Liquid–Liquid Equilibrium for Systems of (Fatty Acid Ethyl Esters + Ethanol + Soybean Oil and Fatty Acid Ethyl Esters + Ethanol + Glycerol)

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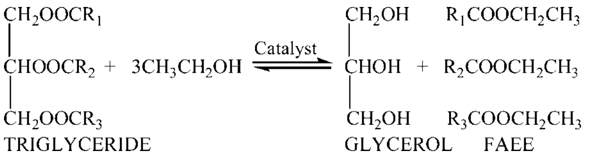
Fatty acid ethyl esters (FAEEs) have great potential for biodiesel fuel production because the raw materials are renewable. Soybean oil (SBO), ethanol, fatty acid ethyl esters, and glycerol are partially miscible in the reaction process. The mutual solubility data of the reaction components are essential for the production design and process operation. In this work, fatty acid ethyl esters were produced by transesterification of soybean oil with ethanol using NaOH as a catalyst. The phase diagrams and tie lines of the fatty acid ethyl esters + ethanol + soybean oil system and fatty acid ethyl esters + ethanol + glycerol system were drawn in the range from (300.15 to 343.15) K. The results indicate that the transesterification reaction is carried out in the ethanol phase. When the temperature increases to 343.15 K, the soybean oil + ethanol mixture becomes a homogeneous phase. The distribution coefficient of fatty acid ethyl esters between the soybean oil phase and the ethanol phase decreases with the increasing concentration of fatty acid ethyl esters. The distribution coefficient of ethanol between the glycerol phase and the fatty acid ethyl esters phase decreases with the increasing concentration of ethanol.

Introduction

There is an increasing worldwide concern for environmental protection and for the conservation of nonrenewable natural resources. Fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs) show large potential applications as diesel substitutes, and they are known as biodiesel.[1,2] FAEE is synthesized from direct transesterification of vegetable oils with ethanol in the presence of a catalyst.[3,4] A wide range of resources could be used for ethanol production: starch-, sugar-, and cellulose-containing raw materials as well as wastes.[5,6] Both ethanol and vegetable oils are renewable and environmentally benign.[7,8] Besides, ethanol has better solvent properties than methanol in biodiesel production.[9] Therefore, FAEE is environmentally attractive. The transesterification reaction of vegetable oil to FAEE with ethanol can be represented as:



$$\begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_2 \\ | \\ CH_2OOCR_3 \\ \text{TRIGLYCERIDE} \end{array} + 3CH_3CH_2OH \overset{\text{Catalyst}}{\rightleftharpoons} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{GLYCEROL} \end{array} + \begin{array}{l} R_1COOCH_2CH_3 \\ \\ R_2COOCH_2CH_3 \\ \\ R_3COOCH_2CH_3 \\ \text{FAEE} \end{array} \quad (1)$$

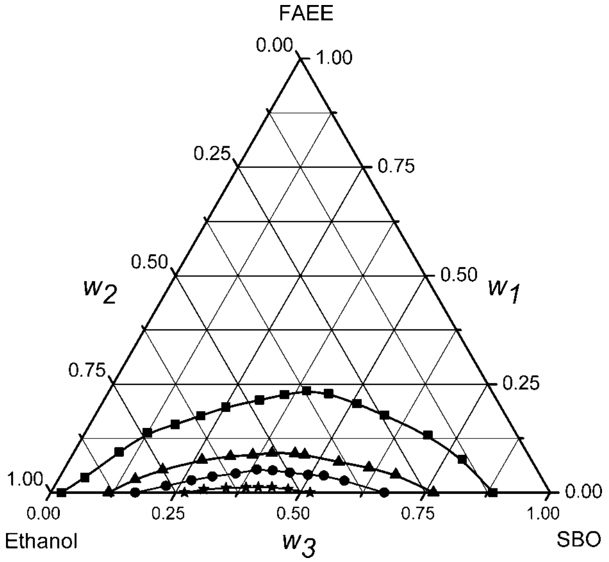


Figure 1. Phase diagram of FAEE (1) + ethanol (2) + SBO (3): ■, 300.15 K; ▲, 323.15 K; ●, 333.15 K; ★, 338.15 K.

