

SOLUBILITIES OF VEGETABLE OILS
IN AQUEOUS ETHANOL

by

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ABSTRACT

In Asiatic countries like India, China and Japan, which produce enormous amounts of oilseeds, the solvent extraction industry has not developed mainly due to the difficulty of obtaining a suitable solvent at a cheap price. The conventional solvents such as normal hexane, trichloroethylene and cyclohexane have to be imported and therefore become enormously costly due to very high import duties and the transit charges. The best way out is therefore to study the suitability of the indigenous solvents for use in the oil extraction industry. Among the solvents produced in plenty in Asia is ethyl alcohol which is available at about half the price of the imported solvents. It is known to be a good solvent for vegetable oils and is bound to become a very popular solvent in Asiatic countries if an economical process for its use is worked out. This investigation pertains to the first phase of the problem.

The most important data necessary in studying the suitability of a solvent for vegetable oil extraction and in designing a commercial plant are the solubility data of the oils in the solvent and the pressures developed by different concentrations of the miscellas at the extraction temperatures.

The literature search revealed that while some data have been published on the miscibilities of cottonseed, peanut, sesame and

soybean oils in aqueous ethanol, no data are available for the other commonly used oils like corn, linseed and tung oils. Further no data whatsoever are available regarding the pressures developed by different concentrations of ethanol miscellas at various extraction temperatures, and hence the need for the present investigation.

An apparatus to determine the solubility of vegetable oils in aqueous ethanol was designed and fabricated. It also enables one to determine the pressures exerted by the alcoholic miscellas at different critical solution temperatures.

A direct and simple method was used to determine the solubilities at different temperatures.

Solubilities of cottonseed, peanut, sesame, soybean, corn, linseed and tung oils in aqueous alcoholic solutions have been determined, and the solubility curves for the seven oils are presented. It is observed that the solubility of the oil increases steadily with temperature, till the critical solution temperature is reached. At and above that temperature oil and aqueous ethanol are miscible in all proportions.

The solubility of the oil decreases with increasing water content of ethanol and vice versa.

For a fixed concentration of aqueous ethanol every oil of known characteristics has a fixed critical solution temperature. The critical solution temperature versus alcoholic composition data, has been

plotted for the seven oils studied. It was observed that the critical solution temperature increases with the water content of alcohol and that the relationship is linear in every case.

The present data on cottonseed, peanut, sesame and soybean oils are in complete agreement with the previously published data and thus confirm the latter. This also establishes the reliability and accuracy of the present method, which has been used to obtain new data on other oils.

The new solubility data of corn, linseed and tung oils are similar to those of cottonseed, peanut, sesame and soybean oils. The solubility curves follow the same pattern and the critical solution temperatures of the three oils vary linearly with concentrations of aqueous ethanol.

The pressure in the system also varies directly with the temperature and the maximum pressure to be used even with 95.4 percent alcohol is about 20 pounds per square inch gage.

INTRODUCTION

The methods of extraction of vegetable oils from the oil seeds are mechanical expression and solvent extraction. In the former, the oil seeds are subjected to external pressure and in the latter use is made of organic solvents, which dissolve the oil when brought into contact with the oil bearing material. Mechanical expression is used to extract oil from oil seeds of very high oil content. However complete removal of oil is not possible even with the best of expellers and the residual cakes from them contain about 5 to 8 percent of oil. The latter could be very conveniently recovered by solvent extraction of the cakes. It has in fact been established that the only way of processing an oil bearing material with low oil content is by extraction with suitable solvents. Solvent extraction when properly done reduces the oil content of the cakes to less than 1 percent in almost all cases.

The most commonly used solvents in the United States are normal hexane and other low boiling petroleum fractions. In European countries benzene, trichloroethylene and cyclohexane have found much favor. In Asiatic countries like India, China and Japan, which produce enormous amounts of oilseeds, the solvent extraction industry has not developed. India had its first solvent extraction plant of 50 tons a day capacity, only a couple of years back which uses normal hexane as a solvent.

However there is an increasing trend to set up many more plants in order to recover oil worth millions of dollars from the oil cakes, which is now being wasted for the lack of proper equipment.

One of the major factors hindering the establishment of the solvent extraction plants in India, has been the difficulty of obtaining a suitable solvent at a cheap price. In India there are resources neither to obtain petroleum fractions nor the other usual solvents like benzene, cyclohexane and trichloroethylene. It has therefore to depend entirely upon foreign countries for the supply of the conventional solvents for its extraction plants. These solvents become enormously costly due to very high import duties and the transit charges. Moreover international events tend to make their supply uncertain and irregular, thus paralyzing the extraction industry. In order therefore to keep its solvent extraction industry absolutely free of foreign dependence, and also because of very high cost of the imported solvents, there is a growing tendency in India to study the suitability of the indigenous solvent for extraction purposes.

Among the solvents available in plenty in India, the cheapest to compare with other imported solvents is ethanol, which is known to be a good solvent for oils, at or above its boiling point. During the last war the Japanese are reported to have used ethanol as a solvent for a batch soybean extraction plant at Dairen, Manchuria (7)(11). Considerable work has been done in this country also at the Northern Regional Research Laboratories, Peoria, Illinois, which has established

alcohol to be a good solvent for soybean oil, producing a meal highly nutritive and of improved flavor (6). Some laboratory scale work done in India (12)(14) has also demonstrated the potentialities of ethyl alcohol for extracting cottonseed and peanut oils.

Although most of the work which has established ethanol as an excellent solvent for soybean oil has been done in the United States, it has not been used at all so far in any commercial plants. The obvious reason is its abnormal cost which is double that for the petroleum solvents, coupled with the high federal tax and supply restrictions. However, in India, the price of alcohol, including the excise duties works out almost half of the cost of the conventional petroleum solvents.

Thus for reasons mentioned earlier and in view of its plentiful supply at rather cheap price, alcohol is bound to become a very popular solvent in India if an economical method for its use is worked out. It may also become very popular in countries like China, Japan and Argentina where alcohol is more cheaply available than the petroleum solvents.

Since the choice of the solvent plays a decisive part in the successful operation of the process it is necessary at this stage to discuss the advantages and disadvantages of alcoholic extraction and to examine closely as to how ethanol compares with the conventional solvents of the extraction industry.

Ethanol as a Solvent

An ideal solvent must be stable, should have a uniform composition and a constant boiling range, which should not exceed 100°C., a low specific heat, and a low freezing point. It should have a selective solvent power for oil, namely it should not extract pigments and mucilagenous matter with the oil. It should easily wet and penetrate the flakes, but should also be easily removable from the residual meal and oil. It should preferably be non inflammable and its vapor be non toxic and non explosive. It must have no corrosive action on the usual materials of construction. It should have a low specific gravity, should be easily available, store well, should not deteriorate in transport and above all it must be cheap (17).

Of course there is no single solvent known that would completely satisfy all the above postulates, hence a compromise has to be made, depending upon the availability and the cost of the solvent.

Alcohol, in addition to having most of the characteristics of an ideal solvent as postulated above such as low specific heat, and low specific gravity, has been shown to possess certain unique advantages when compared to the conventional solvents. It has however a few disadvantages also.

These disadvantages are its inflammability and its use at higher temperatures and pressures. It is also said that alcohol dilutes easily, thus decreasing the solubility and is very difficult to be

removed from the extracted oil.

As regards inflammability, it is common to all the other conventional solvents and the usual precautions have to be taken.

Alcohol has to be used at temperatures at or above its boiling point, consequently the equipment has to be specially designed, which may involve extra initial cost of investment. Since the working temperature in the case of alcohol will be about 90°C . unlike other solvents which are worked at low temperatures, it may be argued that more heat is to be supplied initially to the solvent. But this has an inherent advantage also. The oil dissolves completely in hot alcohol and the major portion of it separates out by just cooling the miscella to about 20°C . (2). The usual method of obtaining the oil in the case of other solvents is by the distillation of the solvent. The use of hot alcohol in fact helps to do away with the "distillation step". This is a unique feature of the use of alcohol (4).

Use of the cooling step for the elimination of distillation, obviously substitutes a step that involves only a sensible heat for one that requires the latent heat of vaporization. Furthermore most of the sensible heat transfer may be effected in heat exchanges since the cooled alcoholic solvent must be reheated for reuse in the extractor. Beckel and coworkers in fact have developed a continuous non distillation extraction process for soybean oil using ethyl alcohol (2). They have investigated the economic aspect of the

method and have found that alcoholic process required theoretically about 7/10 as much energy as the hexane process (4). One other advantage with ethanol is that although impurities are extracted by the alcohol together with the oil, the miscella when cooled to 25-30°C., separates into two layers. The bottom layer consists of pure oil of an excellent quality and little alcohol, while the top layer contains all the impurities, such as resin, pigments, proteins, carbohydrates, hydrocarbons and water and can be reused. Only after several recycles the contaminated alcohol has to be redistilled (2).

The cake obtained from the alcoholic extraction is therefore bound to be of improved and flavor and has been shown so (3)(16). It has also been shown that its nutritive value is higher than the cakes obtained from the other solvents and therefore is bound to command a higher price than the other meals.

