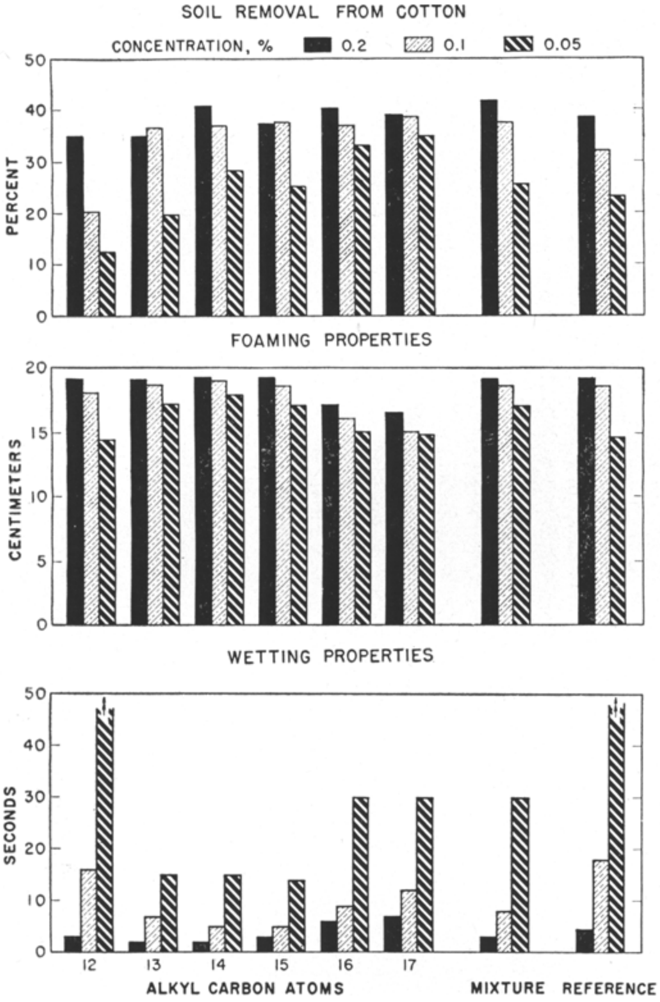

FIG. 2. Surface activity of alkyl sulfates.

ing and moisture pickup than the reference sulfate. However they were equivalent to a commercial sample of coconut fatty-alcohol sulfate.

Conclusion

Detergents prepared from Fischer-Tropsch olefins are thus measurably better than the reference standards prepared from propylene tetramer or lauryl alcohol. The combination of straight and branched chains with both terminal and internal double bonds produces the high level of surface activity found with these synthetic olefins.

Although the optimum molecular weights for the experimental sulfonates are about the same as for sulfonates from polymer olefins, the surface activity is somewhat better. In physical properties these sulfonates are superior to polymer-olefin sulfonates in resistance to caking and in rate of solution. The optimum experimental sulfates, of 14- through 16-carbon atoms, are superior to lauryl sulfate. The branched structure of these alkyl sulfates probably gives rise to their soft, waxy, and hygroscopic character. Total mixtures of these experimental products are better than the respective reference standards.

Both types of detergents prepard from Fischer-Tropsch olefins are about equivalent. The alkylbenzene sulfonates appear to be superior to similar products now in every-day use. Although Fischer-Tropsch olefins are a promising source of raw material for detergents, there is no assurance that they will be commercially available in the near future.

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Alcoholic Extraction of Vegetable Oils. I. Solubilities of Cottonseed, Peanut, Sesame, and Soybean Oils in Aqueous Ethanol

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THE MOST commonly used solvents for the solvent extraction of vegetable oils in the United States are low boiling petroleum fractions, such as normal hexane. In European countries benzene, trichloroethylene, and cyclohexane have been used. Considerable work has been done on the utilization of ethanol and isopropyl alcohol as solvents in this country. Beckel and co-workers developed a continuous non-distillation method for extraction of soybean oil, which theoretically requires only 7/10 of the energy required by the hexane process (1). Ethyl alcohol is said to produce a meal having a higher nutritive

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value and improved flavor (2). In Asiatic countries such as India, China, and Japan, where the natural resources for alcohol production are much greater than for petroleum solvents, the former is bound to become very popular as a solvent if an economical process for its use is worked out.

