	5.45	87.73	4.12	83.90	4.52	11.28	0.30
	45.91	3.99	48.04	2.06	2.37	4.39	89.08	4.16	85.56	3.57	10.60	0.27
	46.92	3.00	48.02	2.06	2.19	3.29	90.32	4.20	87.15	2.71	9.89	0.25
	47.93	2.01	48.00	2.06	1.99	2.21	91.55	4.25	88.79	1.80	9.19	0.22
	48.96	0.99	47.99	2.06	1.82	1.12	92.77	4.29	90.30	0.90	8.60	0.20
	12.97	0.05	83.49	3.49	1.54	0.05	94.42	3.99	91.76	0.05	8.02	0.17
5.58	44.93	4.97	47.25	2.85	1.79	5.20	87.43	5.58	84.89	4.73	10.05	0.33
	45.92	4.03	47.20	2.85	1.63	4.22	88.49	5.66	86.39	3.83	9.47	0.31
	46.93	3.00	47.22	2.85	1.46	3.18	89.64	5.72	88.16	2.84	8.70	0.30
	47.96	2.00	47.19	2.85	1.31	2.13	90.71	5.85	89.76	1.88	8.10	0.26
	48.95	0.98	47.22	2.85	1.19	1.06	91.82	5.93	91.23	0.92	7.61	0.24
	12.91	0.05	82.17	4.87	1.07	0.05	93.26	5.62	92.66	0.05	7.09	0.20

[a] w_{5s}: water mass fraction in the alcoholic solvent.

To test the quality and accuracy of the results obtained, the mass balance of each component was evaluated according to a modified procedure developed by Marcilla et al.[19] The relative deviation ($Er_{i,N}$) of the component i in each N tie line was calculated according to

$$Er_{i,N} = \frac{|m_N^{\mathrm{OC}}(w_{i,N}^{\mathrm{OC}}) - m_N^{\mathrm{OP}}(w_{i,N}^{\mathrm{OP}}) - m_N^{\mathrm{AP}}(w_{i,N}^{\mathrm{AP}})|}{m_N^{\mathrm{OC}}(w_{i,N}^{\mathrm{OC}})} \qquad (1)$$

where $w_{i,N}^{\mathrm{OC}}$ is the mass fraction of the component i associated to the overall mass composition m_N^{OC}, both being gravimetrically attained. m_N^{AP} and m_N^{OP} are, respectively, the masses of the alcoholic and oil phases, calculated using the procedure developed by Marcilla et al.[19] $w_{i,N}^{\mathrm{AP}}$ and $w_{i,N}^{\mathrm{OP}}$ are the mass fractions of the component i in the alcoholic and oil phases, experimentally determined.

The relative deviations ($Er_{i,N}$) varied within the following ranges: (0.00 to 0.01) % for triacylglycerols, (0.00 to 2.47) % for oleic acid, (0.00 to 0.01) % for ethanol, and (0.01 to 4.79) % for water, being that the lowest values were obtained for the greatest compositions. The relative deviations attained between the sum of ($m_N^{\mathrm{OP}} + m_N^{\mathrm{AP}}$) and m_N^{OC} were lower than 0.09 %, with an average value of 0.03 %, confirming the high quality of the experimental data.

Results and Discussion

The refined and cold pressed grape seed oils presented, respectively, free fatty acid mass fractions of 0.03 % and 0.38 %, expressed as oleic acid. The water mass fractions of the crude and refined grape seed oils were determined as 0.12 % and 0.03 %.

Characterizations of the crude and refined grape seed oils in fatty acid compositions are presented in Table 1. It can be seen that the fatty acid compositions of the oil samples used in this study are within the Codex Alimentarius identity specifications, certifying also that the oil samples were actually derived from grape (*Vitis vinifera*) seeds.[7] The high content of linoleic acid (*cis*,*cis*-octadeca-9,12-dienoic acid) found in the crude grape seed oil is also revealed in Table 1.

Table 2 presents the fatty acid composition of the commercial oleic acid. The average molar mass of the commercial oleic acid, estimated from its molar composition, was 276.31 g·mol^{-1}. This value was used to calculate the mass fraction of this component in the equilibrium data.

