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Liquid−Liquid Equilibrium of the Castor Oil + Soybean Oil + Hexane Ternary System

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Liquid−liquid equilibria for the ternary system castor oil + soybean oil + hexane are studied at 298.15 K. Mixtures are equilibrated in a temperature-controlled water bath. After evaporation of hexane, the oil compositions of each phase are determined by a combination of gravimetric measurements and the analysis of fatty acid methyl esters (FAMEs) using gas chromatography. Since castor and soybean triglycerides are a mixture of five or six fatty acids, the castor and soybean fractions are characterized by the relative concentration of ricinoleic acid. Fitting the *K*-ratios for castor oil, soybean oil, and hexane smoothed the liquid−liquid equilibrium data. A computational cross-flow extraction is designed on the basis of the smoothed phase diagram and is experimentally validated.

Introduction

Vegetable oils constitute an important future feedstock in the pharmaceutical, food, and surfactant industries. They are mixtures of triglycerides, which can be a combination of saturated and unsaturated fatty acids attached to glycerol. Unsaturated oils, or oils that contain natural hydroxyl fatty acids, can be valuable in the chemical industry because they can be used in polymerizations to make bio-based plastics.[1] Castor oil, which occurs naturally in the higher plant *Ricinus communis*, is used commercially in large amounts, and its major constituent, ricinoleic acid (12-hydoxy-*cis*-9-octadecenoic acid), is a hydroxyl fatty acid that is used industrially for the preparations of a wide variety of products, such as polyurethanes, detergents, and lubricants.[2] Even though the castor oil fatty acid content is approximately 90% ricinoleic acid, making it a desirable feedstock, castor oil is not grown domestically because of cultivation limitations.[3] Also, castor oil requires careful processing, since it contains a toxic protein, ricin. Therefore, alternative sources of hydroxyl oils are highly desirable. Soybean oil, while available widely in large amounts, does not contain any hydroxyl fatty acids. Vegetable oils such as soybean can be chemically functionalized to generate hydroxyl fatty acids with more than one hydroxyl group.[2]

As oilseeds are genetically engineered to provide new sources of hydroxyl oils, the triglycerides will require fractionation to enrich the hydroxyl content. To characterize the possible fractionations, liquid−liquid equilibria for the ternary system castor oil + soybean oil + hexane are measured at 298.15 K. The *K*-ratios for castor oil, soybean oil, and hexane are calculated and used to smooth the data. A cross-flow extraction is designed using the computational procedures provided by Wankat.[4] Then, the extraction is evaluated experimentally.

Experimental Section

Chemicals. Castor oil [8001-79-4], soybean oil [8001-22-7], and hexane (95.0+% purity, [110-54-3]) were purchased from Aldrich Chemical Co. and were used as received. Potassium hydroxide pellets (Columbus Chemical Industries, Inc., min. 85.0% purity, [1310-58-3]), potassium chloride granules (Spectrum Quality Products, Inc., 99.0% purity, [7447-40-7]), methanol (Fisher Scientific, 99.9% purity, [67-56-1]), and hexane were used to convert the oil samples to fatty acid methyl esters (FAMEs) via esterification. Six FAMEs were purchased from Alltech-Applied Science Labs, including methyl stearate (octadecanoic acid, methyl ester, 99.0+% purity, [112-61-8]), methyl palmitate (hexadecanoic acid, methyl ester, 99.0+% purity, [112-39-0]), methyl oleate (*cis*-9-Octadecenoic acid, methyl ester, 99.0% purity, [112-62-9]), methyl linoleate (*cis*,*cis*-9,12-octadecadienoic acid, methyl ester, 99.0% purity, [112-63-0]), methyl linolenate (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid, methyl ester, 99.0% purity, [301-00-8]), and methyl ricinoleate (12-hydroxy-*cis*-9-octadecenoic acid, methyl ester, 99.0+%, [141-24-2]). A Perkin-Elmer model 8500 gas chromatograph equipped with a FID detector was used for the analysis of the FAMEs. The GC column was an Alltech Associates EC-WAX Econo-Cap capillary column. Each standard was analyzed separately to determine the corresponding retention time. Then, all standards were mixed together into one solution to verify their relative retention times.

