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High-Pressure Phase Equilibria of the Ternary System Oleic Acid + Squalene + Carbon Dioxide

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Vapor−liquid equilibrium data are reported for the ternary system oleic acid + squalene + carbon dioxide in the temperature range of (313 to 333) K and in the pressure range of (14 to 22) MPa. Experiments were performed in a continuous-type equilibrium apparatus where a static mixer promotes the equilibrium between the gas and liquid phases. A low selectivity of carbon dioxide toward squalene was obtained, indicating that the separation is poor. Oleic acid was of technical grade containing other fatty acids in minor quantities. Distribution coefficients of major fatty acids were evaluated in the range described. Equilibrium data were correlated using the Peng−Robinson equation of state with a reasonably good agreement. The interaction parameters of the equation were optimized by minimizing the deviations between the calculated and experimentally determined vapor and liquid-phase compositions and distribution coefficients of each component.

Introduction

The use of supercritical fluid (SCF) technology to separate biological active compounds has been widely practiced over the past decades. The main targets for this technology have been plants and oils from plants so valuable extracts can be obtained. The fact that the extraction solvent, a gas at supercritical conditions, can be regarded as a “green” solvent makes this technology attractive when fractionation and/or recovery of valuable compounds from liquid and solid matrices is involved. To assess the feasibility of a given high-pressure fractionation process, the knowledge of the vapor−liquid equilibria (VLE) is required. It gives information on the distribution coefficients of the substances between the gas and liquid phases and the respective separation factors (which is the ratio of the above coefficients for two specific compounds) as well as on the mutual solubilities of the gas in the liquid feed and of the liquid in the gas phase.

The measurement of high-pressure phase equilibria can be experimentally obtained using different types of equipment as proposed in the literature.[1−4] The use of an in-line mixing device such as a static mixer to promote the VLE at high-pressure conditions has been previously proposed.[5,6] Static mixers promote a rapid and efficient material mixing by the presence of internal elements of different shapes in a length of pipe; the material undergoes a series of flow diversions as it travels through the pipe. A static mixer with 21 elements from Kenics was used in this work to study the phase equilibria of a ternary mixture containing oleic acid (ca. 80 % by weight pure), squalene, and carbon dioxide. Squalene is a naturally occurring tri-terpenoid hydrocarbon, usually used in its natural form in health foods or in its hydrogenated form (squalane) in cosmetic preparations as a moisturizing or emollient agent.[7] The model mixture intends to reproduce part of a more complex mixture that is obtained from the olive oil refining process residue. Oleic acid is the main fatty acid present in olive oil and is representative of the behavior of the free fatty acids fraction in the respective residues. Separation of the oil residue components using high-pressure carbon dioxide is an attractive process since no additional chemicals are involved and the lipid components are not thermal degraded due to the ambient temperatures employed. High-pressure VLE for the ternary system oleic acid + squalene + carbon dioxide has not been reported, which is the aim of this work.

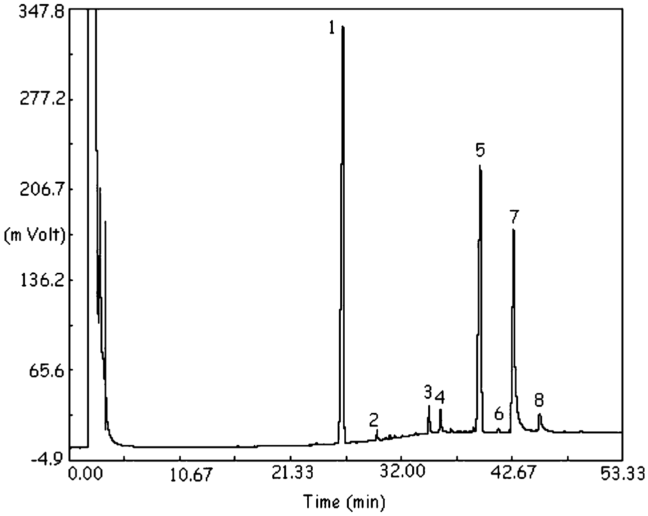

Figure 1. Gas chromatogram of an oil feed sample: 1, squalane (internal standard); 2, myristic acid; 3, palmitic acid; 4, palmitoleic acid; 5, squalene; 6, stearic acid; 7, oleic acid; 8, linoleic acid.

