

Phase Equilibrium Data Pertaining to the Extraction of Cottonseed Oil With Ethanol and 2-Propanol

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THE mutual solubility of glyceridic oils with the lower aliphatic alcohols is comparatively low at room temperature but increases with rise in temperature until they become completely miscible. This fact has been made the basis of a proposed process for the extraction of oil from soybeans (2, 3, 4, 10, 11) and, more recently, from cottonseed (1, 5, 6, 7, 8). The oil is extracted from the flaked oilseed by means of the hot alcohol, and when the resulting homogeneous miscella is cooled, it breaks into two liquid layers, one having a very high oil concentration and the other a very low oil concentration. The major part of the solvent can thus be removed from the miscella without distillation and the solvent-rich layer may be recycled over fresh flakes. The presence of water in the system raises the temperature at which complete miscibility between the oil and the solvent is reached and also affects the concentration of the two liquid phases which separate on chilling. The purpose of the present investigation was to obtain basic solubility data pertaining to the use of ethyl and isopropyl alcohols in the extraction of oil from cottonseed by the proposed process thus augmenting previously reported data (5, 6, 7, 8) which cover only a portion of the range and which were based in part on titration methods. The data reported below were obtained by equilibrium methods and include, on the one hand, mutual solubility data for cottonseed oil in various aqueous solutions of these alcohols and, on the other, tie-line data for the ternary cottonseed oil-alcohol-water systems.

A commercial refined and bleached cottonseed oil was used, having a Wijs iodine value of 108 and a free fatty acid value (as oleic) of 0.46%. Absolute 2-propanol was prepared from analytical grade reagent by refluxing and distilling from calcium oxide followed by fractionation in a Podbielniak column.² It had a density corresponding to 99.96% by weight (9). The absolute ethanol (99.26% by weight) was a portion of a batch which had been purified for use as a spectroscopic solvent. The various aqueous alcohols were prepared by dilution of the absolute alcohols. Their exact concentrations were determined by accurate pycnometric density measurements. All concentrations are expressed in weight percent.

Mutual Solubilities

Mutual solubility data were determined for cottonseed oil and various aqueous alcohols as follows: 90.7%, 94.4%, and 99.3% ethanol, and 90.8%, 96.1%, and 99.9% 2-propanol. The determinations were made by the static sealed-tube method. For each composition, weighed amounts of cottonseed oil and the desired alcoholic solvent were sealed in a glass tube. A glass bead was included to ensure efficient stirring

as the sample tubes were turned end-over-end in a constant temperature bath. Two temperatures a few tenths of a degree apart were found, one at which the mixture was entirely homogeneous and the other at which two liquid phases or a slight turbidity persisted after prolonged agitation. The mean of these two temperatures corrected for both thermometer calibration and emergent stem was taken as the solubility temperature for the given oil-solvent composition. Except for certain ranges of concentration, as mentioned later, the solubility temperature was reproducible to within $\pm 0.2^\circ\text{C}$.

The data are given in Table I and are represented graphically in Figure 1. The broken curves indicate

TABLE I
Mutual Solubility Data for Cottonseed Oil in Aqueous Ethanol and Aqueous 2-Propanol

Oil content wt., %	Solubility temperature, $^\circ\text{C}$. ^a	Oil content wt., %	Solubility temperature, $^\circ\text{C}$. ^a	Oil content wt., %	Solubility temperature, $^\circ\text{C}$. ^a
99.26% Ethanol		94.4% Ethanol		90.7% Ethanol	
2.87	15.2	2.05	47.9	2.12	67.4
11.15	51.5	6.13	72.7	5.50	90.0
18.29	61.7	10.35	82.0	10.31	104.8
41.63	72.4	19.51	92.3	19.61	114.6
49.35	71.0	28.19	98.7	27.24	119.0
58.49	66.2	38.63	100.3	39.19	122.8
66.91	60.7	49.37	99.1	49.29	122.9
79.22	45.8	59.06	96.9	58.73	122.7
87.13	29.0	69.52	90.5	68.82	118.9
94.44	8.9	79.62	77.8	79.35	107.1
.....	94.75	40.8	90.13	84.4
.....	95.11	63.2
99.96% 2-Propanol		96.1% 2-Propanol		90.8% 2-Propanol	
10.95	12.7	9.82	24.9	2.87	22.8
18.97	20.6	20.28	35.8	10.14	49.1
29.48	24.6	29.97	40.6	19.34	60.0
40.03	26.8	39.83	42.4	29.43	66.2
51.66	24.2	49.34	41.0	39.66	70.2
56.32	22.7	60.16	37.7	49.26	72.2
68.64	17.0	70.20	32.1	58.81	74.3
80.00 ^b	79.71	21.7	67.04	73.7
89.96 ^b	89.94 ^b	79.68	67.2
.....	89.10	50.9
.....	94.06	33.0

^a Minimum temperature at which mixture exists as a clear homogeneous liquid.

