Liquid−Liquid Equilibrium for Systems of Canola Oil, Oleic Acid, and Short-Chain Alcohols

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Vegetable oils can be deacidified by liquid−liquid extraction. The difference in polarity between the triglycerides, the principal components of the oil, and the solvent guarantees the formation of two phases and permits the removal of free fatty acids. A knowledge of the equilibrium between the phases of such systems is important, however, if adequate equipment for the implementation of the process is to be designed. The present paper establishes experimental data for systems of canola oil, oleic acid, and alcohols, subsequently adjusting the NRTL and UNIQUAC models to them for the calculation of activity coefficients. The results show the good descriptive quality of the models.

Introduction

Crude vegetable oils contain impurities, especially free fatty acids, yet the presence of these compounds can adversely affect oil quality and stability to oxidation. Most edible oils are produced by alkaline refining (Antoniassi et al., 1998), since this is a highly versatile process applicable for all raw materials; however, it can result in great losses of the neutral oil.

For highly acidic oils, physical refining is also a possibility, as it results in less loss of neutral oil than the traditional process, but more energy is consumed. The process also has certain limitations, since its application is limited to specific raw materials; moreover, the finished product is subject to undesirable alterations in color and a reduction of stability to oxidation (Antoniassi et al., 1998).

Another possible alternative to reduce energy consumption without loss of natural components is deacidification through liquid−liquid extraction, as this process is carried out at room temperature and atmospheric pressure. According to Thomopoulos (1971), this process is based on the difference in solubility of free fatty acids and neutral triglycerides in the solvent, as well as on the difference in boiling points of the solvent and the fatty acids during subsequent separation.

Deacidification of vegetable oils can be conducted using various selective solvents such as acetone, furfural, ethyl acetate, propanol, 2-propanol, butanol, ethanol, methanol, and ethyl-methyl-cetone, although ethanol has been suggested to be the best solvent for the process (Thomopoulos, 1971). Experimental data relating to the equilibrium of such systems are scarce in the literature, despite the necessity for the study and design of equipment which make industrial-scale liquid−liquid extraction feasible for the refining of oils.

The present paper determines liquid−liquid equilibria data for systems of canola oil, oleic acid, and short-chain alcohols at different temperatures, focusing on the effect of the structure of the solvent on the formation of the heterogeneous area and on the selectivity, as well as the distribution of oleic acid in the phases. The parameters of the NRTL and UNIQUAC models were then adjusted to the experimental data for the description of the liquid−liquid equilibrium phases.

Materials

Refined canola oil of the Purilev brand was utilized as a source of triglycerides, and commercial oleic acid of the Riedel−deHaën brand as the source of fatty acids. An initial study determined the chemical composition of these reagents.

The canola oil was analyzed by gas chromatography of the fatty acid methyl esters to determine the fatty acid composition. The official method (1−62) of the AOCS (1988) was adopted, and a Sigma 3B (Perkin-Elmer) gas chromatograph with a flame ionization detector and an integrator was used under the following experimental conditions: stainless steel column with 1/8 in. external diameter and 4 m length, packed with 10% Silar 10C (10% Cianopropilsiloxane in Chromosorb W), nitrogen as the carrier gas at a rate of 25 mL/min, an injection temperature of 225 °C, a column temperature of 175 °C, and a detection temperature of 225 °C. Samples were prepared in the form of fatty acid methyl esters according to the methodology developed by Hartman and Lago (1973).

The fatty acid composition of the canola oil is presented in Table 1.

From this fatty acid composition it was possible to determine the probable triglyceride composition of the oil (Table 2) by using the computational method developed by Antoniosi Filho et al. (1995). For this transition, two aspects should be considered. In first place, the principal triglyceride represents the component of greatest concentration in the isomer set with *x* carbons and *y* double bonds. For this reason, some fatty acids which appear in Table l (M, Po, A, B, E) do not appear explicitly in Table 2; for example, the triglyceride PPoS is part of the 50:1 group, with a principal triglyceride of PPO. Moreover, groups with a total concentration of triglycerides less than 0.5% were ignored.