Experimental Section

Apparatus and Method. Phase equilibria data were obtained in a static mixer apparatus described elsewhere.[8] Briefly, a Kenics static mixer (model 37-04-065) with an internal diameter of 4.928 mm, length of 178 mm, and 21 helical mixing elements was used to promote the equilibrium between the gas and liquid phases. This is achieved by allowing carbon dioxide and the

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Table 1. Vapor−Liquid Equilibrium Data for the Ternary System Oleic Acid (1) + Squalene (2) + CO$_2$ (3)[a]

squalene mass fraction in feed	p/MPa	T/K	x_1	x_2	x_3	y_1	y_2	y_3
0.25	14.00	313.2	0.5465	0.1202	0.3333	0.0064	0.0030	0.9906
	18.00		0.4876	0.1614	0.3510	0.0105	0.0059	0.9837
	22.00		0.4751	0.1696	0.3553	0.0170	0.0057	0.9773
	14.00	333.2	0.5878	0.1186	0.2936	0.0014	0.0007	0.9979
	18.00		0.5759	0.1170	0.3071	0.0066	0.0029	0.9905
	22.00		0.5713	0.1105	0.3182	0.0134	0.0047	0.9819
0.50	14.00	313.2	0.3154	0.3774	0.3072	0.0040	0.0061	0.9899
	22.00		0.2884	0.3241	0.3874	0.0110	0.0146	0.9744
	14.00	323.2	0.3671	0.3313	0.3016	0.0014	0.0040	0.9947
	18.00		0.3877	0.2858	0.3265	0.0061	0.0081	0.9858
	22.00		0.3547	0.2827	0.3626	0.0125	0.0082	0.9793
	14.00	333.2	0.3906	0.3927	0.2166	0.0009	0.0024	0.9967
	18.00		0.4108	0.3241	0.2651	0.0045	0.0063	0.9893
	22.00		0.3343	0.3410	0.3247	0.0072	0.0104	0.9824
0.75	14.00	313.2	0.2705	0.4342	0.2953	0.0032	0.0081	0.9886
	18.00		0.2223	0.4556	0.3221	0.0048	0.0147	0.9805
	22.00		0.2806	0.3665	0.3529	0.0101	0.0151	0.9748
	14.00	333.2	0.3449	0.3908	0.2644	0.0013	0.0031	0.9957
	18.00		0.3192	0.3750	0.3059	0.0039	0.0072	0.9889
	22.00		0.3101	0.3505	0.3394	0.0082	0.0130	0.9788

[a] p is the total pressure. x and y are the mass fractions of each component in the liquid and vapor phases, respectively.

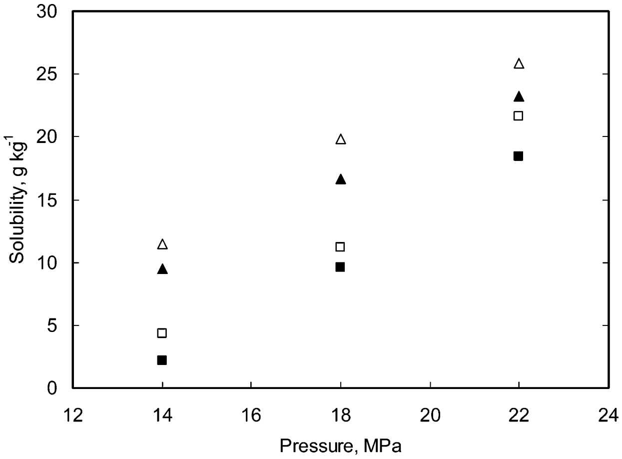

Figure 2. Solubility of the oil in the gas-rich phase as a function of the pressure, for two isotherms (▲, △, 313 K; ■, □ 333 K) and two initial feed compositions, 0.25 mass fraction squalene (solid symbols) and 0.75 mass fraction squalene (open symbols).

oil feed to flow co-currently through the static mixer; by choosing the correct operating conditions, equilibrium is reached at the end of the mixer. Separation of the two equilibrium phases is subsequently accomplished in a gravimetric separation cell; the liquid phase is collected at the bottom of this cell and later analyzed for its carbon dioxide content and solute components. The carbon dioxide-rich phase is further expanded in a second separation vessel. The solutes previously dissolved by carbon dioxide are precipitated, collected at the bottom of this vessel, and later analyzed. Further details of the experimental apparatus and respective procedure can be found elsewhere.[8] The equilibrium pressure in the static mixer was measured with a pressure transducer (model Digibar PE300, from HBM GmbH) with an accuracy of 0.02 MPa. The equilibrium temperature was measured with a thermocouple K-type, with an accuracy of 0.1 K.