Review of Previous Work

The Japanese have reported the use of ethanol as a solvent for the batch extraction of soybeans in a plant at Darien, Manchuria (6, 3). They have also published data on the miscibilities of cottonseed, peanut, sesame, and soybean oils in various ethanol-water mixtures (6, 7).

Harris and co-workers published data on the miscibility of cottonseed oil in constant boiling ethanol (95.6%) (4) based on the cloud-point titration method. More recently Magne and Skau (5) have published the basic phase equilibrium data pertaining to the extraction of cottonseed oil with ethanol of various aqueous concentrations based on work using the static, sealed tube method.

Magne and Skau compared their data of cottonseed oil with the data of Okatomo for soybean oil and found a good agreement. However data are available on cottonseed itself (7), and the same have been plotted in Figure 1. The data of Skau and Magne are also represented there and show a slight variation. The present data, which are also represented, agree very well with the data of the Japanese workers (7).

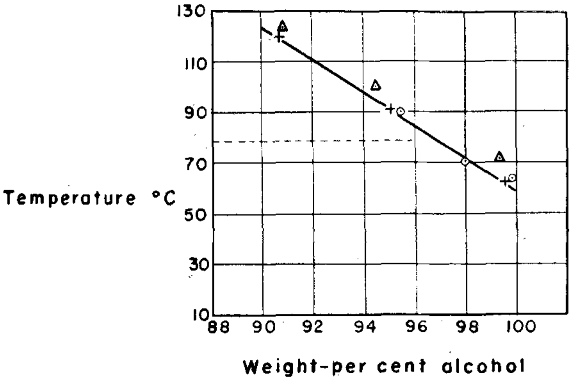

FIG. 1. Variation of critical solution temperatures of cottonseed oil with concentrations of aqueous ethanol.

X—Data of Sato, *et al.* (7).
△—Data of Magne and Skau (5).
⊙—Authors' data.
Dotted line indicates boiling point of pure ethyl alcohol.

Thus the miscibility data for the various oils in different aqueous alcoholic solutions have previously been obtained by the static method only, from which the critical solution temperature and composition data for use in the design of an extraction process can be deduced by only an indirect method, such as suggested by Okatomo (6).

The aim of the investigation was to obtain the desired critical solution temperature *vs.* alcoholic composition data by a direct method while also getting an idea of the working pressures developed by different concentrations of alcohol at various extraction temperatures.

Apparatus

Alcoholic solutions of the oils were prepared in a mild steel vessel 2.5 in. in diameter and about 6 in. high, closed at the bottom, and fitted with a flange at the top. A blind flange with a lead gasket was bolted to the top. Through a packing gland in the center of the flange passed a steel stirrer shaft provided with two blades at the bottom end, and driven by an electric motor. Asbestos thread and high melting grease packing were provided in the gland to prevent leakage. A pressure gauge was also provided to indicate the pressure developed. The vessel was provided with a needle valve 1 in. from the bottom, through which the sample could be withdrawn. The vessel was heated electrically; the temperature was controlled by a variable transformer to ±0.1°C.

Solubility Determination

Known volumes of oil and solvent in ratios such as to provide an excess of oil at a fixed temperature were stirred for 30 min. (determined previously) to obtain the maximum solubility at that temperature. The stirring was stopped, and the mixture was allowed to settle for about 30 min., keeping the temperature constant. A definite volume of the clear supernatant solution was drawn out into weighed conical flasks, which were corked and weighed again to give the weights of solution withdrawn. It was necessary to be extremely careful in withdrawing the samples to prevent evaporation of alcohol. The alcohol in the solution was evaporated on a vigorously boiling water bath, and after all of it has evaporated, the flask was dried in a drying oven at 105°C. to constant weight. From the above data the percentage solubility was calculated.