Alcohol has a great affinity for water. It easily absorbs moisture from the oleaginous material and the solubility of oil in alcohol is considerably reduced. This absorption could be prevented by simply predrying the material to reduce the moisture content to less than 3 percent, so that considerable dilution does not take place. It has been shown by Beckel that in the case of soybean flakes if the moisture content is reduced to about 3 percent, the moisture was not at all lost to alcohol, but instead removed water from the latter, leaving it a better solvent than when first used. He has used the alcohol 85 times without ever having distilled it, and found it a better oil solvent,

than it was at the beginning of the experiment. He also found that the oil content of the flakes was always reduced to less than 1 percent in each case.

As regards the argument that it is not possible to remove the alcohol from the residual oil completely it has been shown in a recent patent taken out by Beckel and Cowan, (5) that after removing the maximum quantity of oil the alcohol remaining in the solvent is completely removed by distilling out with benzene.

It is therefore evident from the above, that ethanol has excellent oil-solvent properties. Its disadvantages are the same as those of the conventional solvents, however it has certain unique properties due to which alcoholic extraction process possesses the following advantages:

1. It is a simple direct process applicable to all oil seeds and oil cakes, as well as to many types of other extractable materials.
2. High grade edible oils can be obtained.
3. Efficiency of extraction is as high as with other solvents.
4. Overall processing costs are less by a third of the costs in other extraction methods. Steam costs are almost three quarters. Solvent loss is lower than with petroleum solvents (4)(13).
5. Alcohol is a non toxic, pure solvent so that even if traces

of solvent remain in the extracted products, these are not rendered inedible.

6. Alcohol extraction results in several valuable by-products which may be recovered, such as, fatty acids, sugars, lecithin, present in oil seeds and oil cakes.

Thus ethyl alcohol with all the above advantages is bound to become a very popular solvent if an economical process for its use is worked out, especially in Asiatic countries like India, China and Japan where ethyl alcohol is produced in plenty and available cheaper than the conventional solvents.

Aim of Investigation

The most important and fundamental data, necessary in studying the suitability of a solvent for vegetable oil extraction and in designing a commercial plant are the solubility data of the oils in the solvent and the pressures developed by different concentrations of the miscellas at the extraction temperatures.

The literature search revealed that while some data have been published on the miscibilities of cottonseed, peanut, sesame and soybean oils in aqueous ethanol solutions, no information is available regarding the pressures developed at the critical solution temperatures.

Besides the above data, which were obtained by the static sealed tube method, have not yet been confirmed by any other method.

Further no data, are available on the solubilities of other commonly used vegetable oils, viz. corn oil, linseed oil and tung oils. The present investigation was therefore taken up to:

1. Confirm the available data on cottonseed, peanut, sesame and soybean oils by using a different method.
2. To determine the solubilities of corn, linseed and tung oils, in various concentrations of aqueous ethanol.
3. To determine the pressures developed by different concentrations of alcoholic miscellas at various critical solution temperatures for all the above oils.

REVIEW OF LITERATURE

The solubilities of linseed, rapeseed, cottonseed, olive, sesame and soybean oils in aqueous ethanol at temperatures up to 25°C. are given in Seidell's book entitled "Solubilities of Organic Compounds" (18).

The Japanese have published data on the mutual solubilities of cottonseed, peanut, sesame and soybean oils (11)(15). Their method is described below:

A mixture composed of a known amount of solvent and about 3.5 cc. of soybean oil is filled into a glass tube (of which one part is wider; diameter of upper portion about 7.0 m.m.; length about 50 m.m.; diameter of lower portion about 10 m.m.; length 30 m.m.) in such a way that as little air remains in it as possible. The glass tube is sealed by fusion, heated gradually in a water bath and shaken occasionally. When a uniform liquid layer is formed, the temperature is gradually decreased while the shaking is continued. The point when the liquid becomes turbid is taken as the saturation point and the solubility is calculated at that temperature.

When dilute alcohol is used as solvent in these experiments a ternary system of soybean oil-alcohol-water is formed. But for the sake of convenience, they assumed dilute alcohol as one compound and

the binary system, soybean oil-alcohol is considered. The above data have been plotted in Figures 3, 5, 7 and 9.

Measamer et al. (10) have determined the equilibrium solubility relationships for trichloroethylene-ethanol system by the following method:

Mixtures of ethanol and trichloroethylene of known compositions varying from 0 to 60 percent trichloroethylene were placed in a three necked balloon flask. An air driven stirrer was operated in the flask through a mercury seal in the center neck. A thermometer was mounted in a stopper in a second neck. Soybean oil was added in small amounts from the burette. After each addition the temperature was raised until the mixture was clear. The arithmetic averages of the clearing and clouding temperatures were taken as the equilibrium temperatures.

Harris and coworkers (8) have published data on the solubility of cottonseed oil in constant boiling ethanol (95.6 percent) based on the cloud point titration method. In this method, water was added from a burette to weighed quantities of oil and alcohol until a permanent cloudiness developed. The titration was conducted in a closed three necked flask, equipped with a thermometer, stirrer, microburette, and immersed in a constant temperature bath.

More recently Magne and Skau (9) also have published mutual solubility data for cottonseed oil with 90.7, 94.4 and 99.3 percent ethanol. The determinations were made by the static sealed tube method which is

described thus:

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 and 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 thermometric calibration and emergent steam was taken as the solubility temperature for the given oil solvent composition. The maxima in the mutual solubility curves, that is the critical solution temperatures and the compositions were found by the method of Okamoto (11), which is based on the Cailletet and Mathias principle.

It will be seen from the above that most of the data on the miscibility of the various oils in different concentrations of ethanol have previously been obtained by the static method only from which the critical solution temperature and ethanol composition data for use in the design of an extraction process can be deduced by only an indirect method, such as suggested by Okamoto (11).

The above data have not yet been confirmed by any other method; besides no data are available for the other most commonly used vegetable oils, viz., corn, linseed and tung oils. Further no data

whatsoever are available regarding the pressures developed by different concentrations of ethanol miscellas at various extraction temperatures, so essential for designing extractors, and hence the need for this investigation.

EXPERIMENTAL

Materials

For the solubility determinations, freshly expelled and unrefined oils were used in every case. For each oil use, its characteristics, acid value, saponification value and iodine value (Wij's) were determined by the standard A.O.C.S. methods (1). The oils used were cottonseed, peanut, sesame, soybean, corn, linseed and tung oils.

Absolute and 91.5 percent alcohol were obtained directly from the stores. Ninety-eight and 95.4 percent ethanol 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 percent.

Analysis of the Miscella

The most practical methods used in the technical literature for determining the composition of the miscellas of hexane and trichloroethylene, are by determining the physical constants such as density and refractive index. Westphal balance and Abbe's refractometer respectively, are commonly used to determine them. Unfortunately the above methods are impracticable in the case of ethanol solutions of vegetable oils.

Both the Westphal balance and the refractometer are used at ordinary temperatures only, at which most of the oil dissolved in ethanol separates out and thus there is no homogeneous solution of the oil left.

In the case of refractometer there are two additional difficulties. The difference in the refractive indices of the pure oil and pure ethanol is of the order of 0.1, and with such a small difference it is impossible to use the refractive index criterion to determine the concentration of the miscella. Secondly the thin film of alcohol evaporated away rapidly in the refractometer even while the determination is being made, thus making the readings erroneous.

Since the above methods do not work, a fairly reliable method was devised and completely standardized for most of the commonly used oils, by the author during his work in India. The accuracy of the method is within ± 0.1 percent.

The method consists of the following steps:

1. The miscella is withdrawn in a 50 cc. weighed Erlenmeyer flask, stoppered immediately and reweighed to give the miscella withdrawn.
2. The alcohol from the miscella is evaporated completely on a vigorously boiling water bath.
3. The flask was dried in a drying oven at 105°C . to a constant weight.

From the above values the amount of oil in the miscella is determined.

Apparatus

The solubility determination apparatus (Figure 1) consisted of a mild steel vessel 2.5 inches in diameter and 6 inches high, closed at the bottom and fitted with a flange at the top. Through a packing gland at the center of the flange passed a steel stirrer shaft driven by an electric motor and provided with two blades at the bottom end. Asbestos thread and high melting grease were provided in the gland to prevent leakage. A pressure gage was provided to indicate the pressure developed. The vessel was provided with a needle valve one inch from the bottom, through which the sample could be withdrawn. The vessel was heated electrically, the temperature being controlled by a variable transformer to $\pm 0.1^{\circ}\text{C}$. Before starting the experiments, the apparatus was tested several times with steam under pressure and ascertained to be leak proof.

Solubility Determination

Known volumes of oil and solvent such as to provide an excess of oil at a fixed temperature (50 cc. oil and 100 cc. ethanol) were stirred for 30 minutes to obtain the solubility at that temperature. The optimum period of stirring to reach saturation was determined as 30 minutes in the earlier work of the author. The stirring was stopped



Figure 1. Solubility determination apparatus

and the mixture allowed to settle for 30 minutes keeping the temperature constant. The optimum period of settling was determined as 30 minutes in the earlier work of the author. A definite volume of the clear supernatant solution was drawn into a weighed conical flask, corked instantaneously and reweighed to give the weight of the 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 the flask was dried in a drying oven at 105°C. to a constant weight. From the above data, the percent solubility was calculated. Triplicate samples were taken for every determination and all the values have been expressed as weight percent alcohol.

With 50 cc. oil and 100 cc. alcohol the theoretical solubility is about 60 percent at the critical solution temperature, depending upon the oil and the concentration of ethanol. In order to establish points further on the solubility curve higher oil-alcohol ratios, 60, 70, 80 cc. oil and 100 cc. alcohol were used and the solubility determined as described above at each of the critical solution temperatures of the various oils used.