General Procedures. Soybean oil is totally miscible in hexane, castor oil is partially miscible in hexane, and the two oils are miscible. Therefore, the construction of the two-phase envelope, on a ternary diagram, is desired to further study the solubility of castor in hexane when castor oil + soybean oil + hexane are mixed together.

1. Equilibration of Samples. Hexane was mixed with a blend of oil in a 36-mL test tube, and the mixture was agitated vigorously for about 10 min. Then, the mixture was allowed to equilibrate overnight in a water bath controlled at 298.15 K. During equilibration, the mixture separated into the β-phase (top, hexane-rich) and α-phase (bottom, oil-rich).

2. Sample Collection. Because a gravimetric step is used in analysis, samples were collected in a manner that provided at least 1 g of oil. To obtain at least 1 g of oil sample for each phase, about 5 g of the liquid was obtained

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using a disposable syringe and needle. For each sample collected, a new syringe and needle were used. The α-phase was easily sampled by inserting the needle tip down into the bottom of the test tube. If any β-phase was also removed, it quickly settled to the top of the syringe. After withdrawal, the sample was transferred into a tared 25-mL round-bottom flask and weighed.

3. Evaporation of Samples. Since the boiling points of castor oil and soybean oil are significantly higher than that of hexane, the solvent was evaporated using a rotovap apparatus. The hexane content was determined by mass loss during evaporation. For the binary mixtures of castor oil + hexane, gravimetric analysis was sufficient to determine mixture compositions. In the multicomponent systems, oil residues of castor + soy were further analyzed via esterification to determine the mass fractions of both castor oil and soybean oil.

4. Esterification of Samples. For the ternary system, the amounts of castor oil and soybean oil must be determined for each residue. The oil residue was esterified to FAMEs and analyzed via gas chromatography. A common esterification method of fats and oils used is AOCS Official Method Ce 2-66.[5] However, this method requires the use of a catalyst, a boron triflouride + methanol complex, which has a limited shelf life, even when refrigerated, and the use of old or too concentrated solutions may result in the production of impurities and the loss of large amounts of polyunsaturated fatty acids.[6] This method also requires the use of heat, which prolongs the esterification process. Therefore, an alternative esterification method was used. The method consisted of dissolving a droplet of oil blend in about 1.5 mL of hexane. Then, about 10 drops of the catalyst 2 M potassium hydroxide in the solvent methanol was added to the solution and allowed to dissolve for just a few seconds. Finally, to salt out the methyl ester into the hexane phase, about 2 mL of aqueous saturated potassium chloride solution was added. We have experimentally verified that this method is comparable with AOCS Method Ce 2-66 within the experimental reproducibility of the AOCS Method. Also, this method is quick and requires no heat or the use and handling of a boron triflouride + methanol complex.

5. Calibration Method. Linoleic acid is the main component fatty acid in soybean oil, making up about 51.5%.[1] Also, the composition of ricinoleic acid in castor oil is about 89.5%. To develop a standard curve, known mixtures of castor oil and soybean oil were esterified and analyzed by gas chromatography. Although castor and soybean triglycerides are a mixture of five or six fatty acids in mixed triglycerides, the GC response of the ricinoleic acid methyl ester is found to be suitable for characterizing castor and soybean mass fractions. Therefore, for each sample, the fractional peak area for ricinoleic acid was calculated by dividing its peak area by the peak areas of palmitic, stearic, oleic, linoleic, linolenic, and ricinoleic acids. The GC calibration curve for castor oil + soy oil esters is shown in Figure 1. In the development of the standard curve, the compositional fatty acid analyses of pure soy oil and pure castor oil were determined. The fatty acid content of soybean oil was 12.3% palmitic acid, 4.8% stearic acid, 24.2% oleic acid, 51.8% linoleic acid, 7.0% linolenic acid, and 0.0% ricinoleic acid, which is comparable with other published soy oil data.[7] Moreover, the fatty acid content of castor oil was 1.3% palmitic acid, 1.4% stearic acid, 3.6% oleic acid, 5.0% linoleic acid, 0.6% linolenic acid, and 88.2% ricinoleic acid, which is also comparable with other published castor oil data.[8]