In this reaction, reactants (ethanol and vegetable oil) are partially miscible. The transesterification reaction takes place mostly in the ethanol phase, where the alkali catalyst exists. Therefore, the reaction rate greatly depends on the solubility of the oil in the ethanol. In the transesterification, the influence of intermediates, monoglyceride (MG) and diglyceride (DG), can be neglected because of their short life spans. Although for classical thermodynamic analysis pure materials should be used, it is expedient for biodiesel production to investigate solubility and stability of systems containing multicomponent liquids of constant composition. FAEE and oil can be thought of as a single component, respectively, even though they are mixtures of fatty acid esters and triglycerides with different chains.[10] Besides, the formation of FAEE and the byproduct glycerol can change the distribution of reaction components in the different phases. The final products exist in two separate phases.

In this work, the FAEE was produced by transesterification of soybean oil (SBO) with ethanol using NaOH as a homogeneous catalyst, and the mutual solubilities of SBO, ethanol, FAEE, and glycerol were measured. The phase diagrams of the FAEE + ethanol + SBO system and the FAEE + ethanol + glycerol system were drawn on the basis of the solubility data. The tie lines of the two systems were obtained by plotting the data in the phase diagram.

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Table 1. Tie Line Data for FAEE (1) + Ethanol (2) + SBO (3) at T/K = 300.15

global composition			ethanol-rich phase			SBO-rich phase			distribution coefficient of FAEE
$100\,w_1^{\mathrm{I}}$	$100\,w_2^{\mathrm{I}}$	$100\,w_3^{\mathrm{I}}$	$100\,w_1^{\mathrm{I}}$	$100\,w_2^{\mathrm{I}}$	$100\,w_3^{\mathrm{I}}$	$100\,w_1^{\mathrm{II}}$	$100\,w_2^{\mathrm{II}}$	$100\,w_3^{\mathrm{II}}$	$(w_1^{\mathrm{II}}/\,w_1^{\mathrm{I}})$
18.16	40.03	41.81	13.86	72.56	13.58	20.28	28.28	51.44	1.46
13.91	53.54	32.55	11.40	77.85	10.75	18.42	24.74	56.8 4	1.62
12.09	45.34	42.57	8.28	83.15	8.57	15.58	21.07	63.36	1.88
7.89	43.42	48.69	4.07	90.46	5.47	11.92	17.21	70.93	2.92

Experimental Section

Materials. Refined soybean oil was purchased from Tianjin Jiali Oil Plant. The chemical composition was determined by an HP 5890 gas chromatograph after SBO was converted to fatty acid methyl esters by transesterification with methanol. The fatty acid consists of palmitic acid (w = 0.125), stearic acid (w = 0.052), oleic acid (w = 0.235), linoleic acid (w = 0.478), linolenic acid (w = 0.100), and traces of other acids. Ethanol, NaOH, and glycerol were analytical reagents (AR) and were purchased from Beihua Fine Chemical Co., Beijing. Analytical reagents (e.g., standards) were of high performance liquid chromatography (HPLC) grade and obtained from Sigma Chemical Co.

Apparatus and Procedures. The FAEE was prepared by transesterification of soybean oil with ethanol using NaOH as a homogeneous catalyst (2 % by mass of oil). The mole ratio of ethanol to oil was 12:1. The reaction temperature was 348.15 K, and the reaction time was 2 h. Ethanol was distilled off under a vacuum after the reaction was completed.[11] To avoid the emulsion, sulfuric acid (1 % by mass of oil) was used as a washing solution to remove the catalyst after removal of the glycerol layer.[12] Then, it was washed with water 4 times. Finally,