The solubility data for the seven oils studied are presented in the next section.

RESULTS AND DISCUSSION

Solubility Data of the Oils

Cottonseed oil

Freshly expelled and unrefined cottonseed oil was obtained from Mrs. Tucker's Products, Sherman, Texas. The following values of the oil were determined:

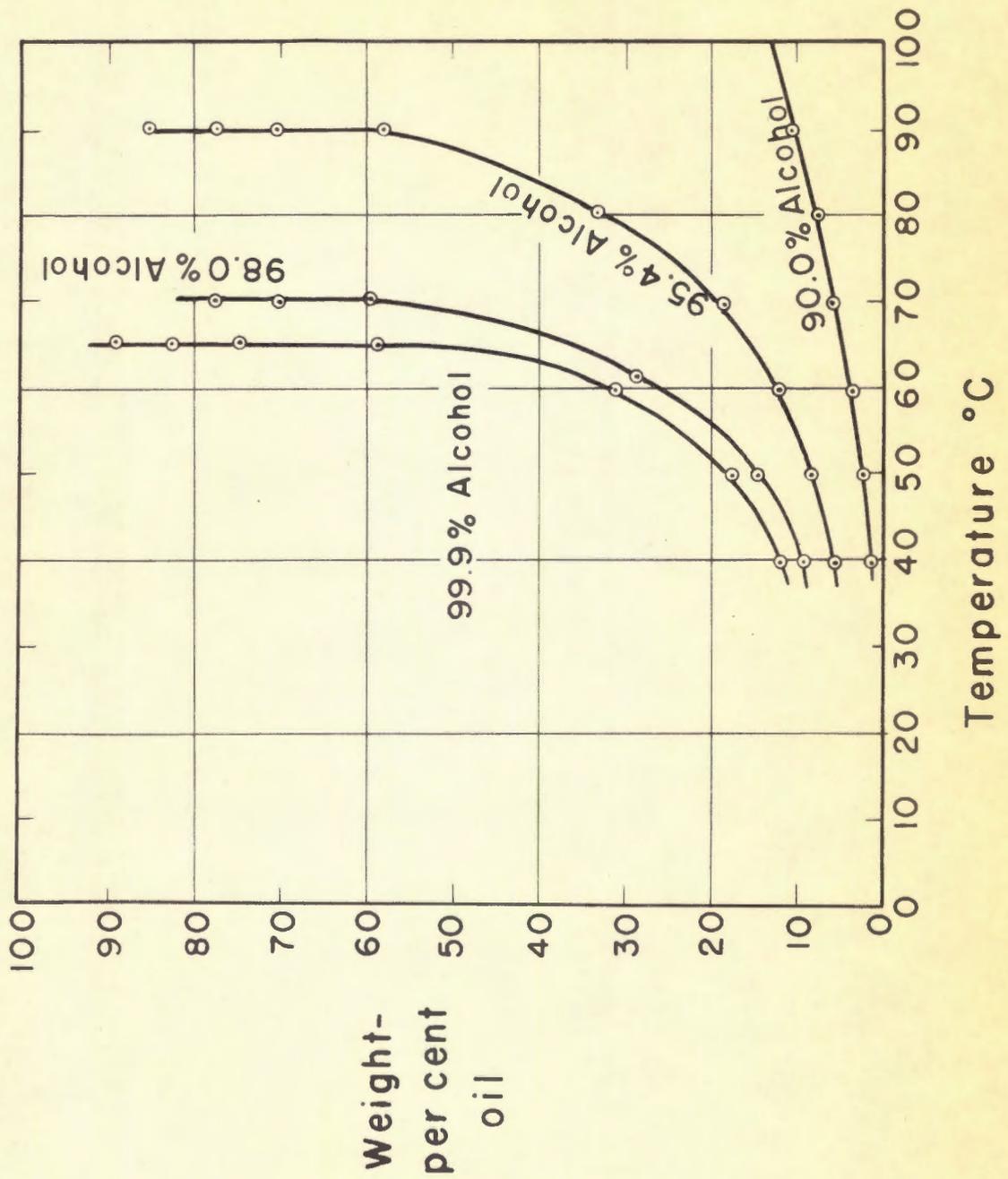
Acid value = 4.56

Iodine value = 105.6

Sap. value = 194.6

The solubility data for this oil are represented^a in Figure 2. It is observed that in all cases the solubility of the oil increases steadily until the critical solution temperature is reached. At the critical solution temperature, the solubility curves become parallel to the y axis, indicating that any amount of oil can be dissolved at that temperature i.e. oil and alcohol are miscible in all proportions at or above that temperature. It is also seen from the figures that with 99.9, 98.0 and 95.4 percent alcohols, the miscibility is attained at 65°, 70° and 90°C. while with 90 percent alcohol the solubility even at 90°C. is only 10.54 percent. With 91.5 percent alcohol it was

^aThe present data are represented by circles in all the figures. The horizontal dotted line in some figures indicates the boiling point of ethanol.



found to be 12.5 percent. This is not plotted in the Figure.

The critical solution temperature versus alcohol composition data have been plotted in Figure 3. It is observed that the critical solution temperature increases with the water content of alcohol and that the relationship is almost linear. The data of Sato, et al. are represented by (x) in Figure 3. The present data show very good agreement with their data (15).

The data of Magne and Skau (9) are represented by the triangles in Figure 3 and show a slight variation. The authors themselves have explained that in their method if the solubility temperature had been taken as the temperature at which two liquid layers appeared, (instead of slight turbidity) their data would have agreed with the Japanese data.

Thus it is seen that the present data on cottonseed oil are in very good agreement with the published data.

Peanut oil

Freshly expelled and unrefined peanut oil was obtained through the courtesy of Law and Company, Atlanta, Georgia. The following values of the oil were determined:

Acid value = 2.72

Iodine value = 94.62

Sap value = 191.9

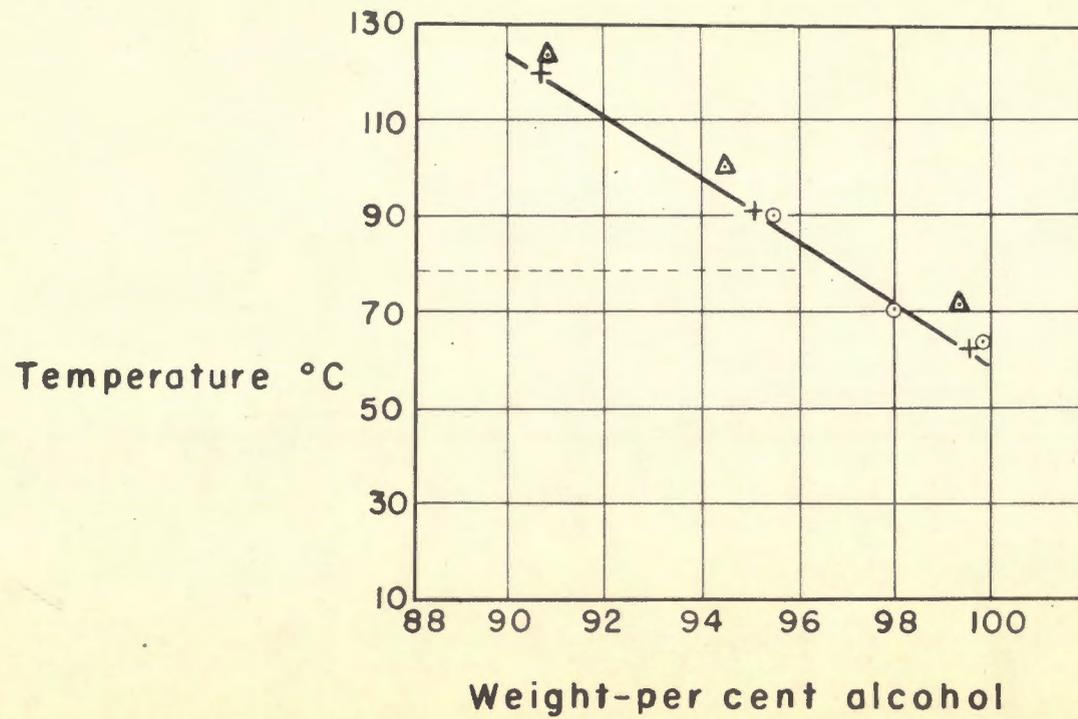


Figure 3. Variation of critical solution temperature of cottonseed oil with alcohol composition

The solubility data for this oil are presented in Figure 4 and indicate that the curves follow the same pattern as that of cottonseed oil. The solubility of the oil increases steadily until the critical solution temperature is reached, at which point the curve becomes parallel to y axis, indicating that oil and alcohol are miscible in all proportions at or above that temperature.

It is also observed that with 99.9, 98.0 and 95.4 percent alcohols, miscibility is attained at 70°, 80° and 95°C. respectively, while the solubility with 90 percent alcohol even at 90°C. is only 8.31 percent. With 91.5 percent alcohol the solubility at 90°C. is 10.2 percent. This is not shown in the Figure.