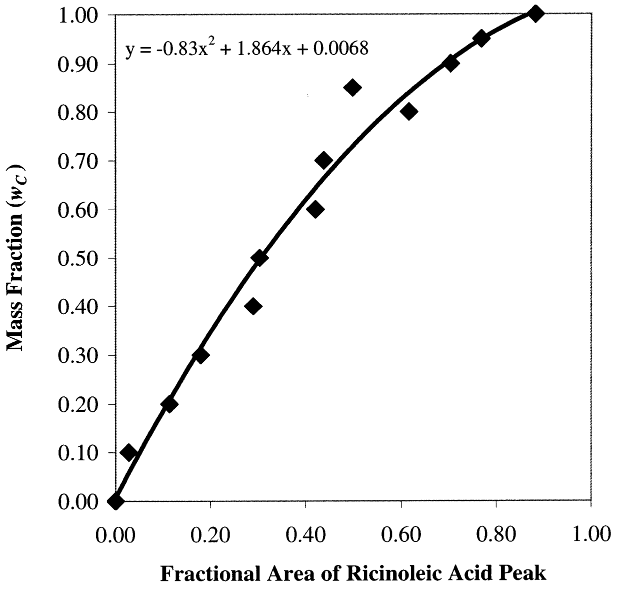

Figure 1. Relation of fractional area of the ricinoleic acid peak to the mass fraction of castor oil in castor/soy FAMEs.

Table 1. Experimental Compositions for LLE in the Binary Castor Oil (1) + Hexane (3) System at 25 °C

w_1^β	w_1^α	w_1^β	w_1^α
0.0741	0.6321	0.0509	0.6222
0.0638	0.6335	0.0400	0.6249
0.0794	0.6256	0.0500	0.6221
0.0636	0.6272	0.0430	0.6314
0.0678	0.6357	0.0349	0.6267
0.0664	0.6307	0.0411	0.6179

Table 2. Experimental Compositions for LLE in the Ternary Castor Oil (1) + Soybean Oil (2) + Hexane (3) + System at 25 °C

w_1^β	w_2^β	w_1^α	w_2^α	w_1^β	w_2^β	w_1^α	w_2^α
0.094	0.109	0.596	0.030	0.094	0.069	0.589	0.027
0.108	0.115	0.603	0.020	0.074	0.043	0.610	0.016
0.150	0.156	0.570	0.047	0.192	0.158	0.488	0.096
0.166	0.125	0.549	0.041	0.209	0.144	0.478	0.103
0.119	0.119	0.604	0.024	0.144	0.114	0.554	0.037
0.112	0.124	0.609	0.021	0.118	0.117	0.601	0.023
0.172	0.113	0.488	0.032	0.101	0.087	0.596	0.023
0.170	0.178	0.572	0.052	0.096	0.074	0.584	0.017
0.109	0.063	0.596	0.019	0.111	0.041	0.613	0.011
0.071	0.133	0.609	0.023	0.134	0.076	0.599	0.010
0.290	0.149	0.432	0.109	0.167	0.053	0.583	0.016
0.219	0.128	0.521	0.051	0.178	0.101	0.549	0.037
0.199	0.146	0.534	0.052	0.189	0.120	0.550	0.033
0.129	0.117	0.582	0.025	0.081	0.060	0.601	0.008
0.116	0.109	0.590	0.032	0.080	0.058	0.611	0.013
0.151	0.147	0.543	0.049	0.155	0.112	0.587	0.021
0.245	0.143	0.498	0.083	0.135	0.128	0.567	0.040
0.176	0.151	0.505	0.069	0.110	0.027	0.612	0.0064
0.192	0.124	0.514	0.046	0.155	0.062	0.571	0.017
0.131	0.125	0.568	0.058	0.176	0.047	0.586	0.012