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Table 1. Fatty Acid Composition of Canola Oil

symbol	fatty acid		M^b (g·mol^{-1})	% molar	% mass
M	miristic	C14:0[a]	228.38	0.0575	0.0469
P	palmitic	C16:0	256.43	7.3757	6.7565
Po	palmitoleic	C16:1	254.41	0.1910	0.1736
S	stearic	C18:0	284.48	2.0964	2.1305
O	oleic	C18:1	282.47	48.0179	48.4533
Li	linoleic	C18:2	280.45	31.9683	32.0275
Le	linolenic	C18:3	278.44	9.2860	9.2365
A	arachidic	C20:0	312.54	0.4809	0.5369
B	behenic	C22:0	340.59	0.2960	0.3602
E	erucic	C22:1	338.58	0.2303	0.2785

[a] In C*x*:*y*, x = number of carbons, and y = number of double bonds. [b] M = molecular weight.

Table 2. Probable Triglyceride Composition of Canola Oil

group	principal triglyceride	M (g·mol^{-1})	% molar	% mass
50:1[a]	PPO	833.37	0.7558	0.7185
50:2	PPLi	831.35	0.5896	0.5591
52:2	POO	859.40	5.7515	5.6384
52:3	POLi	857.39	7.4897	7.3253
52:4	PLiLi	855.37	4.7095	4.5953
52:5	PLiLe	853.36	1.5166	1.4763
54:2	SOO	887.46	1.6612	1.6817
54:3	OOO	885.44	13.5808	13.7172
54:4	OOLi	883.43	24.2201	24.4078
54:5	OLiLi	881.41	22.3229	22.4445
54:6	OLiLe	879.40	12.3093	12.3481
54:7	LiLiLe	877.38	0.8564	0.8571
54:8	LiLeLe	875.36	4.2368	4.2306
total			100.0000	100.0000

[a] In *X*:*Y*, X = number of carbons (except carbons of glycerol), Y = number of double bonds.

Table 3. Fatty Acid Composition of Riedel−deHaën Oleic Acid

fatty acid	% molar	% mass
M	1.8793	1.5427
P	4.8073	4.4311
Po	6.8541	6.2679
S	1.5490	1.5839
O	80.1066	81.3350
Li	4.3664	4.4017
Le	0.4373	0.4377

The average molecular weight calculated for the canola oil was 876.6339 g·mol^{-1}; this oil also has a residual acidity of 0.06%, expressed as oleic acid.

The fatty acid methyl esters of the Reidel−deHaën oleic acid were also analyzed by gas chromatography, using the methodology described above. The fatty acid composition is presented in Table 3. The average molecular weight of the oleic acid was 278.2067 g·mol^{-1}. The solvents used were methanol, ethanol, 2-propanol, and *n*-propanol, all from Merck, with a purity greater than 99.5%.

Experimental Procedure

For the determination of liquid−liquid equilibrium data, equilibrium cells such as those suggested by Silva et al. (1997) were used. The cell temperature was regulated with a thermostatic bath (Cole Parmer, model 12101-15, accurate to ±0.01 °C), and the components were weighed on an A200 S Sartorius analytic balance, accurate to 0.0001 g. The mixture was stirred briskly with a magnetic stirrer (FISATOM, model 752A) for at least 15 min and left to rest for 4 h. After this treatment, the two phases became clear and transparent, and the interface was well defined.

The quantity of fatty acids was determined using potentiometric titration (modified AOCS method Ca 5a-40, 1977) with an automatic buret (Dosimat 715 model from Metrohm); the solvent was determined by evaporation in an EDG vacuum oven (Model EIV-1). The water concentration was determined by Karl Fisher titration. Having determined the concentration of fatty acids and the solvent, the concentration of triglycerides was obtained by difference. All measurements were performed in triplicate, and the standard deviations were ±0.081% for the canola oil, ±0.066% for oleic acid, ±0.027% for alcohols, and ±0.038% for water.

Results

Tables 4−8 present the overall experimental composition of the mixtures and the corresponding tie lines for the systems of interest. All concentrations are expressed as percentage of mass.