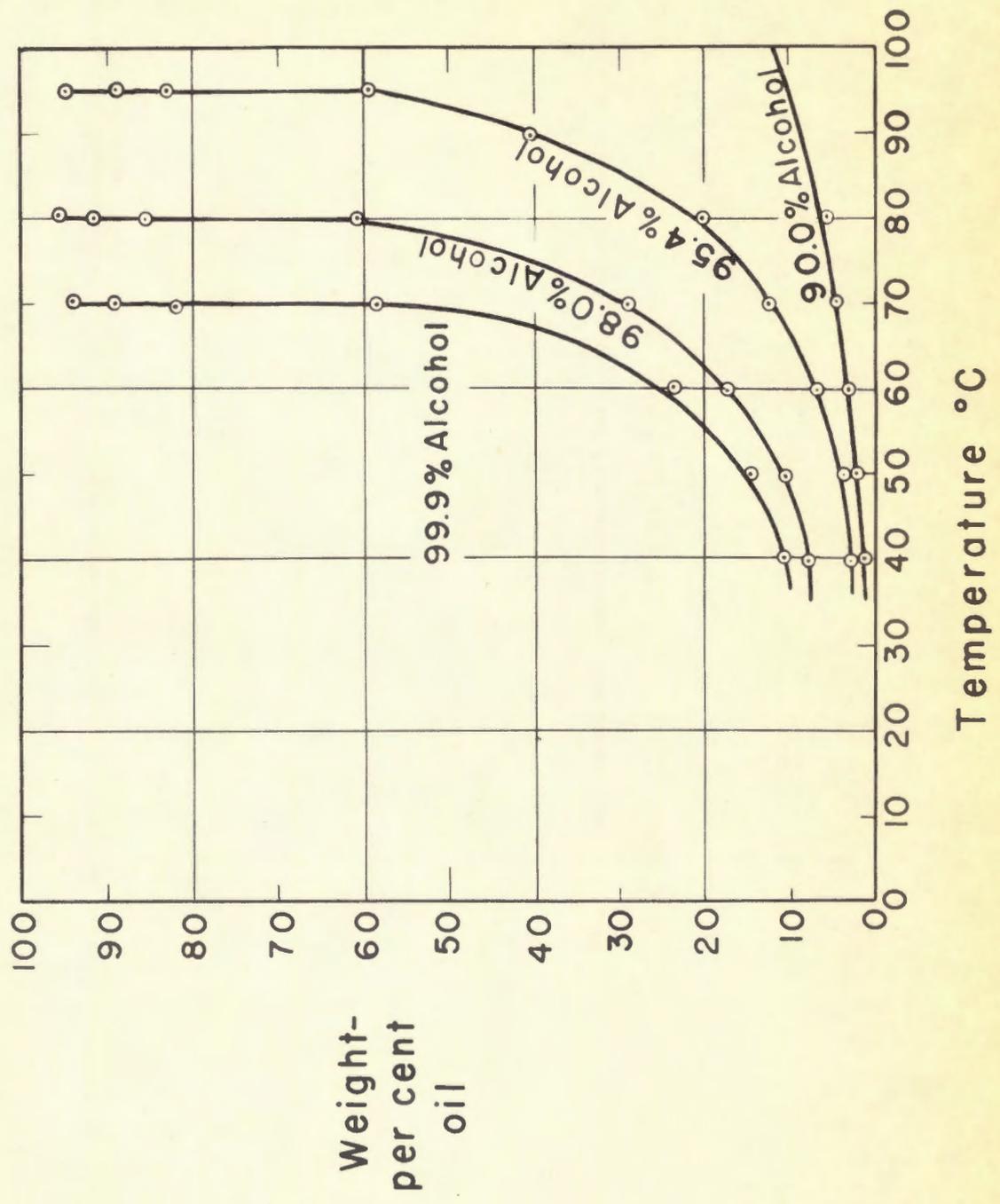
The critical solution temperature versus alcohol composition data are plotted in Figure 5. It is seen that the critical solution temperature increases with the water content of alcohol, and the relationship is linear.

Data of Sato et al. (15) are represented by (x) in the Figure and the present data are found to be in complete agreement with their data.

Sesame oil

The unrefined oil was obtained through the courtesy of Southern Regional Research Laboratories, New Orleans, Louisiana. The following values of the oil were determined:

Acid value = 2.5



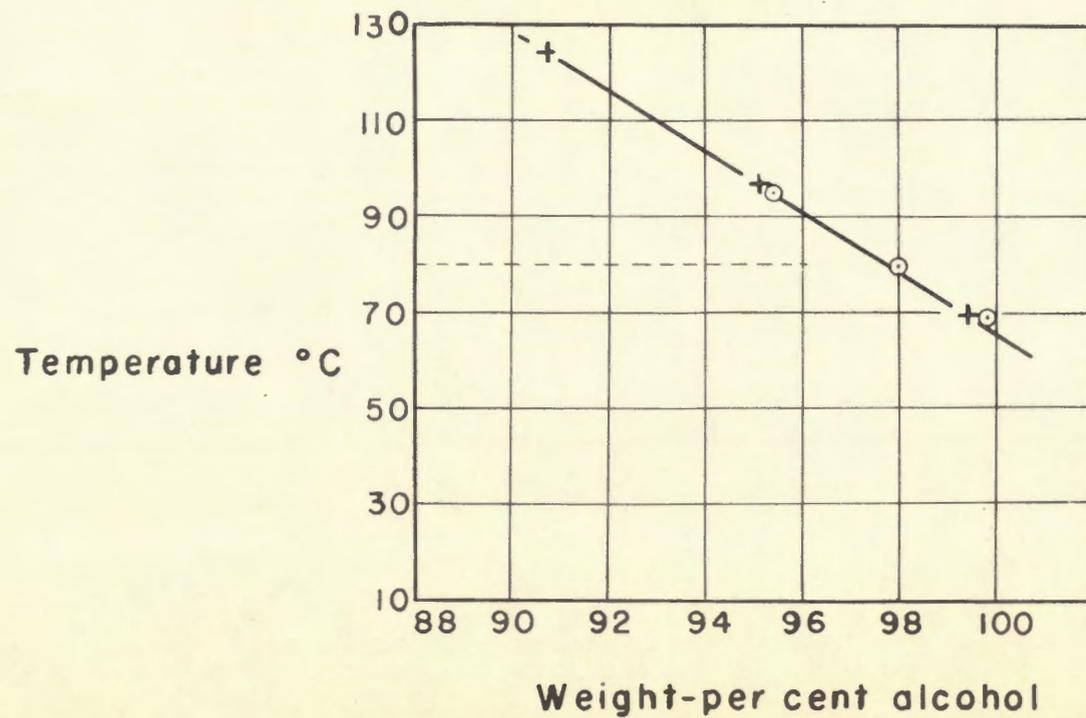


Figure 5. Variation of critical solution temperature of peanut oil with alcohol composition

Iodine value = 112.7

Sap. value = 191.4

The solubility data are plotted in Figure 6. and the curves follow the same general pattern as described earlier. In each case the solubility increases steadily till the critical solution temperature is reached at or above which oil and alcohol are miscible in all proportions.

It is seen that miscibility with 99.9, 98.0 and 95.4 percent alcohol is attained at 65°, 75° and 90°C. respectively, while with 91.5 percent alcohol, the solubility even at 90°C. is only 11.0 percent.

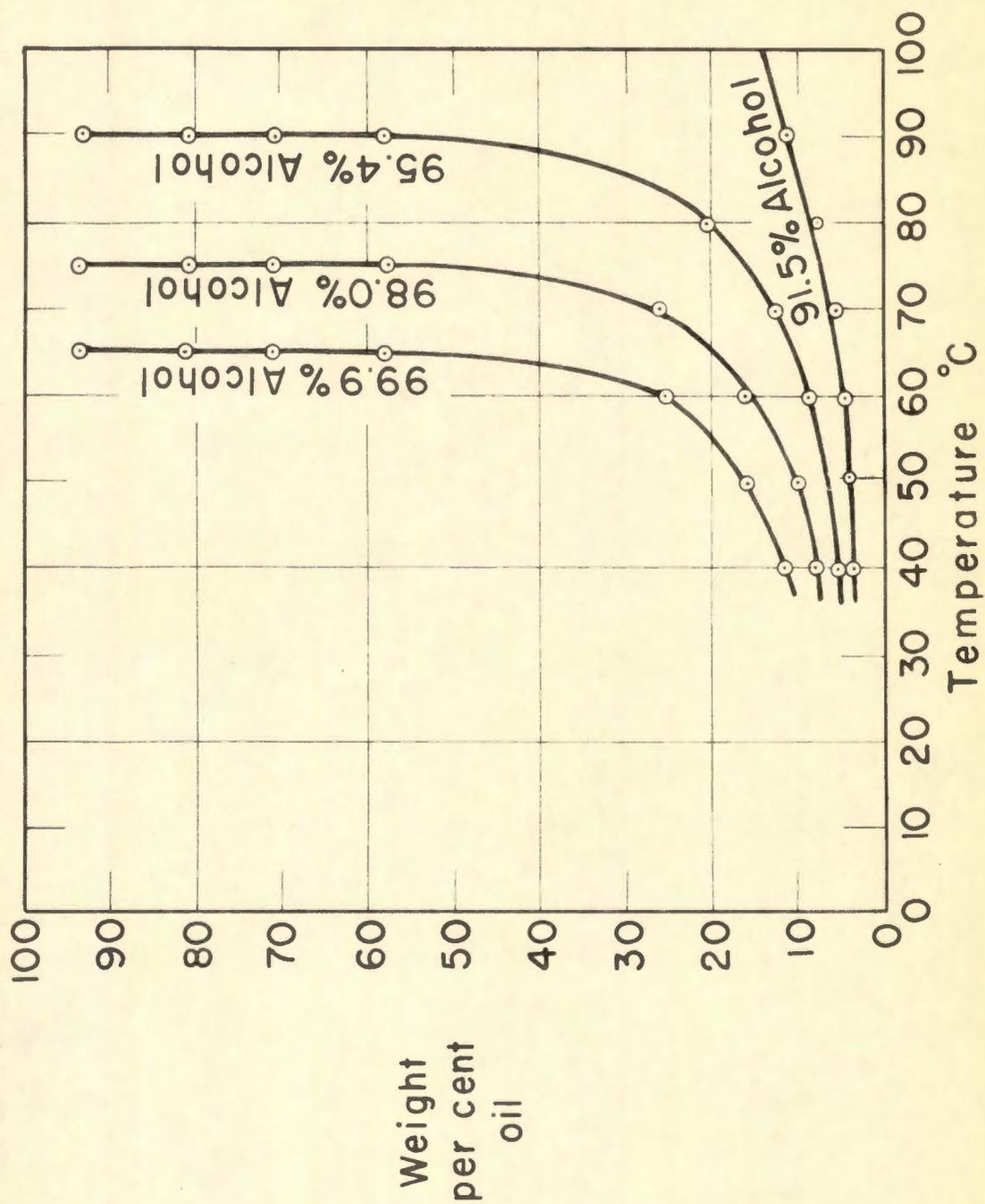
The critical solution temperature versus alcoholic composition data have been plotted in Figure 7 and show complete agreement with the data of Sato et al. (15), represented by (x). It is seen that the critical solution temperature increases with the water content of alcohol and that the relationship is linear.