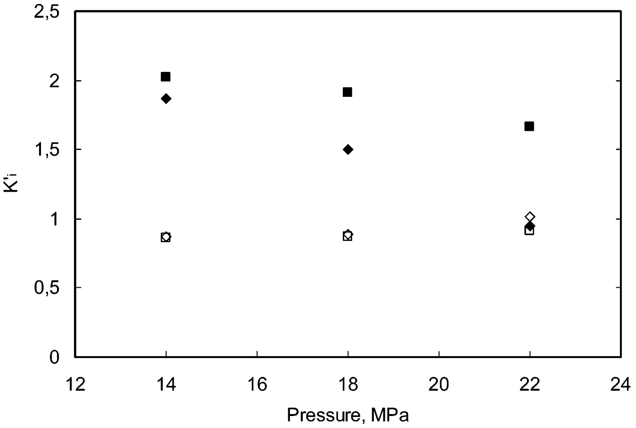

Figure 3. Distribution coefficients in a solvent-free basis as a function of the pressure and temperature, for an oil mixture with an overall composition of 0.25 mass fraction in squalene: ◆, ◇ 313 K; ■, □ 333 K. Solid symbols, squalene; open symbols, oleic acid.

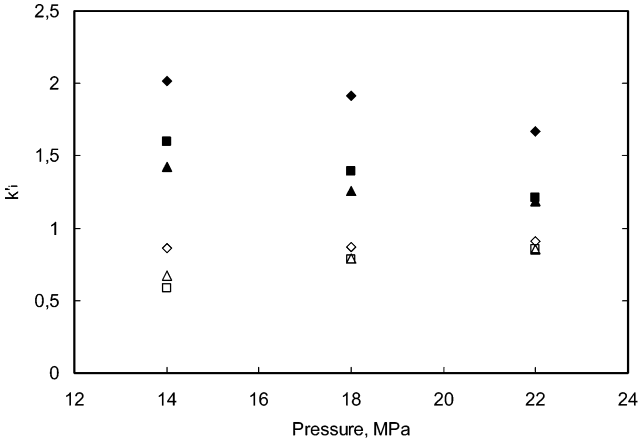

Figure 4. Distribution coefficients in a solvent-free basis as a function of the pressure at 333 K: ◆, ◇ 0.25 mass fraction squalene; ■, □ 0.50 mass fraction squalene; ▲, △ 0.75 mass fraction squalene. Solid symbols, squalene; open symbols, oleic acid.

Each experiment at a given temperature, pressure, and overall composition consisted of at least three measurements of the oil and carbon dioxide compositions in the gas and liquid phases. The reproducibility of the method was checked by randomly selecting a combination of pressure and temperature conditions and repeating the experiment several times. Reproducibility varies by less than 2 % of the mean value. The experimental error for the solubility of oil in carbon dioxide was estimated to be at most ± 0.001 g of oil/kg of CO$_2$ and that for carbon dioxide in oil to be ± 0.01 % by weight.

Materials and Analysis. Carbon dioxide was supplied by Air Liquide with a purity of 99.995 %. Squalene was supplied by Sigma (98 % by weight), and oleic acid was supplied by Riedel-de Haën.

Oleic acid was of technical grade (79.9 % by mass); other major fatty acids present included myristic acid (C14:0) at 2.0 %, palmitoleic acid (C16:1) at 5.2 %, palmitic acid (C16:0) at 5.6 %, stearic acid (C18:0) at 1.0 %, and linoleic acid (C18:2) at 6.4 %.

The squalene content of oil in the liquid and gas-phase samples was determined by gas chromatography (GC) using squalane as the internal standard. The chromatograph was a Thermo Quest Trace GC 2000 with a FID detector; a DB-WAX column, 50 m × 0.320 mm and 1-μm film thickness, from J&W Scientific Inc. was used. The oven temperature was (150 to 250) °C (20 min) at a rate of 3 °C·min^{-1}. The gas chromatogram of a feed sample is shown in Figure 1.