^b Solid separates.

the temperatures above which the equilibrated mixtures were turbid but would not separate into two liquid layers when agitation was stopped. In this range of concentrations the solubility temperature values, shown by the full lines, were less precise because the disappearance of the turbidity with rise in temperature was very gradual. However the temperature determinations were still reproducible to $\pm 0.5^\circ\text{C}$. Outside this concentration range the separation into two distinct liquid phases was relatively sharp and no region of turbidity was encountered.

The maxima in the mutual solubility curves, *i. e.*, the critical solution temperatures and compositions, were found by the method of Okamoto (10), which is based on the Cailletet and Mathias principle. The ethanol curves are fairly symmetrical and centered in the diagram while the 2-propanol curves are less

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²The mention of names of firms or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

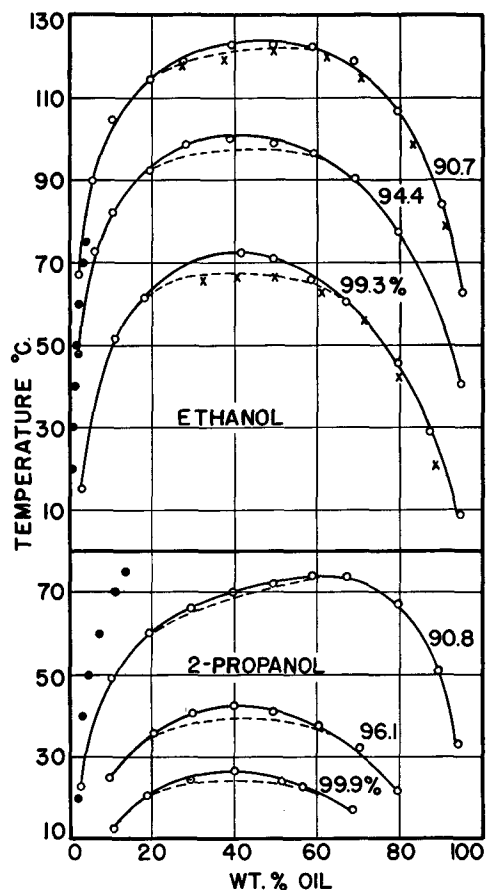


Fig. 1. Limiting solubility curves for cottonseed oil in 90.7, 94.4, and 99.3% (by weight) ethanol and 90.8, 96.1, and 99.9% 2-propanol: ———, complete homogeneity; - - - -, disappearance of two-liquid-layer formation; ●, data of Harris *et al.* (8) for 95.6% ethanol; and ×, data of Okatomo (10) for soybean oil with 99.5% and 90.3% ethanol.

centered and that for 90.8% 2-propanol is relatively unsymmetrical. The data of Okatomo for soybean oil with 99.5% and 90.3% ethanol, represented by the crosses in Figure 1, show good agreement with the curves for 99.3% and 90.7% ethanol. In the light of the high degree of unsaturation of soybean oil as compared to cottonseed oil this suggests that these mutual solubility curves may be applicable to other vegetable oils over a wide range of iodine values. Previously published solubility data (5, 8) for cottonseed oil in constant boiling (95.6%) ethanol and in constant boiling (87.9%) 2-propanol have been plotted as solid circles in Figure 1. The ethanol data are obviously at variance with the present results, but the 2-propanol values can be shown by extrapolation to be in fair agreement.

The critical solution temperature rises with the moisture content of the alcohols (Figure 2). For ethanol the relationship is linear and for the 2-propanol the effect of added water is slightly greater at higher aqueous concentrations. The value for the percentage of oil at the critical solution temperature also increases with the proportion of water in the alcoholic solvent (Figure 3). The change between 100% and 90% ethanol amounts to only 4% (from 40 to 44% oil) and is again practically linear. For 2-propanol the corresponding change amounts to more than 25%; the rate of rise becoming markedly greater as the water content increases. In both Figures 2 and 3