Freshly expelled and unrefined oils were used in each case. Their characteristics are given below:

Soybean Oil—	Acid value Iodine value (Wijs) Sap. value	1.029 129.6 192.2
Cottonseed Oil—	Acid value Iodine value (Wijs) Sap. value	4.56 105.6 194.6
Peanut Oil—	Acid value Iodine value (Wijs) Sap. value	2.723 94.62 191.9
Sesame Oil—	Acid value Iodine value (Wijs) Sap. value	2.5 112.7 191.4

The various aqueous solutions of alcohol were obtained by diluting the absolute alcohol. The concentrations of the alcoholic solutions were determined by determining the densities by picnometer method. All the values are reported as weight percentage.

Results

Soybean Oil. The data (Figure 2) obtained with miscellas composed of soybean oil and aqueous solutions of 95.4, 98.0, and 99.9 ethyl alcohol indicate that in all cases the solubility of soybean oil in alcoholic solutions increases steadily until the critical temperature is reached. At the critical temperature the solubility curves became parallel to the y axis, indicating that any amount of oil can be dissolved at that temperature, *i.e.*, oil and alcohol are completely miscible

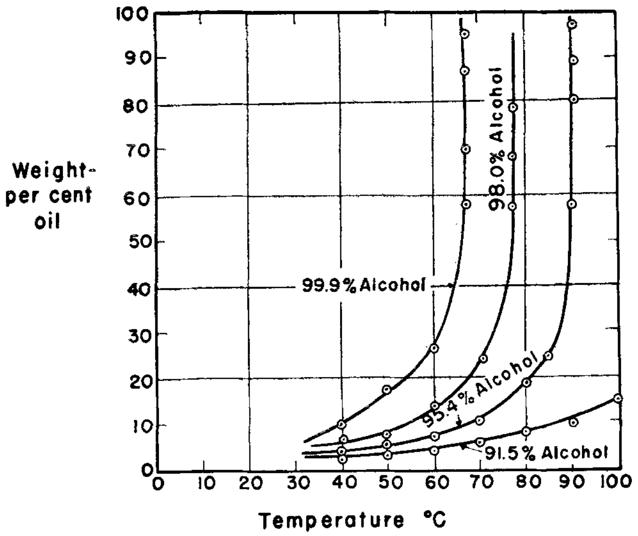

FIG. 2. Variation of solubility of soybean oil in aqueous ethanol with the temperature.

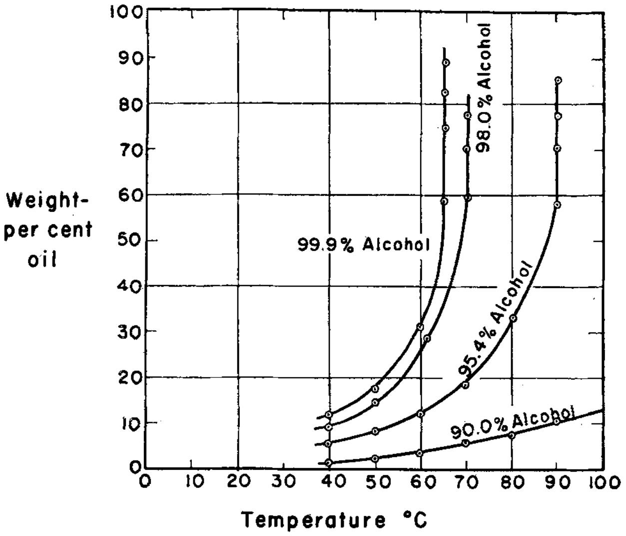

FIG. 4. Variation of solubility of cottonseed oil in aqueous of ethanol with temperature.

in all proportions at or above that temperature. In order to verify this three additional points representing higher oil-alcohol ratios were determined for the 95.40, 98.0, and 99.9% alcohol curves. These all fall on the same vertical temperature line corresponding to the critical solution temperature. The critical solution temperatures *versus* alcoholic concentration data of Okatomo are represented in Figure 3. The present data have also been plotted there and show complete agreement.