Soybean oil

Freshly expelled and unrefined oil was obtained from Swift and Company, Des Moines, Iowa. The following values of the oil were determined:

Acid value = 1.03

Iodine value = 129.6



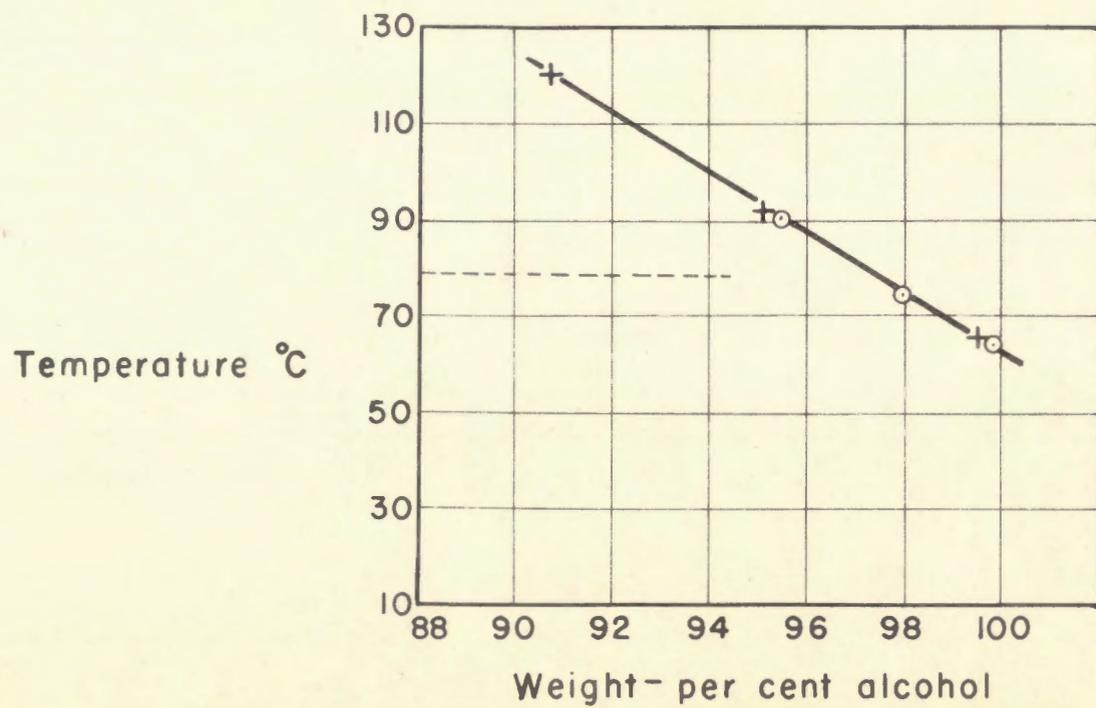


Figure 7. Variation of critical solution temperature of sesame oil with alcohol composition

Sap. value = 191.4

The solubility curves for this oil are presented in Figure 8. It is observed that with 99.9, 98.0 and 95.4 percent alcohols, miscibility is attained at 67°, 78° and 90°C. respectively, while the solubility with 91.5 percent alcohol even at 100°C. is only 15 percent.

The critical solution temperature versus alcohol composition data are plotted in Figure 9, and are found to be in complete agreement with the data of Okatomo (15), represented by (x). It is observed that the critical solution temperature increases with the water content of alcohol and that the relationship is linear.

Corn oil

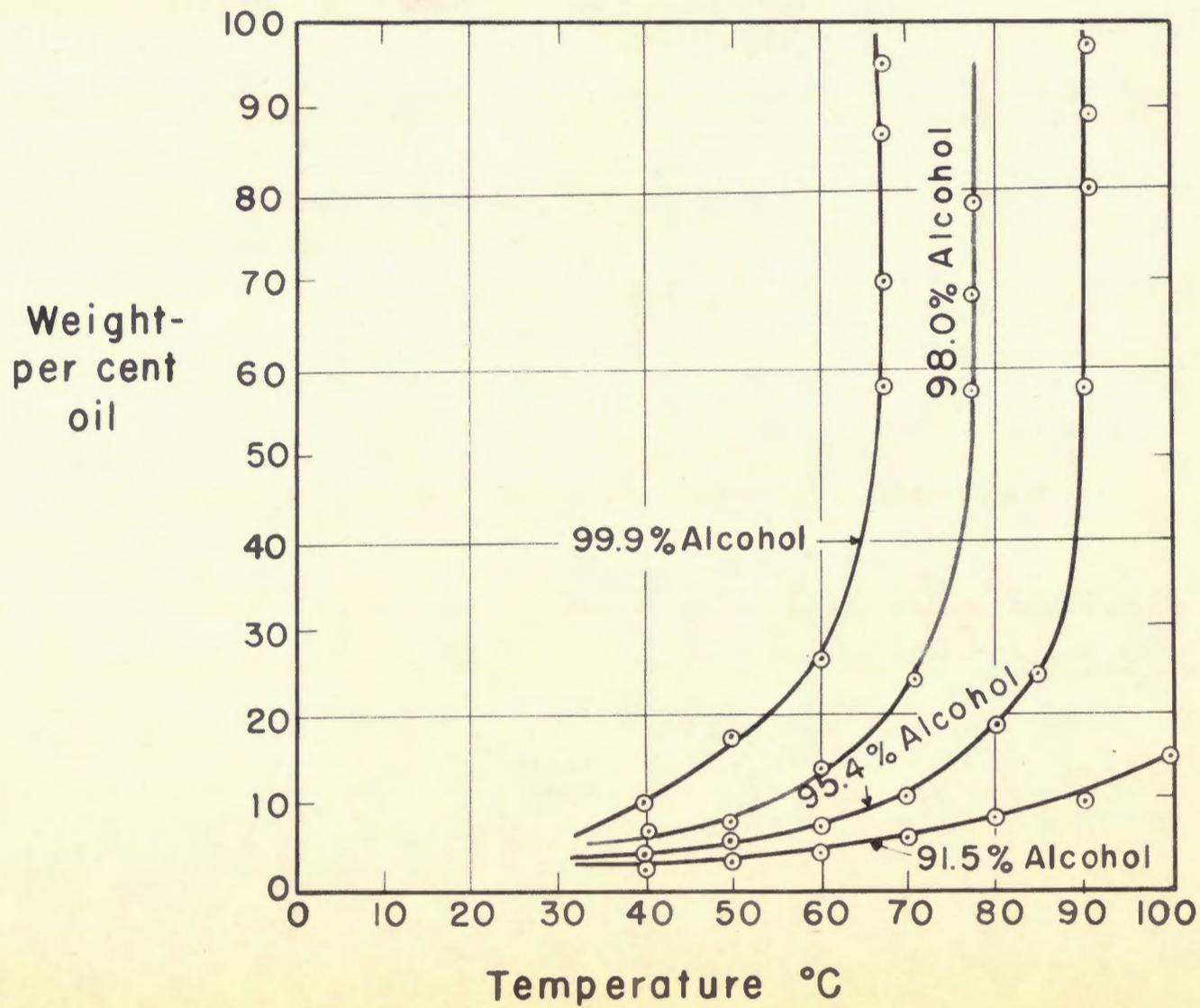
Freshly expelled and unrefined corn oil was obtained from Clinton Foods, Inc., Clinton, Iowa. The following values of the oil were determined:

Acid value = 1.52

Iodine value = 120.2

Sap. value = 189.7

The solubility data for the oil are presented in Figure 10. It is observed that the solubility curves follow the same general pattern as that of the oils presented earlier. In this case miscibility with 99.9, 98.0 and 95.4 percent alcohols is attained at 65°, 75° and 90°C.