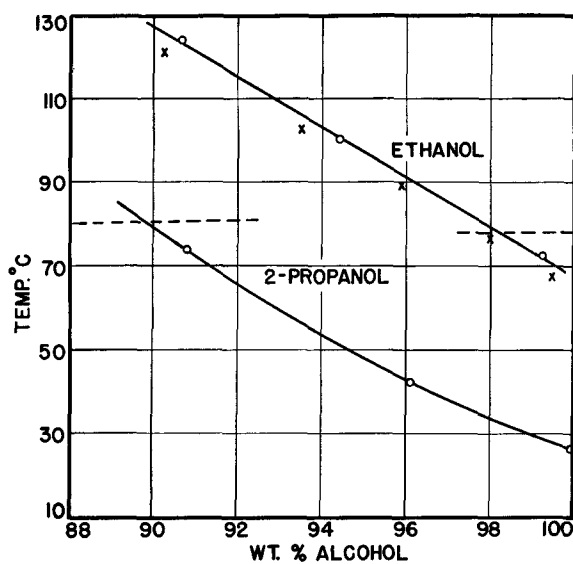


Fig. 2. Moisture content of aqueous ethanol and 2-propanol vs. critical solution temperature with cottonseed oil: - - - -, boiling temperatures of respective aqueous alcohols; ×, data of Okatomo (10) for soybean oil with ethanol.

the data of Okatomo (10) for soybean oil in aqueous ethanol are represented by crosses and show good agreement with the cottonseed oil data. It should be noted that if the solubility temperature had been taken as the temperature at which two liquid layers appeared (instead of a slight turbidity) the curve for ethanol in Figure 2 would agree almost perfectly with Okatomo's data for soybean oil.

Ternary Diagrams and Tie-Lines

Ternary tie-line data for the systems cottonseed oil-ethanol-water and cottonseed oil-2-propanol-water were obtained by equilibrating mixtures of oil, alcohol, and water of known overall composition. The desired proportions of the three components were weighed into a water-jacketed solubility burette of special design, which was then turned end-over-end in a thermostated bath at 30°C. for 48 hours to establish equilibrium conditions. It was then permitted to remain in an upright position until de-emulsification into two clear liquid layers had taken place, after which the conjugate layers were drawn off without change in temperature, each in two-aliquot portions. One portion of each layer was stripped of solvent to determine the oil concentration and the remainder was used for du-

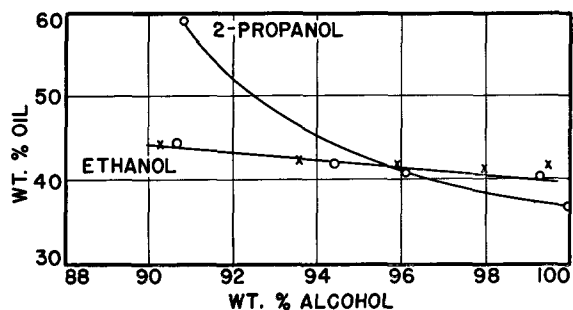


Fig. 3. Moisture content of aqueous ethanol and 2-propanol vs. critical solution concentration with cottonseed oil: ×, data of Okatomo (10) for soybean oil with ethanol.

uplicate determinations of the water content by the Karl Fischer method. The percentage of alcohol was obtained by difference.

The resulting data are given in Table II. Figures 4 and 5 represent the 30°C. ternary isotherms as well as the 30°C. tie-lines for each of the overall concentrations equilibrated. In every case the point representing the original overall concentration fell on the tie-line as required, thus confirming the accuracy of the results. The corresponding results previously published (5, 8) indicated an appreciably lower oil concentration in the alcohol layers, possibly because of the fact that indirect rather than direct methods of analysis were used to determine the ratio of alcohol to water in the mixtures.

TABLE II

Tie-Line Data for Ternary Systems: Cottonseed Oil-Ethanol-Water and Cottonseed Oil-2-Propanol-Water at 30°C.

Original overall composition			Composition of oil phase			Composition of alcohol phase		
Oil wt. %	Alcohol wt. %	Water wt. %	Oil wt. %	Alcohol wt. %	Water wt. %	Oil wt. %	Alcohol wt. %	Water wt. %
Cottonseed oil-ethanol-water								
47.45	47.68	4.87	92.45	7.12	0.43	1.09	88.53	10.38
50.02	49.49	0.51	83.69	16.08	0.23	7.20	91.62	1.18
50.19	45.76	4.05	90.85	8.73	0.42	1.50	89.73	8.77
49.58	48.88	1.54	86.60	13.01	0.39	4.41	91.83	3.76
49.47	42.99	7.54	93.55	6.03	0.42	0.58	83.74	15.68
Cottonseed oil-2-propanol-water								
49.76	37.65	12.59	90.31	8.95	0.74	0.64	72.49	26.87
49.57	40.37	10.06	88.72	10.50	0.78	1.22	77.43	21.35
47.39	44.67	7.94	86.31	12.79	0.90	2.42	81.90	15.68
49.86	45.83	4.31	80.88	17.99	1.13	6.31	84.47	9.22
49.92	46.57	3.51	76.76	22.00	1.24	8.59	84.09	7.32
50.09	47.97	1.93	66.57	32.11	1.32	17.01	78.76	4.23