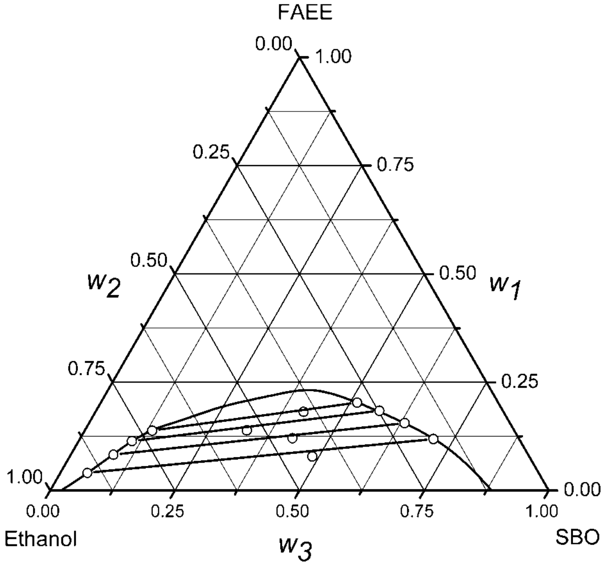

Figure 2. Tie line of the system FAEE (1) + ethanol (2) + SBO (3) at 300.15 K.

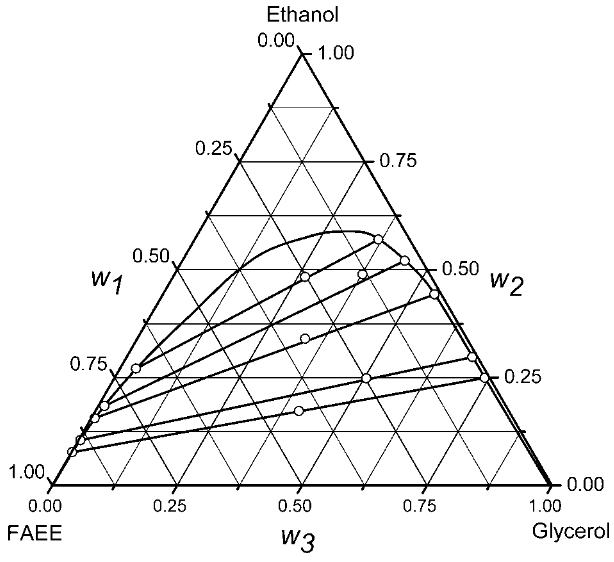

Figure 4. Tie line of the system FAEE (1) + ethanol (2) + glycerol (3) at 300.15 K.

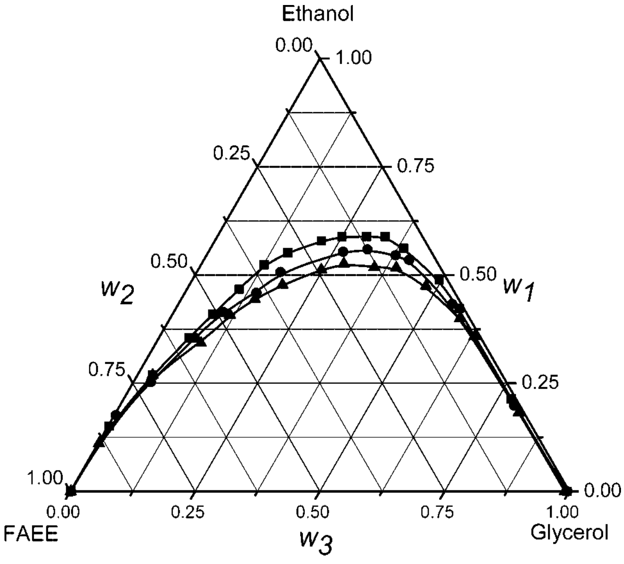

Figure 3. Phase diagram of FAEE (1) + ethanol (2) + glycerol (3): ■, 300.15 K; ●, 323.15 K; ▲, 343.15 K.