Results and Discussion

Experimental Data. Results for the binary castor oil + hexane system are summarized in Table 1. The binodal points for the castor oil + hexane binary system are, in mass fractions of hexane, 0.37 and 0.95. Experimental data for the ternary system are summarized in Table 2 and plotted in Figure 2. In some instances, the experimental tie lines (not shown) cross each other by about 1 mass % in soybean mass fraction. The experimental tie lines cross because the experimental error is greater than 1 mass % in determining soybean oil and castor oil content. We were unable to the reduce error to within 1 mass %. Dominant

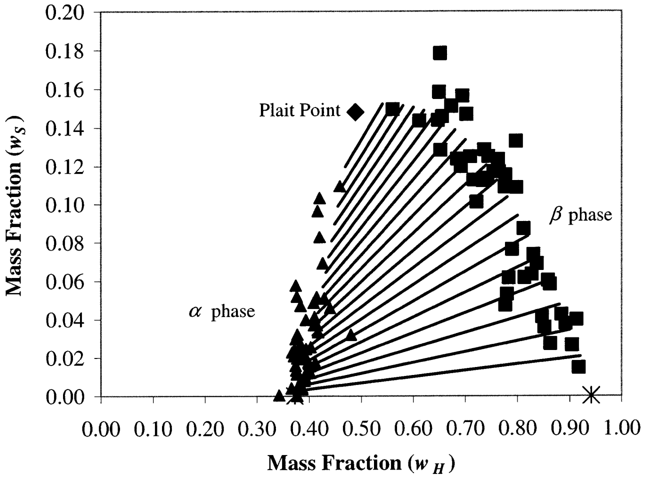

Figure 2. Castor oil (1) + soybean oil (2) + hexane (3) ternary phase diagram at 25 °C.

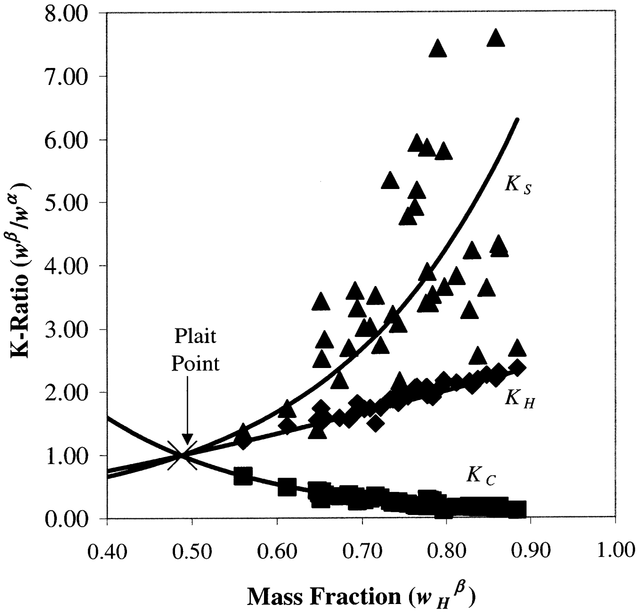

Figure 3. *K*-ratios for soybean oil, castor oil, and hexane. The smooth lines are the functions given in the text.

experimental errors are attributed to the reproducibility of the esterification technique and of the gas chromatography instrumentation. Careful experimental techniques were implemented in all experimental procedures. To reduce gravimetric error, at least 1 g of oil sample was obtained after hexane was driven off, as previously mentioned. Soy and castor oils contain five to six fatty acids characterized in a multistep procedure. Despite careful analytical techniques that were implemented, the experimental error could not be reduced. Note that scatter also exists on the standard curve. We chose to conduct many experiments and smooth the results as described next.

Method for Smoothing of Data. Conventional *K*-ratios, defined as (component fraction in the β-phase)/(component fraction in the α-phase), are plotted as a function of $w_H{}^\beta$ in Figure 3. Although the raw data show scatter, the *K*-ratios are smoothed by fitting with empirical functions. Because the Plait point is difficult to determine accurately from Figure 3 by extrapolating the conventional *K*-ratios, the functions have been adjusted in conjunction with the Hand-type plot of Figure 4, as described next.