Table 2. Distribution Coefficients of the Major Fatty Acids Present in the Oil Mixture in a Solvent-Free Base

	p	T	K'					
squalene mass fraction in feed	MPa	K	oleic acid	myristic acid	palmitic acid	palmitoleic acid	stearic acid	linoleic acid
0.25	14.00	313.2	0.950	1.571	1.050	1.682	0.913	0.960
	18.00		0.943	1.631	1.125	1.680	0.858	1.067
	22.00		0.927	2.095	1.431	1.128	0.840	1.334
	14.00	333.2	0.949	1.563	1.089	1.326	0.807	1.116
	18.00		0.951	1.709	1.055	1.402	0.699	1.059
	22.00		0.945	1.715	1.223	1.375	1.121	0.978
0.50	14.00	313.2	1.008	1.745	1.048	1.211	0.464	0.711
	22.00		1.007	1.367	0.988	1.210	0.521	0.851
	14.00	323.2	1.008	1.222	0.710	1.085	0.825	1.015
	18.00		0.993	1.327	1.120	1.350	0.845	0.757
	22.00		0.925	1.884	1.322	1.430	0.930	1.166
	14.00	333.2	0.936	2.006	0.991	1.448	0.593	1.202
	18.00		0.952	1.780	1.110	1.444	0.819	1.053
	22.00		0.974	1.454	1.219	1.348	0.829	0.855
0.75	14.00	313.2	0.955	1.750	1.638	1.276	0.926	0.936
	18.00		0.954	1.364	0.676	1.861	0.456	1.414
	22.00		0.981	1.437	1.019	1.244	0.923	0.887
	14.00	333.2	0.939	1.928	1.237	1.358	0.779	0.914
	18.00		0.936	1.887	1.278	1.330	1.051	0.947
	22.00		0.949	1.522	1.199	1.300	0.833	1.058

Results and Discussion

Isothermal VLE were measured at (313, 323, and 333) K for the oleic acid + squalene + carbon dioxide system in the pressure range of (14 to 22) MPa. Three different feed compositions were studied in this work: 0.25, 0.50 and 0.75 mass fraction of squalene. The experimental liquid and vapor-phase mass compositions are given in Table 1 for the respective pressure, temperature, and initial feed composition conditions.

Carbon dioxide dissolves appreciably in the oil phase up to, on average, 30 % by weight; nonetheless, this value is relatively independent of the conditions of temperature, pressure, and overall composition, as can be seen from Table 1. The solubility of the oil compounds in the gas-rich phase increased with the density of carbon dioxide (higher pressures and lower temperatures) following the same behavior of other high-pressure systems. Figure 2 shows the solubility of the oil in carbon dioxide (in g_{oil}/kg_{CO2}) as a function of the pressure for two isotherms (313 and 333 K) and two initial feed compositions (0.25 and 0.75 mass fraction of squalene). The highest solubility was obtained for the oil feed with the highest squalene content studied in this work, with a value of 25.8 g_{oil}/kg_{CO2}, which gives an indication that squalene was the most soluble of the oil components in carbon dioxide.

The higher selectivity of carbon dioxide toward squalene is better seen by calculating the distribution coefficients of each oil component in a solvent free basis, K'. This parameter is very useful to access the capability of a supercritical solvent to separate two compounds at a given extraction condition. K' is calculated from the respective compositions:

$$K_i' = \frac{Y_i'}{X_i'} \tag{1}$$

where Y_i' and X_i' stands for the mass fractions in a solvent-free basis of solute i in the vapor phase and in the liquid phase, respectively. The mean uncertainty of calculated K' factors for carbon dioxide, squalene, and oleic acid were estimated to be $\pm$ 0.003, $\pm$ 0.008, and $\pm$ 0.009, respectively.

Figure 3 shows the results obtained for the oil mixture with an overall composition on a CO_2-free basis of 0.25 mass fraction squalene, as a function of the pressure and temperature. As can be seen, carbon dioxide is more selective for squalene than for the fatty acids (K_{SQ}' is higher than 1 while K_{FA}' is lower than 1). The distribution coefficient of squalene increases with the temperature and decreases with the pressure, while that for the fatty acids has only a slight increase with the pressure and the effect of temperature is negligible. A higher initial content of squalene in the oil mixture results in a decrease of the selectivity of carbon dioxide toward this compound as seen in Figure 4. Selectivity of carbon dioxide toward squalene (calculated as the ratio between K'_{SQ} and K'_{FA}) was low for the most part of p/T conditions, ranging from 1 to 2. This indicates a poor degree of separation between squalene and fatty acids. To obtain a high-pure squalene product from such mixtures several processing stages would be required[1] or the fatty acids first methylated in order to get a better separation between squalene and the corresponding methyl esters.[8]