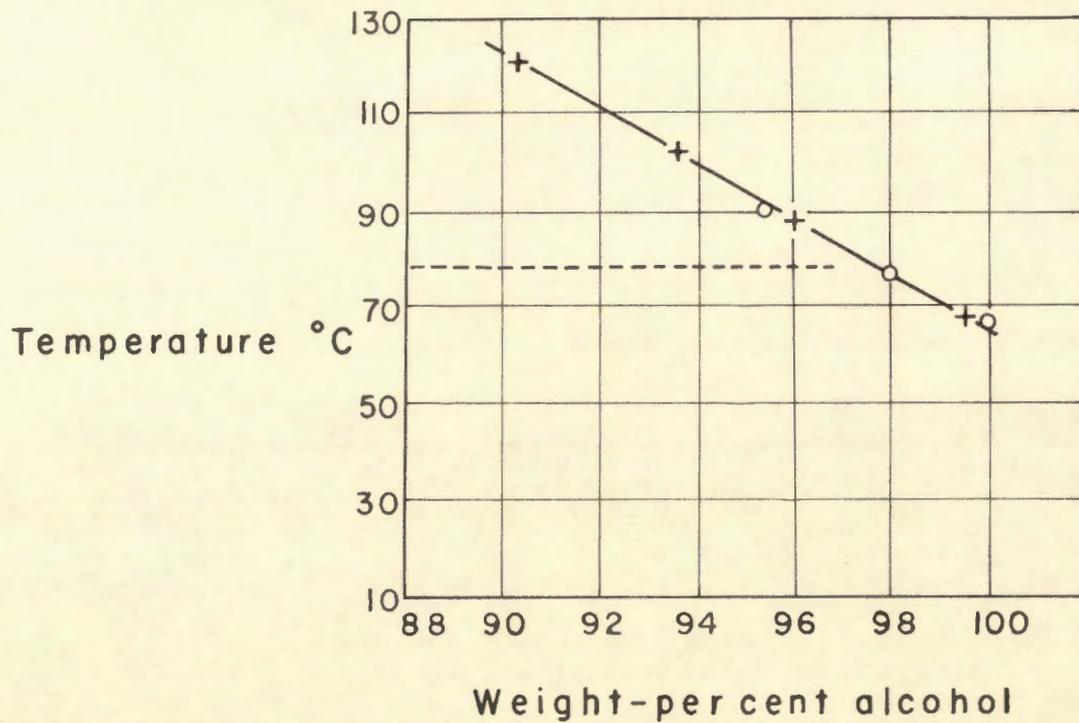
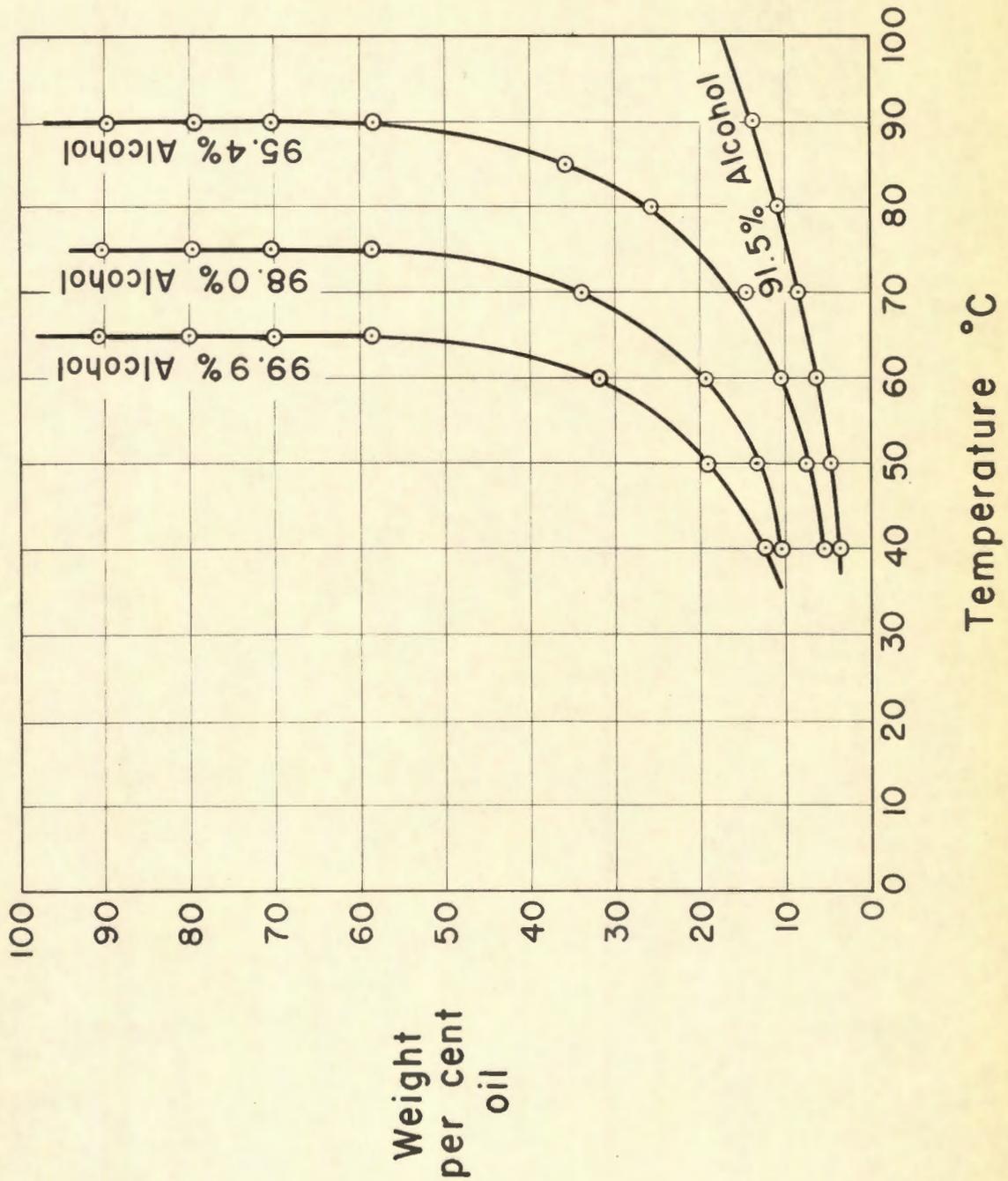


Figure 9. Variation of critical solution temperature for soybean oil with alcohol composition



respectively, while the solubility at 91.5 percent alcohol even at 90°C. is 13.7 percent.

The critical solution temperature versus alcohol composition data are plotted in Figure 11. It is observed that in this case also, the critical solution temperature increases directly with the water content of ethanol and that the relationship is linear.

Linseed oil

Freshly expelled and unrefined linseed oil was obtained from Minnesota Linseed oil Co., Minneapolis, Minnesota, and the following values of the oil were determined:

Acid value	=	1.48
Iodine value	=	182.5
Sap. value	=	191.3

The solubility curves are presented in Figure 12 and show that in this case with 99.9, 98.0 and 95.4 percent alcohols miscibility is attained at 60°, 70° and 80°C. respectively, while with 91.5 percent alcohol the solubility even at 90°C. is only 17.5 percent.

The critical solution temperature versus alcohol composition data are plotted in Figure 13, and as in the previous cases, a linear relationship is observed.