Modeling

The experimental equilibrium data were used to adjust the parameters of the NRTL and UNIQUAC models for the calculation of activity coefficients. Due to the large difference in molecular weights between the components in the systems studied, the mass fraction was used as the unit of concentration, a procedure already utilized by Oishi and Prausnitz (1978) for the calculation of the activity of a solvent in polymeric solutions with the UNIQUAC and UNIFAC methods.

The adjustments were made by treating the system as a pseudoternary one composed of a single triglyceride having the average molecular weight, representing the canola oil, of a representative fatty acid with the molecular weight of the commercial oleic acid, and of the solvent. The values of r_i' and q_i' for the UNIQUAC model were calculated via eq 1, which considers the composition of the oil and the commercial oleic acid; the values are furnished in Table 9. The parameters R_i and Q_i were taken from Magnussen et al. (1981):

$$r_i' = \frac{1}{\overline{M}_i}\sum_j^C x_\mathrm{j}\sum_k^G \nu_k^{(i)} R_k; \quad q_\mathrm{i}' = \frac{1}{\overline{M}_i}\sum_j^C x_\mathrm{j}\sum_k^G \nu_k^{(i)} Q_k \qquad (1)$$

where x_j is the molar fraction of the triglycerides of the canola oil or the fatty acids of the commercial oleic acid and $\overline{M}_i$ is the average molecular weight of the canola oil or the commercial fatty acid.

Following the procedure developed by Stragevitch and d'Avila (1997), adjustments of the parameters were made by minimization of the maximum likelihood objective function:

$$S = \sum_m^D \sum_n^N \left\{ \left(\frac{T_{nm}^{\mathrm{calc}} - T_{nm}^{\mathrm{ex}}}{\sigma_{T_{nm}}} \right)^2 + \sum_i^{C-1} \left[\left(\frac{w_{inm}^{\mathrm{I,calc}} - w_{inm}^{\mathrm{I,ex}}}{\sigma_{w_{inm}^{\mathrm{I}}}} \right)^2 + \left(\frac{w_{inm}^{\mathrm{II,calc}} - w_{inm}^{\mathrm{II,ex}}}{\sigma_{w_{inm}^{\mathrm{II}}}} \right)^2 \right] \right\} \qquad (2)$$

where D is the total number of groups of data and N and C are the total number of tie lines and the total number of components in the group of data m, respectively. T is the temperature, w is the mass fraction, the subscripts i, n, and m are component, tie line, and group number, respectively, and the superscripts I and II are the phases; ex and

Table 4. Ternary Liquid−Liquid Equilibrium Data for the System Canola Oil (1) + Commercial Oleic Acid (2) + Methanol (3)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_3$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$
20	52.41		47.59	99.49		0.51	5.03		94.97
	51.20	4.84	43.96	94.55	4.57	0.88	7.24	5.08	87.68
	51.03	9.42	39.55	90.08	8.64	1.28	9.34	10.39	80.27
	47.65	19.14	33.21	76.44	18.82	4.74	16.58	19.60	63.82
	48.28	23.57	28.15	70.83	23.00	6.17	19.91	24.84	55.24
30	52.58		47.42	99.38		0.62	5.98		94.02
	52.72	3.16	44.12	96.56	2.78	0.66	6.70	3.51	89.80
	51.97	5.88	42.15	93.63	5.33	1.04	8.31	6.35	85.34
	47.95	9.28	42.77	89.31	8.82	1.87	10.85	9.56	79.59
	47.30	13.03	39.67	85.33	12.26	2.41	13.10	13.74	73.16