A Hand-type plot using Bancroft coordinates[9] is created by plotting soybean/hexane mass ratios on the *y*-axis and soybean/castor mass ratios on the *x*-axis. The binodal lines are obtained by plotting ($w_S{}^\beta/w_H{}^\beta$) versus ($w_S{}^\beta/w_C{}^\beta$) and ($w_S{}^\alpha/w_H{}^\alpha$) versus ($w_S{}^\alpha/w_C{}^\alpha$), where the subscripts S, H, and C represent soy oil, hexane, and castor oil, respectively. The Bancroft *K*-ratio, *K*′, line is represented by plotting ($w_S{}^\beta/w_H{}^\beta$) versus ($w_S{}^\alpha/w_C{}^\alpha$). Smoothed binodal lines and the *K*′ line all intersect at the Plait point, and the curvature of the lines is significantly greater than those of the conventional *K*-ratios in Figure 3, providing greater certainty in the location of the Plait point. The smoothed lines are calculated by solving the material balance using the empirical fits of the conventional *K*-ratios from Figure 3. The constants and functions were adjusted until a good representation was obtained in both Figures 3 and 4. The Plait point mass fractions determined by extrapolation of the lines are {0.3636, 0.1480, and 0.4884} for castor oil, soy oil, and hexane, respectively. The equations for the conventional *K*-ratios are

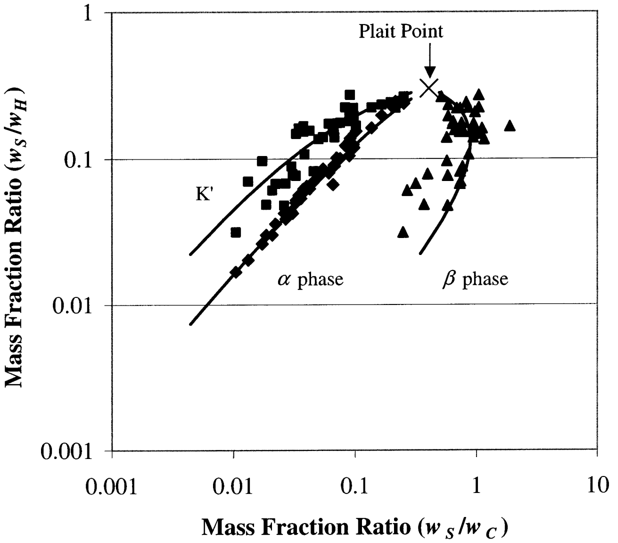

Figure 4. Hand-type plot of LLE in the castor oil (1) + soybean oil (2) + hexane (3) system at 25 °C compared with smoothed calculations using the fitted *K*-ratios presented in Figure 3. *K*′ is the soybean distribution coefficient in Bancroft coordinates.

$$K_C = w_C{}^\beta/w_C{}^\alpha = 13.9\ \exp(-5.4125 w_H{}^\beta) \tag{1}$$

$$K_S = w_S{}^\beta/w_S{}^\alpha = 0.1032\ \exp(4.6505 w_H{}^\beta) \tag{2}$$

$$K_H = w_H{}^\beta/w_H{}^\alpha = 2.7523(w_H{}^\beta)^{1.4128} \tag{3}$$

With these three functions, smoothed tie lines can be generated by choosing the $w_H{}^\beta$ mass fraction along the binodal. The smoothed tie lines are shown in Figure 2. Although the functions represent the individual K_S, K_H, and K_C, they do not provide reliable tie lines when the concentrations are very close to the Plait point concentration, and they should not be used for $w_H{}^\beta < 0.54$.

Extraction Design. The conventional *K*-ratios clearly show potential fractionation of castor oil and soybean oil in hexane. Since the selectivities of castor oil and soybean oil are significantly different in hexane, liquid−liquid extraction of oil mixtures can enrich the α-phase in ricinoleic content.