Table 5. Liquid−Liquid Equilibrium Data for Systems of Refined Grape Seed Oil (2) + Oleic Acid (3) + Ethanol (4) + Water (5) at 298.2 K

	overall composition				alcoholic phase				oil phase			
$100\ w_{5s}$[a]	$100\ w_2$	$100\ w_3$	$100\ w_4$	$100\ w_5$	$100\ w_2$	$100\ w_3$	$100\ w_4$	$100\ w_5$	$100\ w_2$	$100\ w_3$	$100\ w_4$	$100\ w_5$
0.00	44.71	4.99	50.30		10.43	5.72	83.85		75.32	4.30	20.38	
	46.01	3.99	50.00		9.27	4.60	86.13		77.35	3.41	19.24	
	46.97	3.00	50.03		8.54	3.45	88.01		79.25	2.62	18.13	
	47.94	1.99	50.07		7.49	2.33	90.18		81.22	1.72	17.06	
	48.96	0.98	50.06		6.82	1.17	92.01		83.37	0.84	15.79	
	29.94	0.01	70.05		5.96	0.01	94.03		85.34	0.01	14.65	
4.00	45.12	4.99	47.88	2.01	3.52	5.38	87.25	3.85	82.32	4.52	12.80	0.36
	45.97	4.02	47.99	2.02	3.09	4.33	88.66	3.92	83.97	3.67	12.03	0.33
	47.04	3.00	47.95	2.01	2.90	3.24	89.90	3.96	85.67	2.73	11.30	0.30
	47.85	1.96	48.17	2.02	2.60	2.14	91.25	4.01	87.30	1.77	10.65	0.28
	49.01	0.98	47.99	2.02	2.33	1.09	92.56	4.02	88.95	0.91	9.89	0.25
	34.91	0.01	62.47	2.61	2.16	0.01	93.80	4.03	90.38	0.01	9.38	0.23
5.58	44.99	4.98	47.22	2.81	2.44	5.24	86.80	5.52	83.41	4.74	11.44	0.41
	46.02	4.00	47.18	2.80	2.22	4.22	88.00	5.56	85.05	3.85	10.74	0.36
	46.98	2.99	47.22	2.81	2.03	3.14	89.19	5.64	86.63	2.85	10.19	0.33
	47.93	2.01	47.25	2.81	1.76	2.13	90.43	5.68	88.24	1.93	9.53	0.30
	49.00	1.02	47.18	2.80	1.66	1.13	91.43	5.78	89.78	0.97	8.97	0.28
	44.98	0.02	51.92	3.08	1.65	0.02	92.53	5.80	91.37	0.02	8.36	0.25

[a] w_{5s}: water mass fraction in the alcoholic solvent.

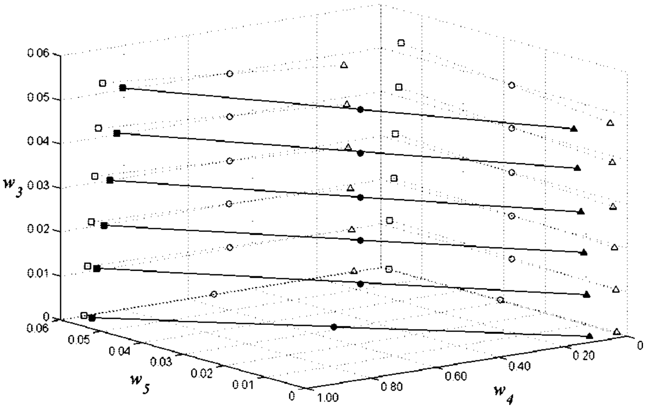

Figure 2. System of refined grape seed oil (2) + oleic acid (3) + ethanol (4) + water (5) at 298.2 K, $100\ w_{5s} = 5.58$: ●, overall composition; ▲, oil phase; −, tie line.

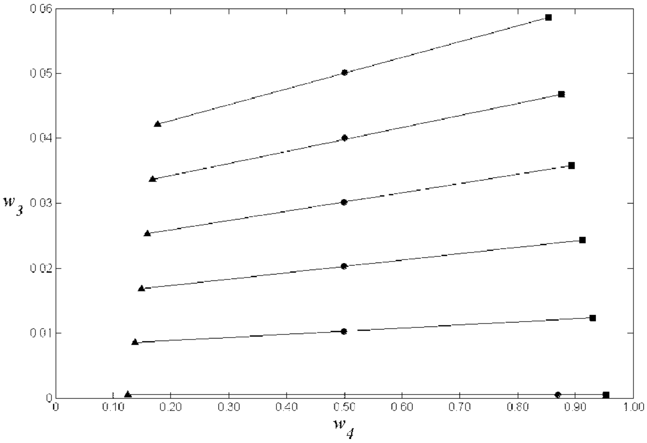

Figure 3. System of crude grape seed oil (1) + oleic acid (3) + ethanol (4) at 290.7 K: ●, overall composition; ■, alcoholic phase; ▲, oil phase; −, tie line.