Table 5. Ternary Liquid−Liquid Equilibrium Data for the System Canola Oil (1) + Commercial Oleic Acid (2) + Ethanol (4)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_4$	$100w_2$	$100w_1$	$100w_4$	$100w_2$	$100w_1$	$100w_4$	$100w_2$	$100w_1$
20	52.73		47.27	95.28		4.72	12.65		87.35
	53.06	2.90	44.04	90.13	3.37	6.50	15.32	2.34	82.28
	52.80	5.87	41.33	84.23	6.56	9.21	18.93	4.88	76.19
	50.84	7.80	41.36	79.43	8.78	11.79	21.98	6.84	71.19
	50.84	9.61	39.55	74.05	10.55	15.40	25.38	8.47	66.15
	50.16	11.05	38.78	67.14	11.90	20.96	31.11	10.11	58.78
30	54.20		45.80	93.90		6.10	15.56		84.44
	52.15	1.25	46.60	91.51	1.40	7.09	16.93	1.17	81.90
	50.08	2.48	47.44	89.13	2.77	8.10	18.30	2.31	79.39
	50.87	3.30	45.83	87.20	3.70	9.10	19.55	2.92	77.53
	51.65	4.13	44.22	85.26	4.64	10.10	20.80	3.54	75.66
	50.74	5.05	44.21	83.05	5.70	11.25	21.89	4.38	73.73
	49.82	5.97	44.21	80.84	6.76	12.40	22.98	5.21	71.81
	48.10	7.97	43.93	74.48	8.97	16.55	27.24	7.35	65.41
	48.98	9.19	41.83	67.55	9.95	22.50	34.34	8.66	57.00

Table 6. Ternary Liquid−Liquid Equilibrium Data for the System Canola Oil (1) + Commercial Oleic Acid (2) + Isopropanol (5)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_5$	$100w_2$	$100w_1$	$100w_5$	$100w_2$	$100w_1$	$100w_5$	$100w_2$	$100w_1$
10	57.65		42.35	90.84		9.16	21.89		78.11
	53.81	1.68	44.51	86.59	1.85	11.56	24.92	1.49	73.59
	56.22	3.25	40.53	82.35	3.61	14.04	27.90	2.89	69.20
	58.08	4.95	36.97	76.33	5.37	18.30	32.44	4.63	62.93
20	70.04		29.96	84.95		15.05	30.76		69.24

Table 7. Ternary Liquid−Liquid Equilibrium Data for the System Canola Oil (1) + Commercial Oleic Acid (2) + *n*-Propanol (6)

	overall composition			alcohol phase			oil phase		
T (°C)	$100w_6$	$100w_2$	$100w_1$	$100w_6$	$100w_2$	$100w_1$	$100w_6$	$100w_2$	$100w_1$
10	58.73		41.27	67.74		32.26	40.77		59.23

Table 8. Quaternary Liquid−Liquid Equilibrium Data for the System of Canola Oil (1) + Commercial Oleic Acid (2) + Ethanol (4) + Water (7)

	overall composition				alcohol phase				oil phase			
T (°C)	$100w_4$	$100w_2$	$100w_1$	$100w_7$	$100w_4$	$100w_2$	$100w_1$	$100w_7$	$100w_4$	$100w_2$	$100w_1$	$100w_7$
30	49.65		47.01	3.34	92.13		1.38	6.49	8.40		91.31	0.29
	48.17	2.25	46.34	3.24	89.43	2.23	1.85	6.49	9.47	2.16	88.00	0.37
	47.63	6.08	43.08	3.21	84.81	6.37	2.65	6.17	12.20	6.13	81.14	0.53
	47.63	9.83	39.33	3.21	79.65	10.52	4.01	5.82	15.44	10.03	73.85	0.68
	47.36	12.19	37.26	3.19	76.02	13.42	5.07	5.49	17.82	12.45	68.88	0.85
	46.56	15.20	35.10	3.14	70.59	16.70	7.52	5.19	21.28	15.82	61.80	1.10

calc are experimental and calculated. $\sigma_{T_{nm}}$, $\sigma_{w^{I}_{inm}}$, and $\sigma_{w^{II}_{inm}}$ are the standard deviations observed for temperature and composition for both liquid phases. Tables 10 and 11 present the adjusted parameters for the two models.

The experimental data were compared to the calculated values by liquid−liquid flash using the adjusted parameters. The percent of deviation of the experimental mass fractions from the calculated ones can be found in Table 12. The average percent of deviation was calculated as follows:

$$\Delta w = 100\sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{C}[(w_{in}^{I,ex} - w_{in}^{I,calc})^2 + (w_{in}^{II,ex} - w_{in}^{II,calc})^2]}{2NC}} \qquad (3)$$