Since the curves in Figure 1 represent limiting solubilities at the various temperatures, ternary isotherm data over part of the range may be derived from them directly and by interpolation. In this way a series of isotherms may be constructed for the two ternary systems. The points on the 30°C. isotherms so obtained show good agreement with the 30°C. isotherm constructed from the tie-line data in Figures 4 and 5.

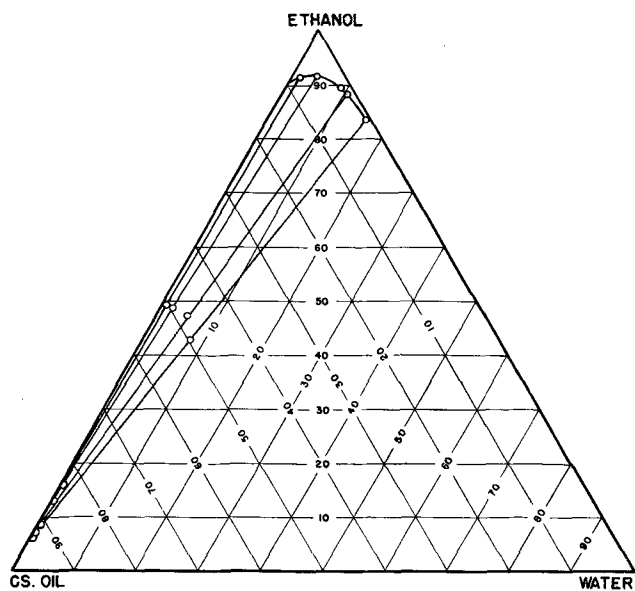


FIG. 4. Ternary isotherm and tie-lines for cottonseed oil-ethanol-water system at 30°C.

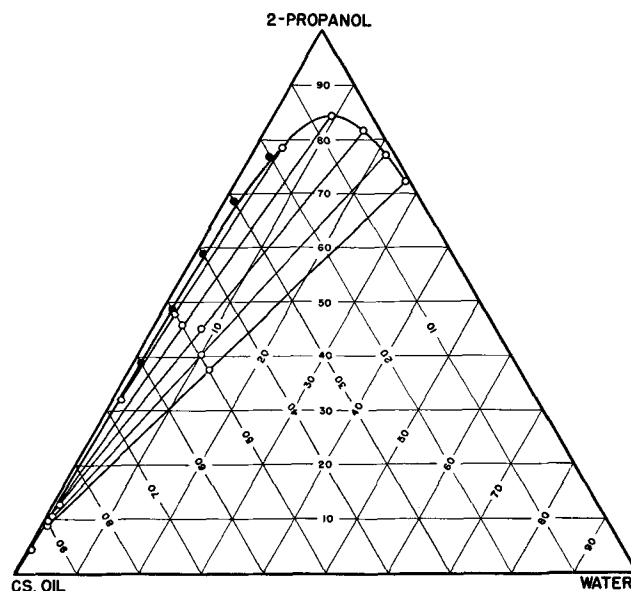


FIG. 5. Ternary isotherm and tie-lines for cottonseed oil-2-propanol-water system at 30°C.; ●, data interpolated from Figure 1.

Figure 6, derived from Table II, shows the distribution of ethanol and 2-propanol, respectively, between the oil and water layers.