Consider a feed (solvent free basis) composition is 0.10 and 0.90 for soybean oil and castor oil, respectively. Suppose the desired final soybean oil mass fraction in the raffinate stream is 0.020. Such a separation is possible in

Table 3. Comparison of Experimental and Predicted Compositions for a Single-Stage Hexane Extraction of Soybean Oil from a Soybean Oil + Castor Oil Mixture[a]

	Extraction Comparison	
	computational	experimental
w_{S0}^{β}	0.000	0.000
w_{C0}^{β}	0.000	0.000
w_{H0}^{β}	1.000	1.000
w_{S0}^{α}	0.100	0.099
w_{C0}^{α}	0.900	0.901
w_{H0}^{α}	0.000	0.000
w_{S1}^{β}	0.044	0.031
w_{C1}^{β}	0.071	0.082
w_{H1}^{β}	0.885	0.887
w_{S1}^{α}	0.005	0.000
w_{C1}^{α}	0.614	0.625
w_{H1}^{α}	0.380	0.375

[a] The top six rows represent the feed compositions, and the bottom six rows represent the α and β phase compositions after equilibration.

a single stage. For example, mixing of the feed with hexane in a mass ratio of 1:2 results in a composition (mass fractions) for castor oil, soybean oil, and hexane, respectively, of {0.306, 0.034, and 0.660}. From the tie line with this composition, the β and α compositions are {0.071, 0.044, and 0.885} and {0.614, 0.005, and 0.380}, respectively. After removal of the solvent, the oil compositions are {0.617 and 0.383} and {0.992 and 0.008}. The extraction process was conducted experimentally, using the same parameters as those for the design. The computational and the experimental extraction results are compared in Table 3.

Conclusions

The liquid−liquid equilibrium of the castor oil + soybean oil + hexane ternary system has been studied at 298.15 K. Liquid−liquid extraction using hexane is promising for separation because of the significant difference between the castor oil and soybean oil *K*-ratios ($K_S > 1$ and $K_C < 1$). Soon, vegetable oil will become a major renewable feedstock in the chemical industry, perhaps replacing the use of petroleum for many products. Castor oil is a valuable resource, especially since it is a dominant source of an 18 carbon hydroxylated fatty acid with one double bond. Enrichment of this hydroxylated fatty is therefore highly desirable. Liquid−liquid extraction is just one way of fractionating oils and remains a priority research area for biological and plant-derived feedstocks.[10]

Literature Cited

(1) Bockisch, M. *Fats and Oils Handbook*; AOCS Press: Champaign, IL, 1998.
(2) Weber, N.; Vosmann, K.; Fehling, E.; Mukherjee, K. D.; Bergenthal, D. Analysis of Hydroxylated Fatty Acids from Plant Oils. *J. Am. Oil Chem. Soc.* **1995**, *72* (3), 361−368.
(3) Armstrong, W. P. 2001. *Wayne's Word*: March 1999. http://waynesword.palomar.edu/plmar99.htm#intro (7 July 2002).
(4) Wankat, P. C. *Equilibrium Staged Separations: Separations in Chemical Engineering*; Prentice Hall P T R: Upper Saddle River, NJ, 1988; pp 586, 599−601.
(5) AOCS Official Method Ce 2-66: Preparation of Methyl Esters of Long-Chain Fatty Acids. In *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th ed.; Firestone, D., Ed.; AOCS Press: Champaign, IL, 1994.
(6) Christie, W. W. *Lipid Analysis*, 2nd ed.; Pergamon Press: Oxford, 1982; p 53.
(7) Schwab, A. W.; Pryde, E. H. Triglyceride-Methanol Microemulsions. *J. Dispersion Sci. Technol.* **1985**, *6* (5), 563−574.
(8) *Technical Bulletin 100: Urethanes, Castor Oil, Chemical Derivatives*; CasChem, Inc.: 1982.
(9) Robbins, L. A.; Cusack, R. W. Liquid−Liquid Extraction Operations and Equipment. *Perry's Handbook for Chemical Engineers*, 7th ed.; Perry, R. H., Green, D. W., Maloney, J. O., Eds.; McGraw-Hill: New York, 1997; pp 15-6−15-8.
(10) *Vision 2020: 2000 Separations Roadmap*; American Institute of Chemical Engineers: New York, 2000.

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