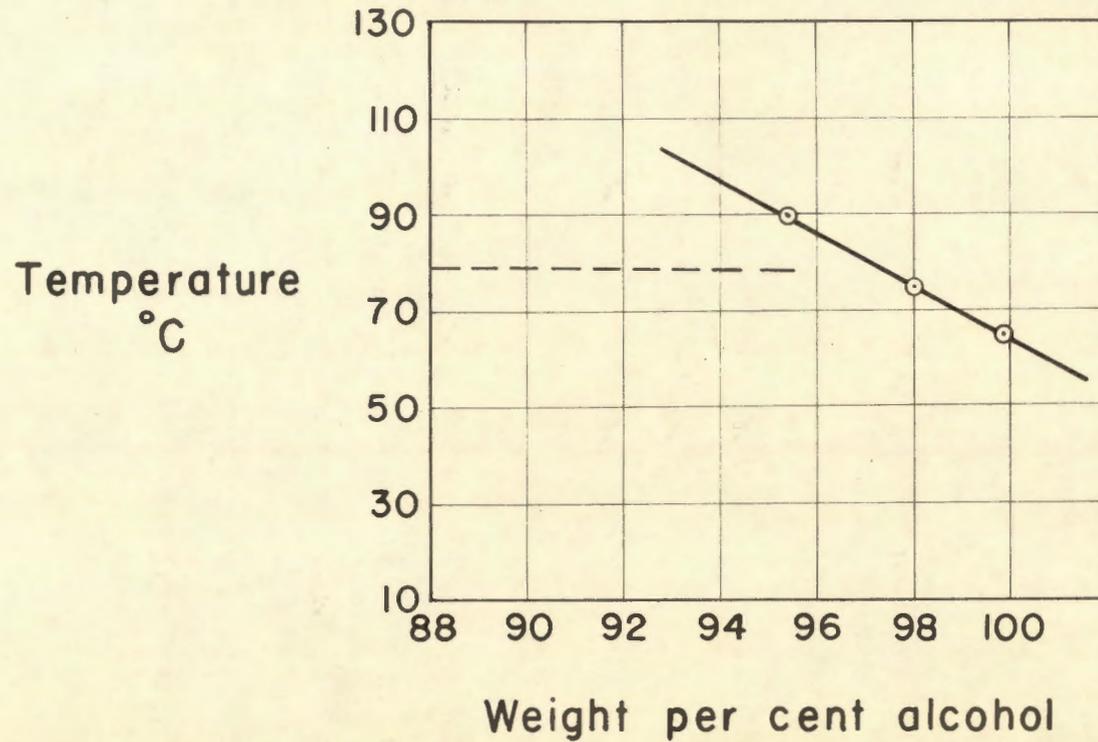
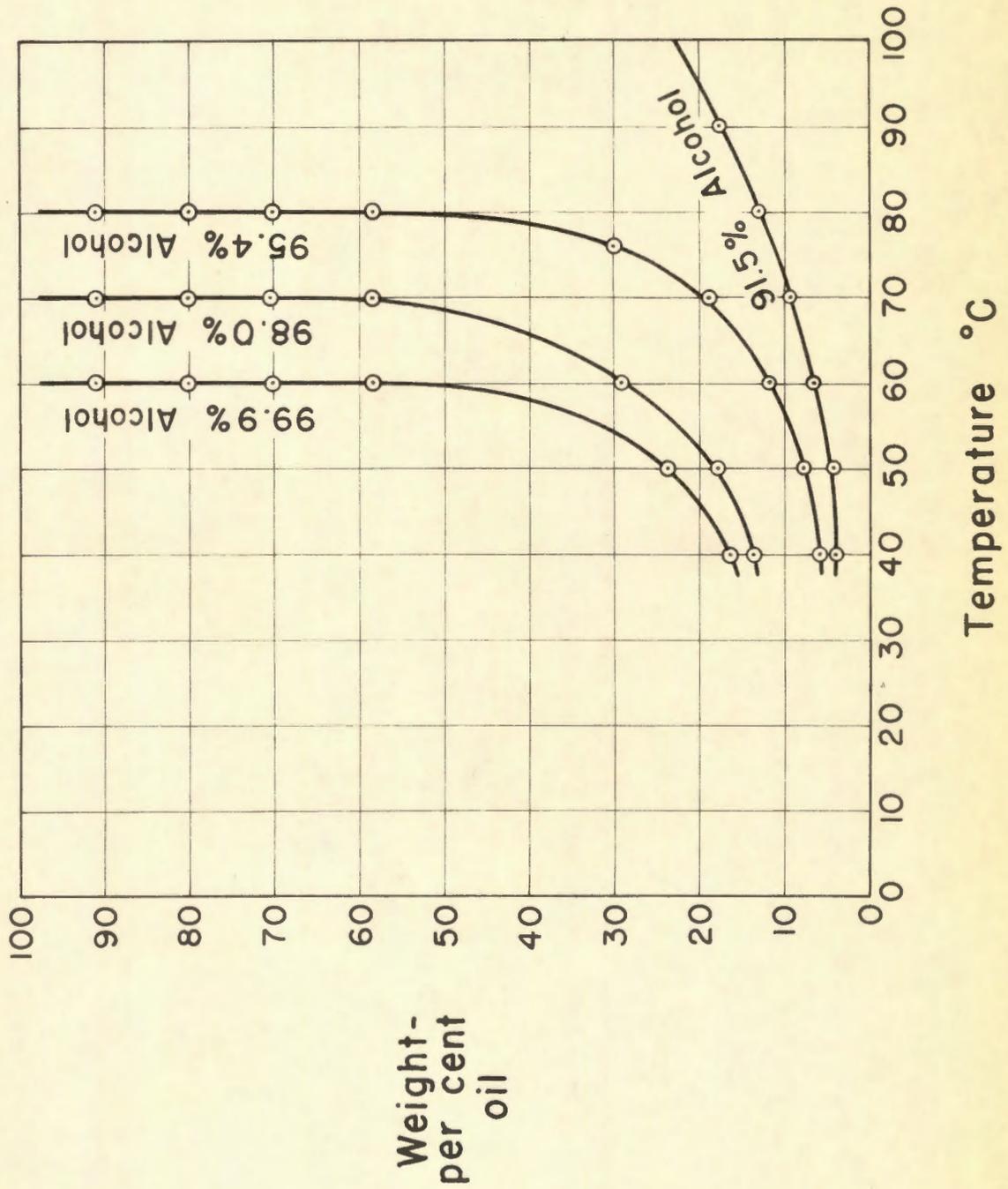


Figure 11. Variation of critical solution temperature of corn oil with alcohol composition



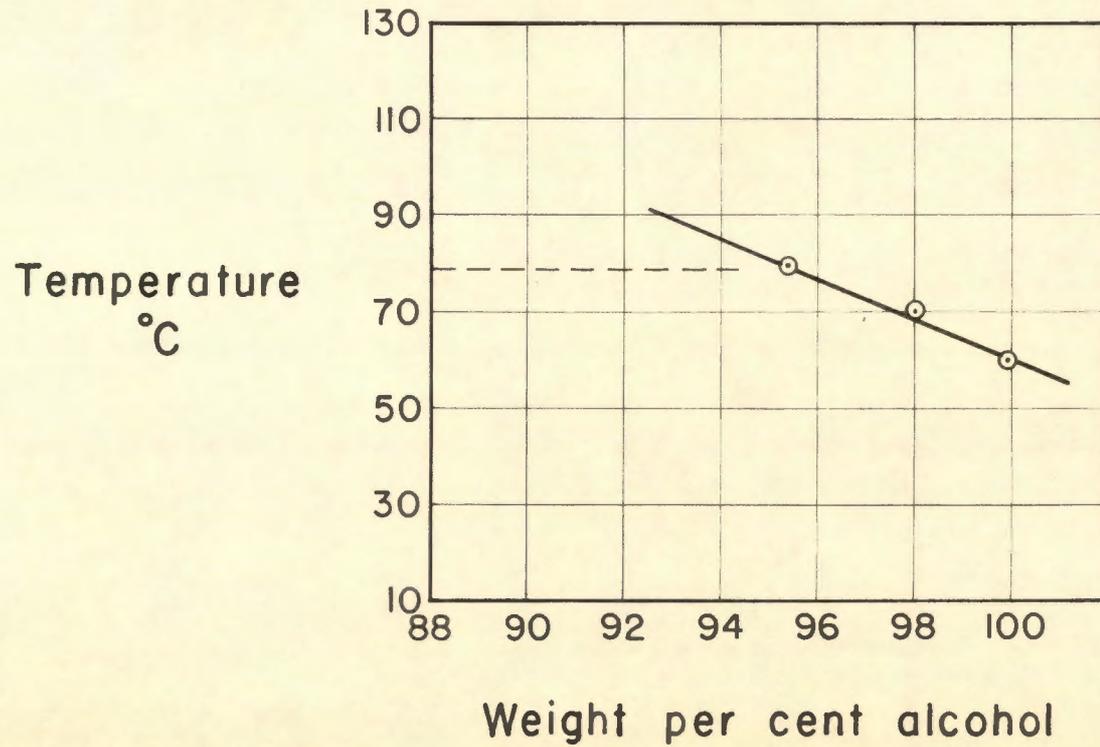


Figure 13. Variation of critical solution temperature of linseed oil with alcohol composition

Tung oil

This oil was obtained through the courtesy of Southern Regional Research Laboratories, New Orleans, Louisiana. The following values of the oil were determined:

Acid value = 1.52

Iodine value = 168.7

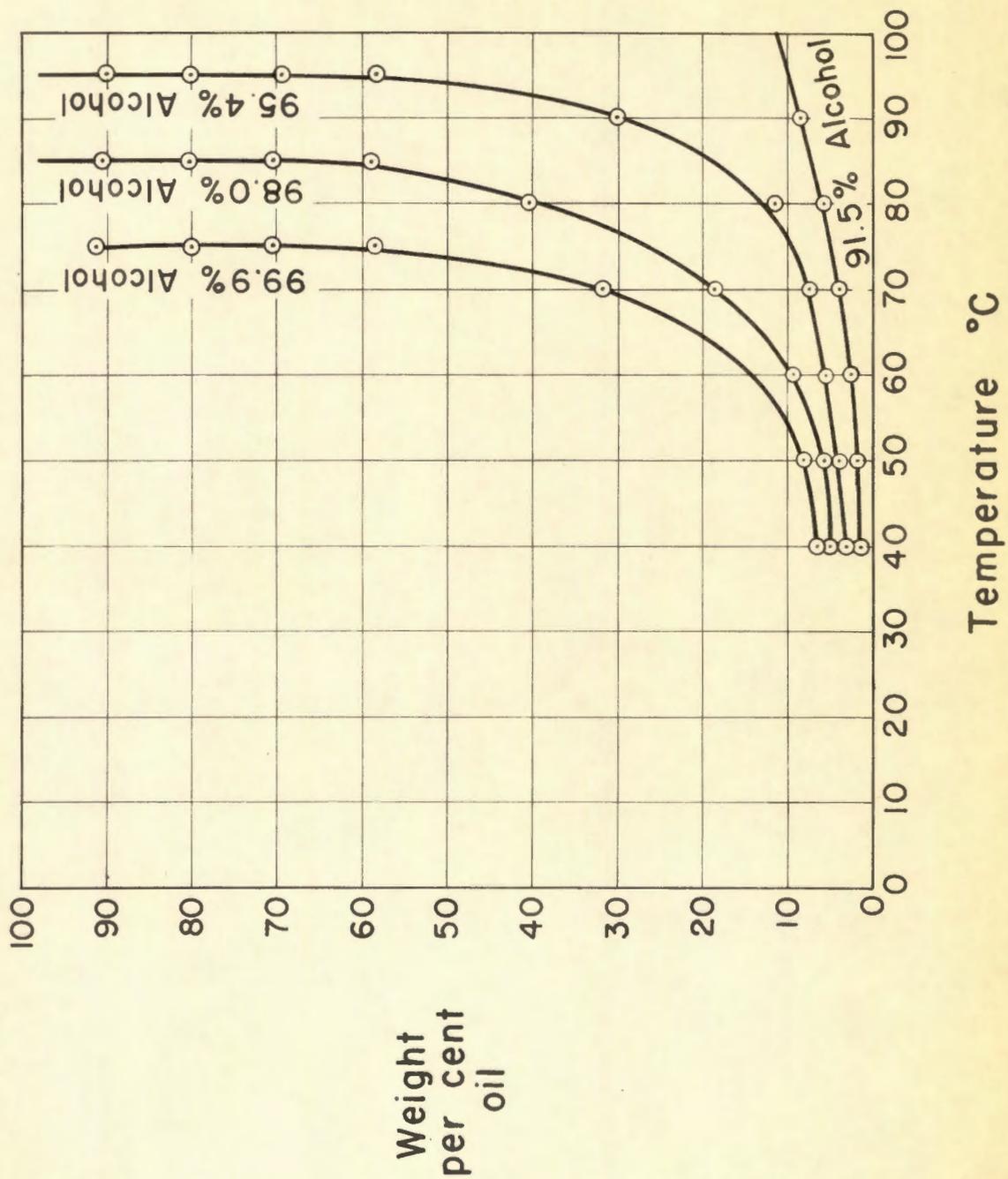
Sap. value = 192.5

The solubility curves are plotted in Figure 14 and indicate that for this oil miscibility with 99.9, 98.0 and 95.4 percent alcohol is attained at 75°, 85° and 95°C. respectively, while the solubility with 91.5 percent alcohol at 90°C. is only 8.5 percent.

The critical solution temperature versus alcohol composition data are plotted in Figure 15 and indicate, as in all other cases before, a linear relationship.

Pressure in the System

The pressures developed in the apparatus, which are made up of the atmospheric pressure and the vapor pressures of aqueous ethanol at different temperatures were read directly from the pressure gage fixed to the apparatus. The pressure gage readings for different alcoholic concentrations at various temperatures are given below in pounds per square inch.



Temperature
°C

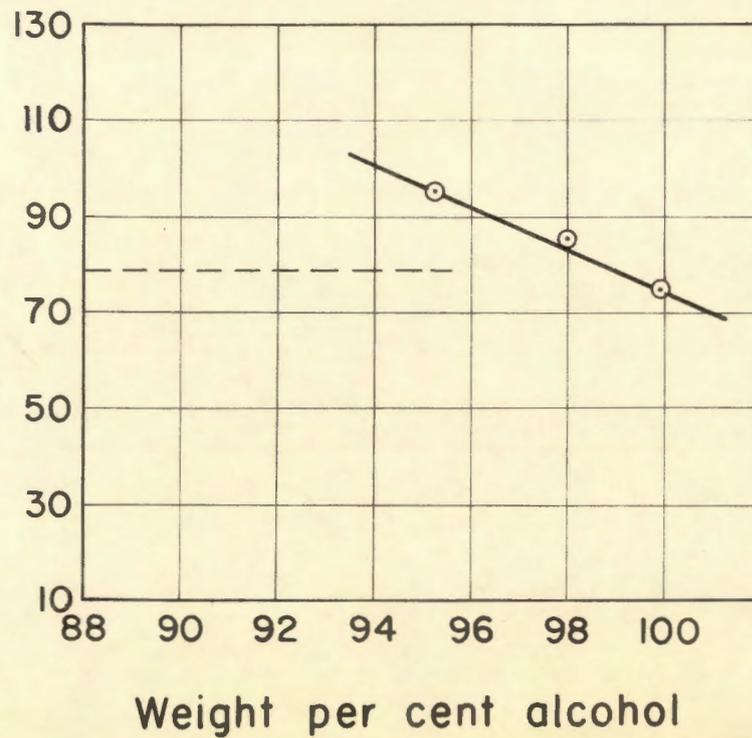


Figure 15. Variation of critical solution temperature of tung oil with alcohol composition

<u>Concentrations of alcoholic solution</u>	<u>Temperatures °C.</u>					
	50	60	70	80	90	95
95.4 percent	2	4	8	15	17	20
98.0 percent	2	4	8	15	18	
99.9 percent	2	4	10	15		

It is seen therefore, that the pressure in the vessel increases with the temperature. However, the gage readings for all the three concentrations are practically the same, since their boiling points differ very slightly, thus producing variations in vapor pressure too small to be recorded by the pressure gage.

The data obtained show that the maximum pressure to be used even with 95.4 percent alcohol is about 20 pounds per square inch gage.

CONCLUSIONS

1. The solubility of the oil increases steadily with temperature, till the critical solution temperature is reached.
2. Oil and aqueous ethanol are miscible in all proportions at or above the critical solution temperature.
3. The solubility of the oil decreases with increasing water content of ethanol and vice versa.
4. For a fixed concentration of aqueous ethanol, every oil of fixed characteristics has a fixed critical solution temperature.
5. The critical solution temperature increases linearly with the water content of ethanol for every oil studied.
6. The present data on cottonseed, peanut, sesame and soybean oils are in complete agreement with the published data and thus confirm the latter.
7. The above established also the reliability and accuracy of the present method, which has been used to obtain new data on corn, linseed and tung oils.
8. The new solubility data of corn, linseed and tung oils are similar to those of cottonseed, peanut, sesame and soybean oils. Solubility curves follow the same pattern and the critical solution temperatures of the three oils vary linearly.
9. The pressure in the system varies directly with temperature.

10. The maximum pressure to be used in the extractor is approximately 20 pounds per square inch gage.

LITERATURE CITED

1. Am. Oil Chem. Soc. Official and tentative methods. 2nd ed. Chicago. The Society. 1946.
2. Beckel, A. C. Alcoholic extraction of oil from soybeans. Paper presented at cooperative soybean oil mills conference, Northern Regional Research Laboratory, Peoria, Illinois. May 25-27, 1948. (Mimeo. rept.)
3. _____, Belter, P. A., and Smith, A. K. Solvent effects of on the products of soybean oil extraction. Jour. Am. Oil Chem. Soc. 25: 7-9. 1948.
4. _____. The nondistillation alcohol extraction process for soybean oil. Jour. Am. Oil Chem. Soc. 25: 10-11. 1948.
5. Beckel, A. C. and Cowan, J. C. Continuous recycling of an alcoholic solvent in oil extraction. U. S. Patent 2,586,108. February 5, 1952.
6. _____, and Smith, A. K. Alcohol extraction improves soya flour flavor and color. Food Industries. 16: 616. 1944.
7. Gross, W. H. Modern practice in solvent extraction. Chem. and Met. Eng. 48: 80-86. 1941.
8. Harris, W. D., Bishop, F. F., Lyman, C. M. and Helpert, R. Isopropanol as a solvent for extraction of cottonseed oil. I. Preliminary investigations. Jour. Am. Oil Chem. Soc. 24: 370-375. 1947.
9. Magne, F. C., Skau, E. L. Phase equilibrium data pertaining to the extraction of cottonseed oil with ethanol and 2-propanol. Jour. Am. Oil Chem. Soc. 30: 288-291. 1953.
10. Measamer, S. G., Sweeney, O. R., and Arnold, L. K. Solvent extraction of soybean oil by mixtures of trichloroethylene and ethyl alcohol. Iowa Academy of Science. 54: 189-197. 1947.
11. Okatomo, S. Studies on the alcoholic extraction of soybean oil. Contemporary Manchuria. 1, no. 3: 83-101. 1937.

12. Rao, Y. K. R. Alcohol extraction of cottonseed. The Bulletin of Central Food Technological Research Institute. Mysore, India. 2, no. 12: 305-306. 1953.
13. _____. Pilot plant for solvent extraction of oilcakes. Jour. of Scientific and Industrial Research, India. 11A: 414-415. 1952.
14. _____. Solvent extraction of oilcakes by alcohol. Jour. of Scientific and Industrial Research, India. 12A: 373-379. 1953.
15. Sato, M., Inaba, T., and Kitagawa, K. The alcohol-extraction process of fatty oils--mutual solubilities of some vegetable oils. Jour. Soc. Chem. Ind. Japan (Suppl. Bind.). 37: 718-721. 1934.
16. _____. The alcohol extraction process of fatty oils--mutual solubilities of some vegetable oils. Jour. Soc. Chem. Ind. Japan (Suppl. Bind.). 38: 50B. 1935.
17. Schwitzer, M. K. Continuous process of fats. London. Leonard Hill Ltd. 1951.
18. Seidell, A. Solubilities of organic compounds. Vol. 2. 3rd ed. New York. D. Van Nostrand Co. 1941.

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