Cottonseed Oil. The data for cottonseed oil are shown in Figure 4 and indicate that complete miscibility with 99.9, 98.0, and 95.4% alcohols is attained at 65°, 80°, and 90°C., respectively. With 90.0% alcohol the maximum solubility even at 90°C. is only 10.54%.

The critical solution temperatures *versus* alcoholic concentrations data have been plotted in Figure 1 and show complete agreement with the Japanese data.

Peanut Oil. The data for peanut oil (Fig. 5) indicate that with 99.9, 98.0, and 95.4% alcohols, the complete miscibility is attained at 70°, 80°, and 95°C., respectively, while the maximum solubility with 90% alcohol even at 90°C. is only 8.31%.

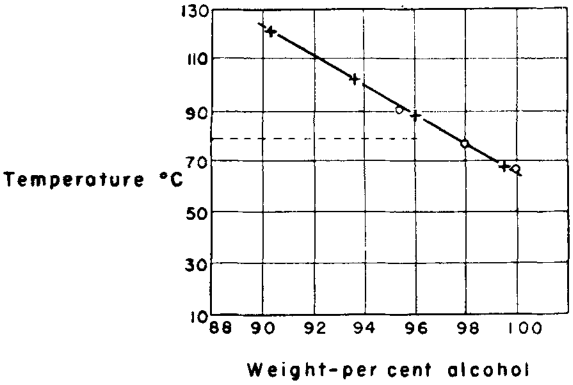

FIG. 3. Variation of critical solution temperatures of soybean oil with concentrations of aqueous ethanol.

X—Data of Okatomo (6).

⊙—Authors' data.

Dotted line indicates boiling point of pure ethyl alcohol.

The critical solution temperature *versus* alcoholic concentrations data have been plotted in Figure 6 and show complete agreement with the Japanese data (7).

Sesame Oil. The data for sesame oil are shown in Figure 7 and indicate that complete miscibility with 99.9, 98.0, and 95.4% alcohol is attained at 65°, 75°, and 90°C., respectively. With 91.5% alcohol the maximum solubility even at 90° is only 11%.

The critical solution temperature *versus* alcoholic concentrations data have been plotted in Figure 8 and show complete agreement with the Japanese data (7).

Thus it is seen that in all cases the critical solution temperature increases with the moisture content of alcohol, and for all of them the relationship is linear (Figs. 1, 3, 6, and 8).

Pressure in the System

The maximum pressure in the vessel, which was the result of both vapor and air pressure, was needed for design purposes and was determined by the pressure gauge. The pressure gauge readings recorded for dif-

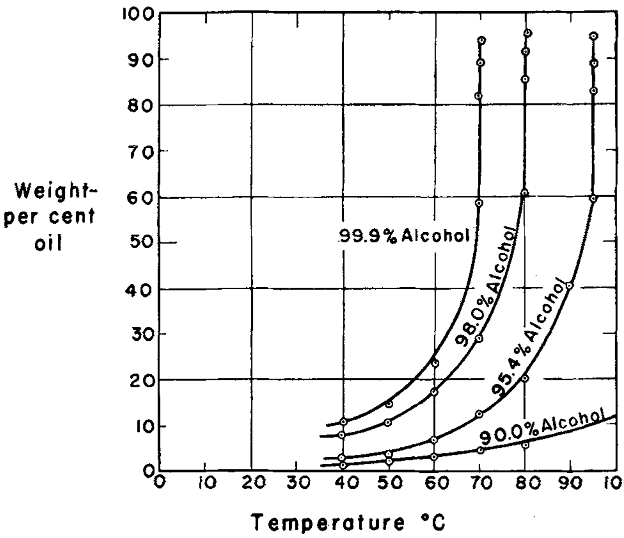

FIG. 5. Variation of solubility of peanut oil in aqueous ethanol with temperature.