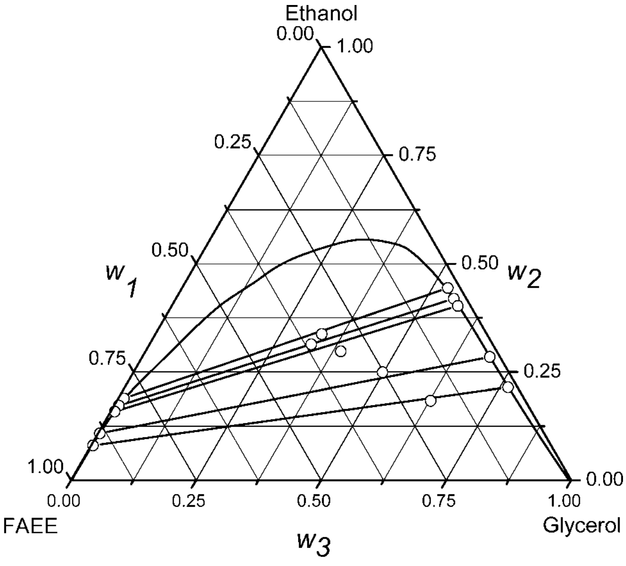

Figure 5. Tie line of the system FAEE (1) + ethanol (2) + glycerol (3) at 323.15 K.

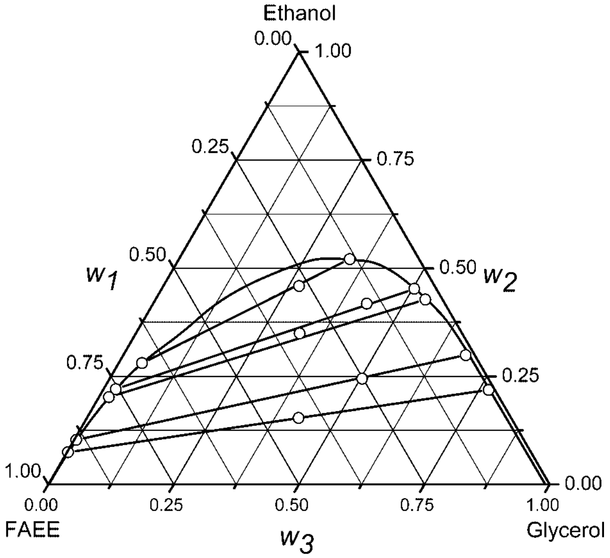

Figure 6. Tie line of the system FAEE (1) + ethanol (2) + glycerol (3) at 343.15 K.

the FAEE was dried at 378.15 K for 3 h. The total content of FAEE in the product was 99.2 %.

(a) Phase Diagram of the FAEE + Ethanol + SBO System. The phase boundary was determined by turbidimetric analysis using the titration method under isothermal conditions.[10] The test tube was placed in a water bath with a magnetic stirrer. The temperature was controlled with a thermostatic bath (with an uncertainty of ± 0.1 K). SBO was titrated to ethanol with a buret. The point when the solution changed from transparent to turbid was considered to be the saturation point of SBO in ethanol. Ethanol was also titrated in SBO with a buret. The point when the solution changed from transparent to turbid was considered to be the saturation point of ethanol in SBO. FAEE was titrated in the mixtures of different initial mass fractions of SBO and ethanol. The points when the mixtures changed from turbid to transparent were considered to be the saturation points of FAEE in SBO + ethanol solutions. The quality was obtained by detecting the mass changes of the test tube with an analytical balance (with an uncertainty of ± 0.0001 g).[13,14]

(b) Tie Lines of the Phase Diagram of the FAEE + Ethanol + SBO System. Mixing SBO, ethanol, and FAEE under 1 h agitation, the two-phase equilibria of different ratios in the heterogeneous zones were obtained, and the mixture was kept in an isothermal water bath for 4 h. The mixture was separated into two phases. The upper phase was enriched with ethanol, and the lower layer was enriched with SBO. According to the phase rule, the degrees of freedom are 3 when a ternary system is in equilibrium with two phases. At a fixed temperature and pressure, only one component can independently change its composition. Samples of the two phases were taken, and the ethanol was removed by evaporation in an oven at 368.15 K for 15 h. The contents of ethanol in the two phases were obtained. The contents of FAEE and SBO in two phases were obtained from the phase diagram of SBO + ethanol + FAEE. The tie lines were obtained by plotting the data in the phase diagram and connecting the two points.