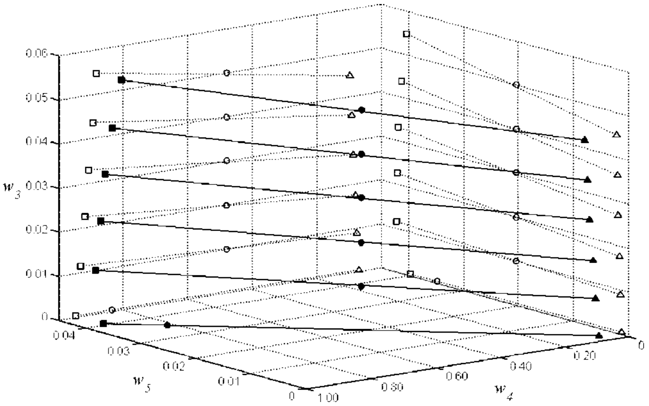

Figure 4. System of crude grape seed oil (1) + oleic acid (3) + ethanol (4) + water (5) at 283.2 K, $100\ w_{5s} = 4.00$: ●, overall composition; ■, alcoholic phase; ▲, oil phase; −, tie line.

The overall compositions and the corresponding tie lines for the studied systems are presented in Tables 3, 4, and 5. All compositions are expressed in mass fractions.

The alignment between the phases and overall compositions was evaluated by the determination coefficient (R^2) of all tie lines. High experimental accuracy was confirmed from values ranging from 0.97 to 1.00, as also verified in Figures 2, 3, and 4.

According to Treybal[20] and Godfrey and Slater,[21] the solvent selectivity (β_{21}) and the distribution coefficient of the solute (m_2) have an important role in the selection of solvents for the liquid−liquid extraction process. The parameters β_{21} and m_2 are, respectively, defined as

$$\beta_{21} = \frac{w_2^{\mathrm{AP}} w_1^{\mathrm{OP}}}{w_2^{\mathrm{OP}} w_1^{\mathrm{AP}}} \tag{2}$$

$$m_2 = \frac{w_2^{\mathrm{AP}}}{w_2^{\mathrm{OP}}} \tag{3}$$

where w_1 and w_2 represent the mass fractions of triacylglycerols and oleic acid and the superscripts AP and OP stand for alcoholic and oil phases, respectively.

To verify the effect of temperature (T) and the solvent's water mass fraction (w_{5s}) in parameters m_2 and β_{21}, response surface methodology was carried out using eq 4,[22,23] a complete second-order model with linear interaction for factors T and w_{5s}. The models were adjusted from coded values of the variables T and w_{5s}.

$$Y = C_0 + C_1 w_{5s} + C_2 w_{5s}^2 + C_3 T + C_4 T^2 + C_5 T w_{5s} \tag{4}$$

The C_i regression coefficients were then estimated by the least-squares fitting method and evaluated using the t test at 5

Table 6. Estimated Models Coefficients for Parameters m_2 and β_{21}

	C_i[a]	SE[b]	t	p-value	C_i[a]	SE[b]	t	p-value
C_0	1.2858	0.0071	181.23	0.000	43.9100	1.6210	27.084	0.000
C_1	−0.1427	0.0039	−36.94	0.000	26.1810	1.8980	13.791	0.000
C_2	−0.0253	0.0085	−2.98	0.004				
C_3	−0.0331	0.0039	−8.44	0.000	−11.9090	1.9860	−5.998	0.000
C_5	0.0233	0.0046	5.07	0.000	−7.6280	2.3250	−3.281	0.002

[a] Coefficient values. [b] Standard errors of coefficients.

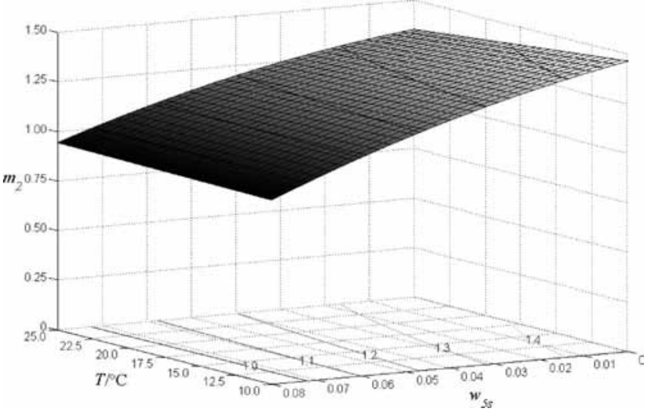

Figure 5. Effect of the water mass fraction in the solvent (w_{5s}) and temperature (T) in the oleic acid distribution coefficient (m_2).