Table 9. Parameters r_i' and q_i' for Canola Oil, Riedel−deHaën Oleic Acid, and Short-Chain Alcohols

compound	r_i'	q_i'
canola oil (1)	0.044 012	0.035 659
commercial oleic acid (2)	0.044 120	0.037 476
methanol (3)	0.059 332	0.063 916
ethanol (4)	0.055 905	0.056 177
2-propanol (5)	0.054 065	0.052 007
water (7)	0.051 068	0.077 713

Table 10. NRTL Parameters for the Systems Canola Oil (1) + Oleic Acid (2) + Methanol (3), Canola Oil (1) + Oleic Acid (2) + Ethanol (4), Canola Oil (1) + Oleic Acid (2) + Ethanol (4) + Water (7), and Canola Oil (1) + Oleic Acid (2) + 2-Propanol (5)

T (°C)	pair ij	A_{ij} (K)	A_{ji} (K)	α
20	12	−228.130	−85.432	0.200 01
	13	−427.020	2549.600	0.200 04
	23	−1176.800	2237.400	0.200 01
	14	−94.972	1538.900	0.418 75
	24	−1252.200	1666.700	0.200 36
30	12	−226.62	−84.303	0.207 57
	13	−534.21	2776.6	0.200 00
	23	−1293.0	2413.0	0.200 05
	14	−95.552	1514.3	0.459 06
	24	−1349.5	1726.5	0.200 15
	17	1926.0	1586.1	0.200 01
	27	−335.59	3000.0	0.468 11
	47	870.17	−836.66	0.216 46
10	12	−229.41	−86.784	0.200 00
	15	−151.94	1302.2	0.470 00
	25	−900.36	1063.9	0.250 16

Table 11. UNIQUAC Parameters for the Systems Canola Oil (1) + Oleic Acid (2) + Methanol (3), Canola Oil (1) + Oleic Acid (2) + Ethanol (4), Canola Oil (1) + Oleic Acid (2) + Ethanol (4) + Water (7), and Canola Oil (1) + Oleic Acid (2) + 2-Propanol (5)

T (°C)	pair ij	A_{ij} (K)	A_{ji} (K)
20	12	276.880	−224.890
	13	390.730	−62.549
	23	132.910	−62.700
	14	241.060	−49.959
	24	−27.228	−18.710
30	12	308.64	−233.63
	13	360.61	−50.713
	23	298.89	−148.91
	14	229.22	−46.158
	24	−35.259	−7.6708
	17	351.43	−151.23
	27	336.60	−267.29
	47	−132.64	−382.54
10	12	245.34	−216.24
	15	166.55	−36.742
	25	−47.947	−28.221

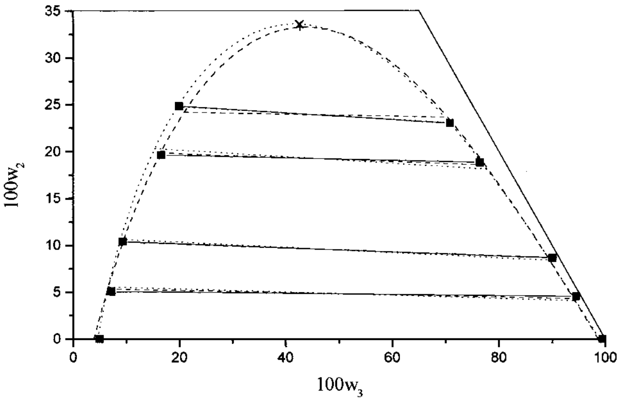

Figure 1. System of canola oil (1) + oleic acid (2) + methanol (3) at 20 °C: (■) experimental; (- - -) NRTL; (···) UNIQUAC; (+) plait point NRTL; (×) plait point UNIQUAC.

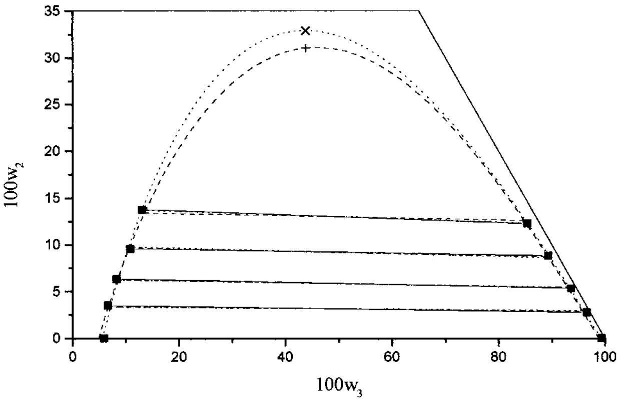

Figure 2. System of canola oil (1) + oleic acid (2) + methanol (3) at 30 °C: (■) experimental; (- - -) NRTL; (···) UNIQUAC; (+) plait point NRTL; (×) plait point UNIQUAC.