Oleic acid was of technical grade. A fractionation effect in the relative distribution of the major fatty acids between the two equilibrium phases occurred at the high-pressure conditions involved. The distribution coefficients of the main fatty acids are given in Table 2 for the respective equilibrium conditions. Figure 5 shows the distribution coefficients at 333 K and a feed with 0.5 mass fraction in squalene, as a function of the pressure. The fatty acids were fractionated by carbon dioxide according with their molecular masses and degrees of saturation following

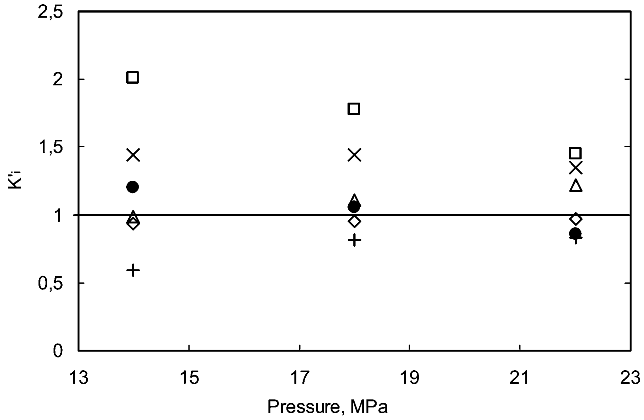

Figure 5. Distribution coefficients of the main fatty acids present in the oil mixture as a function of the pressure at 333 K and 0.50 mass fraction in squalene; □, myristic acid; △, palmitic acid; ×, palmitoleic acid; +, stearic acid; ◇, oleic acid; ○, linoleic acid.

Table 3. Estimated Pure Component Physical Properties

compound	T_c/K	P_c/MPa	ω
CO_2	304.10	7.380	0.225
oleic acid	786.79	1.355	1.187
squalene	782.129	1.1121	1.9083

Table 4. Optimized Interaction Parameters of the Ternary System with the PR-EOS and the Quadratic Mixing Rule

	OA-SQ	OA-CO_2	SQ-CO_2
k_{ij}	−0.0207	0.113839	0.083502
l_{ij}	−0.0981	0.0855	−0.0443

	x	y	K_i
ARD	8.45×10^{-2}	1.75×10^{-1}	2.19×10^{-1}

a pattern similar to that observed by other authors.[9−10] The lower molecular mass fatty acids were concentrated in the gas phase as indicated by a distribution factor higher than 1.

Correlation

The experimental *pTxy* data were correlated with the Peng−Robinson cubic equation of state (PR-EOS)[11] and the quadratic mixing rule, with adjustable binary interaction parameters, k_{ij} and l_{ij}. The actual multicomponent system was assumed to be a pseudo-ternary-system made of oleic acid (considered to be the representative of the fatty acids fraction) + squalene + carbon dioxide.

The pure component parameters a_i and b_i were determined from the pure component critical properties and acentric factor data. In the case of carbon dioxide, critical properties are known from experimental measurements.[12] The properties of pure oleic acid and pure squalene had to be estimated, as no experimental data are available. We have used estimated data collected from the literature.[13,14] For oleic acid, they were estimated by the group contribution method proposed by Lydersen.[14] On the case of squalene, the critical data were estimated by fitting the Soave−Redlich−Kwong EOS to reported vapor pressure curve.[13] Table 3 shows the critical properties and acentric factors used in this work.

Correlation of the ternary system with the PR-EOS with the quadratic mixing rule was made using a non-commercially available program for high-pressure phase equilibria calculation, PE.[15] The fitting of the PR-EOS to the ternary system was made by finding the best set of binary interaction parameters that minimized the deviations between the calculated and experimental liquid and gas-phase compositions as well as the distribution coefficients of all the components of the mixture. The objective function to be minimized is

$$F_{ob} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i^{exp} - x_i^{EOS})^2} + \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i^{exp} - y_i^{EOS})^2} + \sqrt{\frac{1}{n}\sum_{i=1}^{n}(K_i^{exp} - K_i^{EOS})^2} \quad (2)$$

where *n* is the number of data. The whole set of experimental data was used in this correlation.