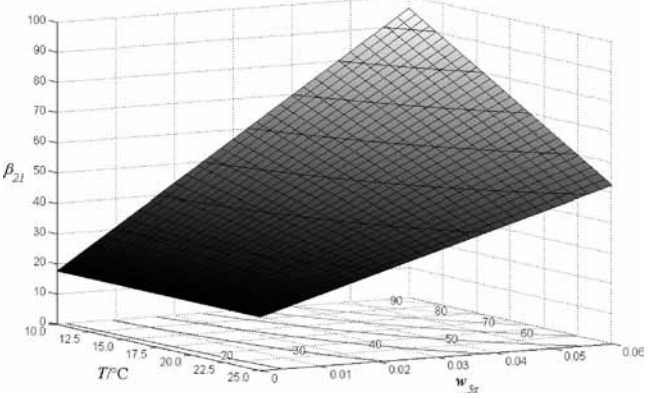

Figure 6. Effect of the water mass fraction in the solvent (w_{5s}) and temperature (T) on the selectivity (β_{21}).

% of significance. The final results of the regressions analysis are presented in Table 6. The adjusted models for parameters m_2 and β_{21} had determination coefficients (R^2) of 0.97 and 0.83, respectively.

It can be observed in Figure 5 that, for the range of studied variables, the increase in w_{5s} caused the decrease of the oleic acid distribution coefficient in higher proportions than T. The reduction of T, on the other hand, led to an increase of m_2 in all the levels of w_{5s}. This was probably due to lower reduction of the solubility of free fatty acids in the alcoholic phase when compared to the oil phase. However, in higher values of w_{5s}, the effect of T was revealed to be smaller.

Gonçalves et al.[7] reported distribution coefficients of oleic acid ranging from 0.80 to 0.92 for systems composed of corn oil + oleic acid + ethanol + water at 298.2 K, with water mass fractions of 8.00 % in the alcoholic solvent. For the given solvent water content and temperature, an oleic acid distribution coefficient of 0.93 was found, according to eq 4 and coefficients presented in Table 6 for m_2.

It can be seen in Figure 6 that w_{5s} has a greater effect than T on the solvent selectivity for the systems studied. The increase of w_{5s} resulted in a significant enhancement of all systems selectivity. This behavior can be explained by the increase and reduction of the triacylglycerol compositions in the oil and alcoholic phases, respectively. This synergic effect, allied to small modifications in the compositions of the oleic acid in both phases, led to higher values of selectivity. Although T had a greater effect at higher compositions of water in the solvent, its reduction caused an increase in the system selectivity at all levels of w_{5s}.

The high mass composition of water in the alcoholic solvent and low temperature used in this study were satisfactory, according to response surface methodology, for use in a liquid−liquid extraction process once, for such conditions, high solvent selectivity and oleic acid distribution coefficients greater than unity were found. This would provide lower losses of neutral grape seed oil in a deacidification process using countercurrent liquid−liquid extraction columns.

Conclusions

The addition of water in the alcoholic solvent increased the selectivity of all systems studied without compromising the oleic acid distribution coefficient, once values greater than unity were determined in all treatments. The reduction of temperature increased the selectivity of all systems, even more so in alcoholic solvents with high water compositions, and caused the enhancement of the oleic acid distribution coefficient. However, in the specific case of the grape seed oil, due to its higher commercial value, it is presumed that greater energy expenses to operate in lower temperatures could be overcome by smaller neutral oil losses.

Acknowledgment

The authors would like to thank the Miolo Winery, whom kindly supplied grape seeds, for the accomplishment of this work.

Literature Cited

(1) Simopoulos, A. P.; Cleland, L. G. Omega-6/Omega-3 Essential Fatty Acid Ratio: The Scientific Evidence. *J. Hum. Nutr. Dietet.* **2003**, *17*, 165–166.

(2) Böchzelt, H.; Graf, N.; Haas, W.; Lomsek, J.; Pöltl, G.; Wagner, S. Wertstoffgenerierung aus dem "Abfallprodukt". *Traubentrester*; Joanneum Research: Graz, 2003.