Table 12. Average Deviations in Phase Composition

	Δw (%)	
system	NRTL	UNIQUAC
canola oil/oleic acid/methanol, 20 °C	0.53	0.55
canola oil/oleic acid/methanol, 30 °C	0.38	0.25
canola oil/oleic acid/ethanol, 20 °C	0.83	0.77
canola oil/oleic acid/ethanol, 30 °C	0.83	0.83
canola oil/oleic acid/2-propanol, 10 °C	0.12	0.16
canola oil/oleic acid/ethanol/water, 30 °C	1.09	0.28

The high deviation of the NRTL model for canola oil/commercial oleic acid/ethanol/water showed that it was not possible to obtain a group of parameters that describes, with accuracy, the liquid−liquid equilibrium of the ternary system (canola oil/commercial oleic acid/ethanol) and of the quaternary system (canola oil/commercial oleic acid/ethanol/water). The addition of water causes a high impact in the liquid−liquid equilibrium, mainly decreasing the mutual solubility oil−ethanol and the distribution coefficient of the commercial oleic acid.

The experimental data for the systems of canola oil, oleic acid, and anhydrous 2-propanol at 20 °C and of canola oil, oleic acid, and anhydrous *n*-propanol at 10 °C were not used, since they formed only a minimal heterogeneous area.

Figures 1−5 show the experimental and calculated tie lines and the calculated binodal curve.

For the systems studied, the information about mutual solubility of the oil and solvent is contained in the base tie line of each diagram. It can be seen that for a given temperature the mutual solubility increases with an increase in the length of the carbon chain of the solvent.

Figure 6 presents the distribution at 30 °C for the systems with methanol and ethanol as solvents. The coefficient of distribution (eq 4) with ethanol is somewhat larger than 1, while that for methanol is somewhat smaller. These results suggest that methanol has a somewhat lesser capacity for extraction of fatty acids, which can be explained by the lower polarity of the ethanol chain in relation to that of methanol. For the same reason, ethanol also dissolves more canola oil, thus presenting less selectivity than methanol.

$$k_i = \frac{w_i^{\mathrm{II}}}{w_i^{\mathrm{I}}} \qquad (4)$$

The mutual solubility of oil and solvent for all systems increases with an increase in temperature. A comparison of Figures 1 and 2 and of Figures 3 and 4 shows that the decrease in temperature from 30 to 20 °C caused a small

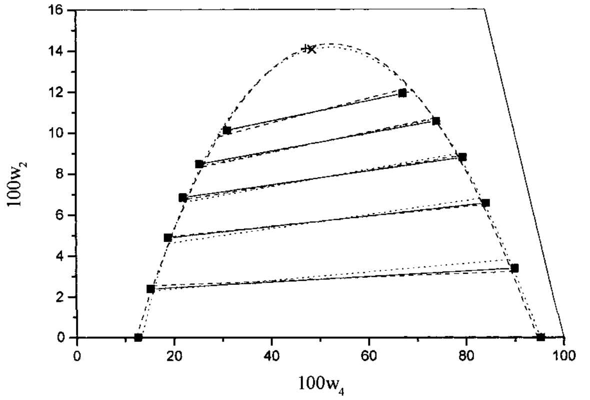

Figure 3. System of canola oil (1) + oleic acid (2) + ethanol (4) at 20 °C: (■) experimental; (- - -) NRTL; (···) UNIQUAC; (+) plait point NRTL; (×) plait point UNIQUAC.