Table 4 shows the optimum set of values determined for the oleic acid + squalene + carbon dioxide system together with the average relative deviation obtained for each fitted equilibrium variable. In average, the fitting of the liquid and gas-phase compositions and of the distribution coefficients was relatively good. The highest deviation was obtained for the distribution coefficients of oleic acid and squalene (27.1 % and 24.8 %, respectively), which can be attributed to the small magnitude of the respective compositions in the gas rich phase. Figures 6 and 7 show a comparison between the predicted and experimental distribution coefficients of squalene at 333 K and at 14 MPa, respectively. A reasonable agreement was obtained between the data calculated by the PR-EOS and the experimentally determined. More important, the EOS was able to correctly predict the variation of K'_{SQ} with the operating parameters, pressure, temperature, and composition. This signifies that the PR-EOS can be used as a thermodynamic tool for design and optimization of a SCF extraction plant.

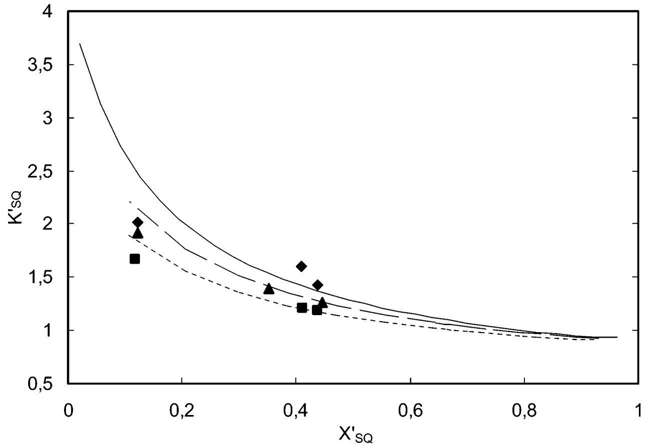

Figure 6. Experimental and predicted distribution coefficients of squalene at 333 K as a function of the pressure and squalene mole fraction in the liquid phase (solvent-free basis), X'_{SQ}. Lines, calculated data from PR-EOS; symbols, experimental data. ◆, —, 14 MPa; ▲, — —, 18 MPa; ■, ···, 22 MPa.

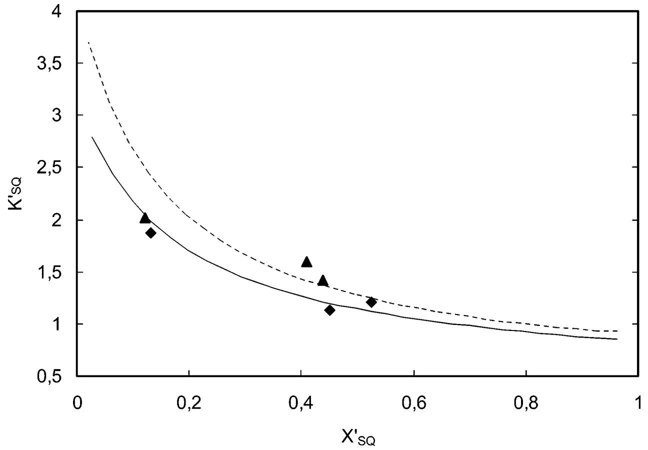

Figure 7. Experimental and predicted distribution coefficients of squalene at 14 MPa as a function of the temperature and squalene mole fraction in the liquid phase (solvent-free basis), X'_{SQ}. Lines, calculated data from PR-EOS; symbols, experimental data. ◆, —, 313K; ▲, ···, 333 K.

Conclusions

VLE of the system oleic acid + squalene + carbon dioxide was determined in the pressure range of (14 to 22) MPa and the temperature range of (313 to 333) K. A continuous-type equilibrium apparatus where a static mixer promotes the equilibrium between the gas and liquid phases was used for this purpose. A higher selectivity of carbon dioxide toward squalene was obtained; this selectivity decreased with pressure and initial squalene content of the feed mixture but increased with the temperature. Oleic acid was of technical grade containing other fatty acids in minor quantities. A fractionation of these acids between the two equilibrium phases occurred according with their molecular masses and degree of saturation. The VLE data were correlated with the PR-EOS with the quadratic mixing rule. An average relative deviation of the predicted distribution coefficients of the three components of the mixture of around 20 % was obtained. The PR-EOS was able to correctly describe the behavior of the selectivity of carbon dioxide with the operating parameters.

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