Discussion

In extracting the oil from cottonseed it is of course advantageous to use a solvent which is miscible with the oil in all proportions. With aqueous ethanol or 2-propanol it would therefore be preferable to use a temperature above the critical solution temperature but not exceeding their normal boiling points. Extraction above the boiling point of the solvent would necessitate the use of a pressurized system. The boiling points of aqueous ethanols over the range of concentrations shown in Figure 2 are all within 0.2° of 78.3°C. Those for the aqueous 2-propanol fall on a straight line, between 82.4°C. for the absolute alcohol and 80.4°C. for the 88% 2-propanol. These are represented over pertinent ranges by broken lines. It is apparent from Figure 2 that 98.4 to 100% ethanol or 90 to 100% 2-propanol would be miscible with oil

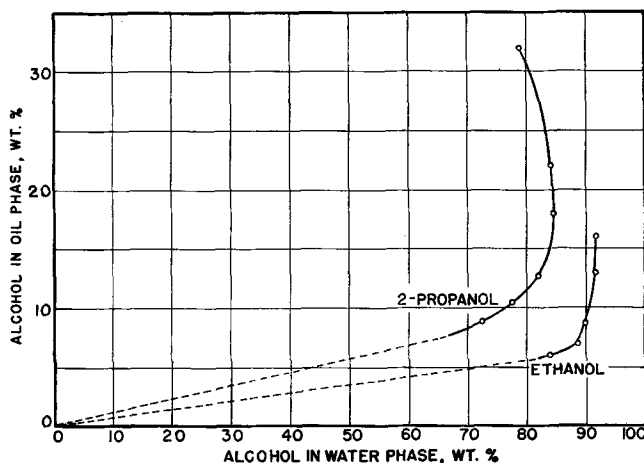


FIG. 6. Distribution of alcohol between oil and water phases in the cottonseed oil-ethanol-water and cottonseed oil-2-propanol-water systems at 30°C.

in all proportions below the boiling point of the solvent and would therefore be satisfactory solvents so far as the extraction step is concerned. It should be kept in mind that the presence in the oil of fatty acids, carbohydrates, and phosphatides may considerably alter the oil-alcohol solubility relation.

Figures 4 and 5 however show that the efficiency of the separation of the oil from the solvent at 30°C. increases as the percentage of water in the alcoholic solvent increases. Therefore from the point of view of the complete process 98.4% ethanol or 90% 2-propanol would theoretically be the optimum concentrations for use as solvent. Practically, the percentage of water in the system would be difficult to control precisely because it would depend upon the amount of moisture in the original and extracted cottonseed (2). In any case the constant boiling mixtures of ethanol (95.6%) and 2-propanol (87.9%) would present the disadvantage of requiring pressures above atmospheric during the extraction in order to attain complete miscibility with the oil.

Summary

Basic phase relation data have been obtained relative to the extraction of cottonseed oil with ethanol and 2-propanol, especially as affected by water in the solvent. Mutual solubility diagrams have been constructed for cottonseed oil with ethanol and 2-propanol of various aqueous concentrations. Tie-line data at 30°C. have been obtained for the ternary ethanol-cottonseed oil-water and 2-propanol-cottonseed oil-water systems. These combined data will be of assistance in the selection of the most desirable temperatures and moisture concentrations in the solvent extraction of cottonseed with these alcohols. Comparison with results previously published for soybean oil suggests that the mutual solubility data for cottonseed oil and

aqueous ethanols are applicable to other vegetable oils over a wide range of iodine values.

In general, the results indicate that 2-propanol is the more desirable solvent since complete miscibility with the oil can be attained at temperatures below its normal boiling point even at moisture contents as high as 10% by weight whereas ethanol can tolerate only about 1.5% of water. High moisture contents result in more effective separation of the oil from the solvent when the miscella is cooled after extraction. Constant boiling aqueous ethanol and 2-propanol present the disadvantage of requiring greater than atmospheric pressure during extraction in order to attain complete miscibility with the oil.

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The Compositions of Some Unhydrolyzed Naturally Occurring Waxes, Calculated Using Functional Group Analysis and Fractionation by Molecular Distillation, with a Note on the Saponification of Carnauba Wax and the Composition of the Resulting Fractions¹

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THE biological and economic importance of the naturally occurring waxes is largely a result of their unique physical properties. In spite of much fine work in the past 140 years, resulting in the identification of numerous compounds isolated from many of the naturally occurring waxes, there is still not one of these complex mixtures whose exact chemical composition is known. Aliphatic acids, hydroxy acids,

primary and secondary aliphatic alcohols, sterols, ketones, and hydrocarbons have been isolated in varying amounts from many waxes after initial saponification. But it is not enough to know the chemical composition of the hydrolysis products if we are to understand and possibly duplicate the unique physical properties of the waxes. We must also know the extent and manner of combination of the acids and alcohols.

Isolation of one or more substances from an unhydrolyzed wax may be used to establish a partial knowledge of its composition. For example, extraction (20) and adsorption separation (chromatography) (2, 17)

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