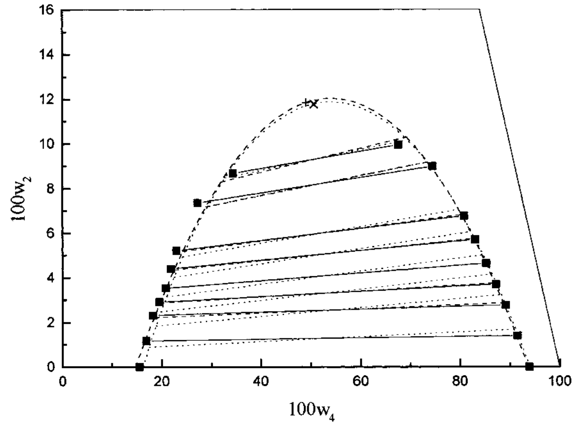

Figure 4. System of canola oil + oleic acid (2) + ethanol (4) at 30 °C: (■) experimental; (- - -) NRTL; (···) UNIQUAC; (+) plait point NRTL; (×) plait point UNIQUAC.

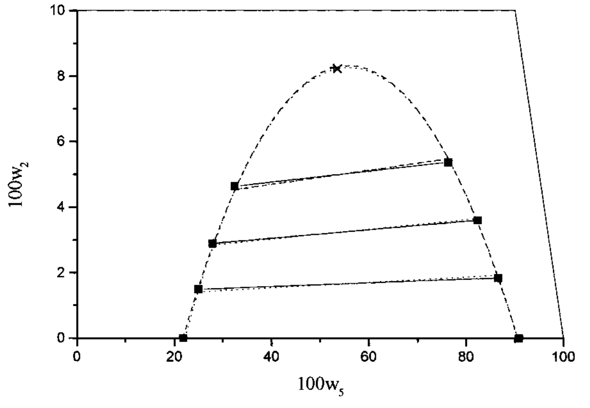

Figure 5. System of canola oil (1) + oleic acid (2) + 2-propanol (5) at 10 °C: (■) experimental; (- - -) NRTL; (···) UNIQUAC; (+) plait point NRTL; (×) plait point UNIQUAC.

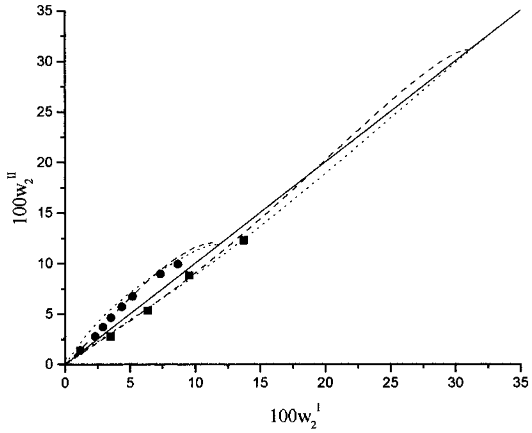

Figure 6. Distribution at 30 °C for systems of canola oil (1) + oleic acid (2) + methanol (3) and of canola oil (1) + oleic acid (2) + ethanol (4): (■) methanol; (●) ethanol; (- - -) NRTL; (···) UNIQUAC.

increase in the two-phase region. In no case, however, did a significant change in the distribution coefficient occur. The increase in the heterogeneous region with only slight alterations in the distribution coefficient increases the selectivity of solvents upon a reduction of temperature.

Conclusion

For any given temperature, the increase in the length of the carbon chain of the solvent led to a reduction in selectivity and an increase in the coefficient of distribution. For those solvents tested, methanol was the most selective solvent, but its distribution coefficient was less than 1. Ethanol and 2-propanol both have distribution coefficients greater than 1, but ethanol is more selective. The size of the heterogeneous area increases with a decrease in temperature, especially for the system with ethanol.

The adjusted NRTL and UNIQUAC models expressed as mass fractions proved adequate and furnished practically identical liquid−liquid equilibria, even when commercial reagents with a very large number of components were used. It should be noted that, especially in the case of the UNIQUAC model, the good adjustments obtained in the present experiment are in contrast to those reported earlier in the literature (Zhang and Hill, 1991), as these authors were unable to obtain good adjustments for systems including a commercial reagent. It is probable that the great chemical similarity between the triglycerides of the canola oil and of the fatty acids in the commercial oleic acid may have contributed to the success of the use of the UNIQUAC model.

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