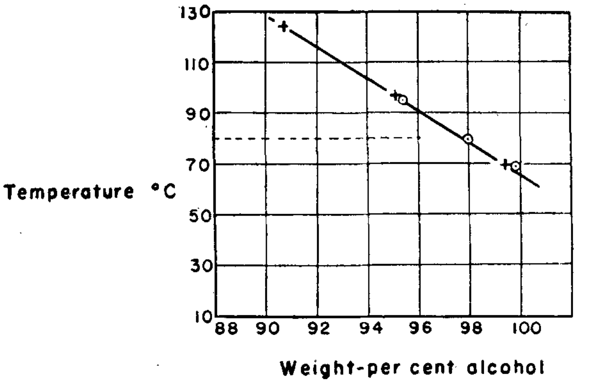

FIG. 6. Variation of critical solution temperatures of peanut oil with concentrations of aqueous ethanol.
X—Data of Sato, *et al.* (7).
⊙—Data of authors.
Dotted line indicates the boiling point of pure ethyl alcohol.

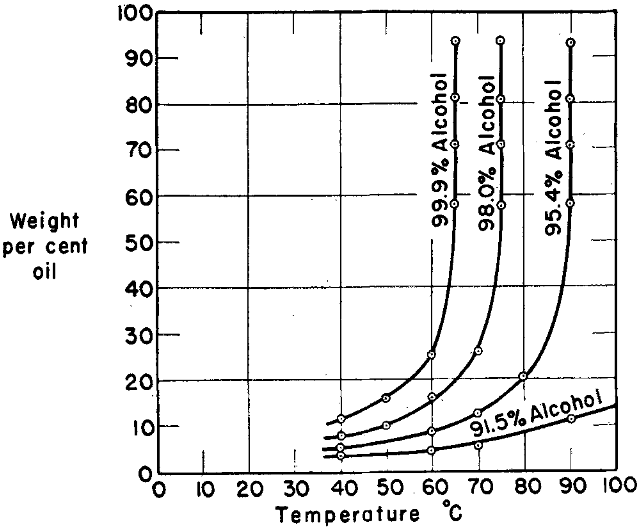

FIG. 7. Variation of solubility of sesame oil in aqueous ethanol with temperature.

ferent alcoholic compositions at various temperatures are given below in pounds p.s.i.

Concentration of alcoholic solution	Temperatures °C.					
	50	60	70	80	90	95
95.42%..............................	2	4	8	15	17	20
98.0 %..............................	2	4	8	15	18	
99.9 %..............................	2	4	10	15		

It is seen therefore that the pressure in the vessel increases with the temperature. However the gauge readings for all the three concentrations are practically the same since their boiling points differ very slightly, thus producing variations in vapor pressures too small to be recorded by the pressure gauge. The maximum pressure to be used even with 95.4% alcohol is about 20 p.s.i.g.

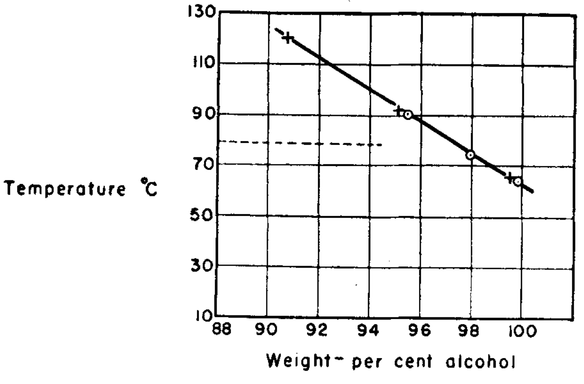

FIG. 8. Variation of critical solution temperatures of sesame oil with concentrations of aqueous ethanol.
X—Data of Sato, *et al.* (7).
⊙—Data of authors.
Dotted line indicates the boiling point of pure ethyl alcohol.

Summary

Solubilities of cottonseed, peanut, sesame, and soybean oils in aqueous alcoholic solutions at various temperatures were determined directly. Solubility curves for the four oils in aqueous alcoholic solutions are presented.

The critical solution temperatures *versus* alcoholic concentrations data have been plotted and are in complete agreement with the previously published data of Japanese workers in each case. It is observed that the critical solution temperature increases with the moisture content of the alcohol, and in each case the relationship is linear. The pressure in the system also varies directly with the temperature, the maximum being approximately 20 p.s.i.g.

Acknowledgments

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