(3) Martinenghi, G. B. *Chimica e Tecnologia Degli Oli, Grassi e Derivati*, 2nd ed.; Ulrico Hoepli: Milano, 1948.

(4) Lo, T. C.; Baird, M. H.; Hanson, C. *Handbook of Solvent Extraction*; John Wiley & Sons: New York, 1983.

(5) Araújo, J. M. A. Química de Alimentos. *Teoria e Prática*, 2nd ed.; Editora UFV: Viçosa, 1999.

(6) Shaw, D. J. *Introduction to Colloid and Surface Chemistry*; Butterworth: London, 1970.

(7) *Codex Alimentarius. Codex Standard for Named Vegetable Oils, Codex Stan-210 (Amended 2003)*; Codex Alimentarius: Rome, 2003.

(8) Rodrigues, C. E. C.; Filipini, A.; Meirelles, A. J. A. Phase Equilibrium for Systems Composed by High Unsatured Vegetable Oils + Linoleic Acid + Ethanol + Water at 298.2 K. *J. Chem. Eng. Data* **2006**, *51*, 15–21.

(9) Gonçalves, C. B.; Batista, E.; Meirelles, A. J. A. Liquid−Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15K. *J. Chem. Eng. Data* **2002**, *47*, 416–420.

(10) Rodrigues, C. E. C.; Pessôa Filho, P. A.; Meirelles, A. J. A. Phase equilibrium for the system rice bran oil + fatty acids + ethanol + water + γ oryzanol + tocols. *Fluid Phase Equilib.* **2004**, *216*, 271–283.

(11) Batista, E.; Monnerat, S.; Kato, K.; Stragevich, L.; Meirelles, A. J. A. Liquid−Liquid Equilibrium for Systems of Canola oil, Oleic acid, and Short Chain Alcohols. *J. Chem. Eng. Data* **1999**, *44*, 1360–1364.

(12) Shah, K. J.; Venkatesan, T. K. Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils. *J. Am. Oil Chem. Soc.* **1989**, *66*, 783–787.

(13) Kim, S.; Kim, C.; Cheigh, H.; Yoon, S. Effect of Caustic Refining, Solvent Refining and Steam Refining on the Deacidification and Color of Rice Bran Oil. *J. Am. Oil Chem. Soc.* **1985**, *62*, 1492–1495.

(14) Thomopoulos, C. Méthode de désacidification des huiles par solvent sélectif. *Rev. Fr. Corps Gras.* **1971**, *18*, 143–150.

(15) *IUPAC. Standard methods for analysis of oils, fats and derivatives*, 7th ed.; Blackwell Scientific Publications, 1987; IUPAC Method 2.301; Report of IUPAC Working Group WG 2/87.

(16) Silva, L. H. M.; Coimbra, J. S. R.; Meirelles, A. J. A. Equilibrium Phase Behavior of Poly(ethylene glycol) + Potassium Phosphate + Water Two Phase Systems at Various pH and Temperatures. *J. Chem. Eng. Data* **1997**, *42*, 398–401.

(17) *AOCS. Official methods and recommended practices of the American Oil Chemists' Society*, 3rd ed.; AOCS Press: Champaign, IL, 1988.

(18) Taylor, B. N.; Kuyatt, C. E. *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results*; NIST Technical Note 1297, 1994.

(19) Marcilla, A.; Ruiz, F.; García, A. N. Liquid-Liquid-Solid Equilibria of Quartenary System Water-Ethanol-Acetone-Sodium Chloride at 25°C. *Fluid phase Equilib.* **1995**, *112*, 273–289.

(20) Treybal, R. E. *Liquid Extraction*, 2nd ed.; McGraw Hill: New York, 1963.

(21) Godfrey J. C.; Slater, M. J. *Liquid-liquid extraction equipment*; John Wiley & Sons: Chichester, 1994.

(22) Box, G. E. P.; Hunter W. G.; Hunter J. S. *Statistics for experimenters: an introduction to designs, data analysis and model building*; John Wiley & Sons: New York, 1978.

(23) Box, G. E. P.; Drapper, N. R. *Empirical Model-Building and Response Surfaces*; John Wiley & Sons: New York, 1987.

Received for review January 13, 2008. Accepted April 29, 2008. The authors wish to recognize the National Counsel of Technological and Scientific Development (CNPq) and The Research Support Foundation of the state of Minas Gerais (FAPEMIG) for their financial support.

JE800034C