(c) Phase Diagram of the FAEE + Ethanol + Glycerol System. The titration method was the same as procedure (a). The saturation point of FAEE in glycerol was obtained by titration of FAEE in glycerol. The saturation point of glycerol in FAEE was obtained by titration of glycerol in FAEE. Ethanol was titrated in the mixture of FAEE + glycerol. The point when the solution changed from turbid to transparent was considered to be the saturation point of ethanol in FEAA + glycerol solutions.

(d) Tie Lines of the Phase Diagram of the FAEE + Ethanol + Glycerol System. The measurement procedure was the same as procedure (b). The upper phase was enriched with FAEE, and the lower layer was enriched with glycerol. The tie lines were obtained by plotting the data in the phase diagram and connecting the two points.

Results and Discussion

Phase Diagram of the FAEE + Ethanol + SBO System. SBO is barely soluble in ethanol because the polarity of ethanol is far greater than that of SBO. However, both SBO and ethanol are soluble in FAEE. Figure 1 shows the phase diagram of FAEE + ethanol + SBO. It indicates that the solubility of ethanol in SBO is slightly greater than that of SBO in ethanol. The solubility of SBO in ethanol gradually increased with an increasing amount of FAEE. At last, the ternary mixture becomes a homogeneous solution when the mass fraction of FAEE increases to 23.42 % at 300.15 K. In addition, the solubility in the ternary mixture changes insignificantly with temperature in the range from (300.15 to 338.15) K. When the temperature reached 343.15 K, FAEE, ethanol, and SBO were

Table 2. Tie Line Data for FAEE (1) + Ethanol (2) + Glycerol (3) at Different Temperatures

global composition			ethanol-rich phase			SBO-rich phase			distribution coefficient of FAEE
100 w_1^{I}	100 w_2^{I}	100 w_3^{I}	100 w_1^{I}	100 w_2^{I}	100 w_3^{I}	100 w_1^{II}	100 w_2^{II}	100 w_3^{II}	($w^{\mathrm{II}}/w_1^{\mathrm{I}}$)
T/K = 300.15									
23.48	51.91	24.61	69.71	27.07	3.22	6.23	56.99	36.78	2.11
13.01	50.6	36.4	80.31	18.44	1.24	3.39	52.05	44.56	2.82
32.4	33.98	33.63	83.71	15.57	0.73	1.35	44.32	54.34	2.85
24.73	24.83	50.45	89.15	10.46	0.39	1.06	29.70	69.24	2.84
42.00	17.25	40.76	92.16	7.71	0.13	0.99	24.94	74.07	3.23
T/K = 323.15									
32.96	33.72	33.32	79.92	18.88	1.20	2.55	46.20	55.25	2.45
36.26	31.38	32.36	81.77	17.26	0.97	2.53	41.92	55.55	2.43
31.14	29.79	39.07	83.30	15.90	0.80	2.54	40.26	57.21	2.53
25.21	24.93	49.86	88.78	10.85	0.37	2.00	28.46	69.54	2.62
18.91	18.35	62.73	91.54	8.07	0.38	1.84	21.51	76.66	2.66
T/K = 343.15									
27.00	45.88	27.12	67.26	28.08	4.67	13.70	51.57	33.76	1.84
15.55	41.83	42.63	75.27	22.00	2.47	4.36	45.23	50.40	2.06
32.39	34.93	32.68	77.79	20.18	2.03	3.38	42.73	53.89	2.12
25.18	24.45	50.37	89.24	10.29	0.47	1.77	29.90	68.33	2.91
42.36	15.38	42.26	92.31	7.47	0.22	1.22	21.83	76.95	2.92

mutually dissolved, and the system FAEE + ethanol + SBO became a homogeneous phase. So, the transesterification reaction can be accelerated at higher temperature and higher content of FAEE.

Tie Lines of FAEE + Ethanol + SBO. For the ternary mixture in a heterogeneous area, there are two liquid phases. Table 1 shows the tie line data for the FAEE + ethanol + SBO system at 300.15 K. It indicates that the distribution coefficient of FAEE between the SBO phase and the ethanol phase decreases with the increasing mass fraction of FAEE. The amounts of FAEE and SBO remaining in the two phases were calculated from the phase diagram after the ethanol contents were determined. Figure 2 shows the lines of the FAEE (1) + ethanol (2) + SBO (3) system. The mass fraction of FAEE in SBO is higher than that in ethanol.

In the ethanol phase, the mass fraction of SBO is w_3^{I}, and the mass fraction of FAEE is w_1^{I}. The relationship of w_3^{I} and w_1^{I} at 300.15 K can be estimated by the following equation (SD stands for the standard deviation)

$$w_3^{\mathrm{I}} = 0.80697 w_1^{\mathrm{I}} + 0.00200, \ \mathrm{SD} = 0.005 \tag{2}$$

In the SBO phase, the mass fraction of FAEE is w_1^{II}, and the mass fraction of ethanol is w_2^{II}. w_1^{II} can also be expressed as a function of w_2^{II}:

$$w_1^{\mathrm{II}} = 0.75887 w_2^{\mathrm{II}} - 0.00771, \ \mathrm{SD} = 0.005 \tag{3}$$

Phase Diagram of the FAEE + Ethanol + Glycerol System. As shown in Figure 3, both FAEE and glycerol are completely soluble in ethanol. But FAEE and glycerol are partially soluble in each other. In the initial period of reaction, most of the glycerol goes into the ethanol phase. From Figure 3, the solubility in the ternary mixture increases with increasing temperature. The phase diagram indicates that the glycerol byproduct has a low solubility in FAEE, and it is easy to separate after removal of the ethanol.

Tie Lines of the FAEE + Ethanol+ Glycerol System. Figures 4 to 6 show the lines of the FAEE (1) + ethanol (2) + glycerol (3) system at different temperatures. The amount of ethanol and glycerol remaining in the FAEE phase can be calculated from the solubility phase diagram. Table 2 shows the tie line data for FAEE + ethanol + glycerol at different temperatures. It indicates that the distribution coefficient of ethanol between the glycerol phase and the FAEE phase decreases with increasing ethanol.

In the FAEE phase, the mass fraction of FAEE, w_1^{I}, can also be expressed as a function of the mass fraction of ethanol, w_2^{I}

at 300.15 K:

$$w_1^{\mathrm{I}} = -1.15792 w_2^{\mathrm{I}} + 1.01361, \ \mathrm{SD} = 0.004 \tag{4}$$

at 323.15 K:

$$w_1^{\mathrm{I}} = -1.07647 w_2^{\mathrm{I}} + 1.00339, \ \mathrm{SD} = 0.001 \tag{5}$$

at 343.15 K:

$$w_1^{\mathrm{I}} = -1.20686 w_2^{\mathrm{I}} + 1.01620, \ \mathrm{SD} = 0.005 \tag{6}$$

In the glycerol phase, the mass fraction of ethanol is w_2^{II}, and the mass fraction of glycerol is w_3^{II}. The relationship between w_2^{II} and w_3^{II} at different temperatures can be estimated by the following equations:

at 300.15 K:

$$w_3^{\mathrm{II}} = -1.13699 w_2^{\mathrm{II}} + 1.03097, \ \mathrm{SD} = 0.014 \tag{7}$$

at 323.15 K:

$$w_3^{\mathrm{II}} = -0.93347 w_2^{\mathrm{II}} + 0.96139, \ \mathrm{SD} = 0.018 \tag{8}$$

at 343.15 K:

$$w_3^{\mathrm{II}} = -0.35212 w_2^{\mathrm{II}} + 1.08387, \ \mathrm{SD} = 0.040 \tag{9}$$

Conclusions

The measurement of mutual solubility of soybean oil, ethanol, FAEE, and glycerol shows the solubility is temperature sensible in the range of (300.15 to 343.15) K. The distribution coefficients of FAEE and ethanol change with the reaction process. It provides basic data for the transesterification of soybean oil to FAEE with ethanol using a homogeneous catalyst.

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