# Liquid-Liquid Phase Equilibrium of Systems Triolein–Furfural–n-Heptane and Trilinolein–Furfural–n-Heptane

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Phase equilibrium data at various temperatures for the system triolein–furfural–n-heptane are presented. Binary curves were developed from cloud-point measurements. Tie lines were developed by special techniques involving refractive index measurements. Data are also presented for the system trilinolein–furfural–n-heptane. Calculations which indicate (with reservations the difficulty of separation of various mixtures of triolein, trilinolein, and the mixed triglycerides are made.

THE SYSTEM triolein-furfural-n-heptane was studied as a part of an investigation of the separation of fats according to the degree of unsaturation by extraction. Binodal curves were obtained over the range 30° C. to 75° C. Tie lines were obtained at 30° C., 50° C., and 70° C.

## TRIOLEIN–FURFURAL–n-HEPTANE

**Materials.** Reagent grade furfural (Fisher Scientific Company) was vacuum distilled twice at 37° C. It was kept from contact with the atmosphere and stored under vacuum for no longer than three or four days before use. The refractive index, $n_D^{20}$, was 1.52606 [literature value 1.52608 (4)].

Highly purified n-heptane (Eastman Kodak Company) was used without further purification. The refractive index, $n_D^{30}$ was 1.3829 [literature value 1.38292 (4)].

Triolein of purity estimated to be greater than 98% (Hormel Foundation) was used without further purification. The refractive index, $n_D^{30}$, was 1.46573 [literature values $n_D^{50} = 1.4586$, $n_D^{40} = 1.4621$ (6) corresponding to $n_D^{30} = 1.4656$].

**Solubility Measurements (Binodal Curves).** Binodal curves at various temperatures for the ternary system furfural-n-heptane-triolein were obtained by measuring cloud point temperatures of mixtures and correlating the results. A series of mixtures of n-heptane and triolein of known composition was prepared. The composition of one such mixture is represented by the point $S$ along the side $BC$ of the ternary diagram shown in Figure 1. All mixtures of n-heptane and triolein were miscible under the conditions of the study. Various amounts of mixture $S$ were weighed into glass tubes of approximately 2-ml. volume. Suitable amounts of furfural were weighed into the tubes and the tubes were sealed. The compositions of the final mixtures are shown as marks along line $AS$ in Figure 1.

The cloud point temperature of each mixture was measured in the following manner: The mixture in the sealed tube was brought to a homogeneous transparent solution by heating it in a water bath equipped with an agitator. The bath temperature was lowered at a rate of 0.1° C. per minute while the tube was shaken vigorously. The temperature at which the first slight turbidity appeared was recorded as the cloud point temperature. The cloud point of most samples could be measured with an accuracy of ±0.1° C.

Other ternary mixtures were made in a similar manner, starting with different known mixtures of n-heptane and triolein. The cloud point temperature of each mixture was measured as before.

The cloud point temperatures for each series of mixtures with a constant ratio of n-heptane to triolein depends only on the fraction of furfural present. Therefore, the data

could be correlated by plotting temperature vs. weight fraction furfural using the weight ratio of n-heptane to triolein plus n-heptane as the parameter (Figure 2). Binodal curves at selected temperatures were determined from this correlation (Figure 3).

**Phase Equilibrium–Tie Lines.** Tie lines are usually obtained by analyzing each phase of two phases in equilibrium, or by starting with a known mixture consisting of two phases in equilibrium and analzing only one phase. The method
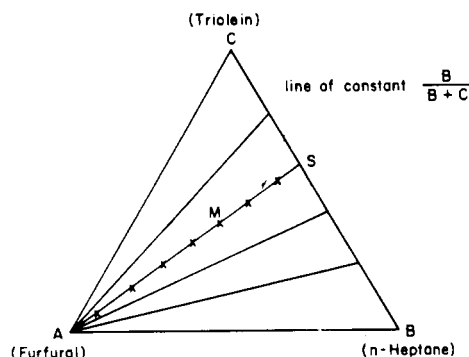


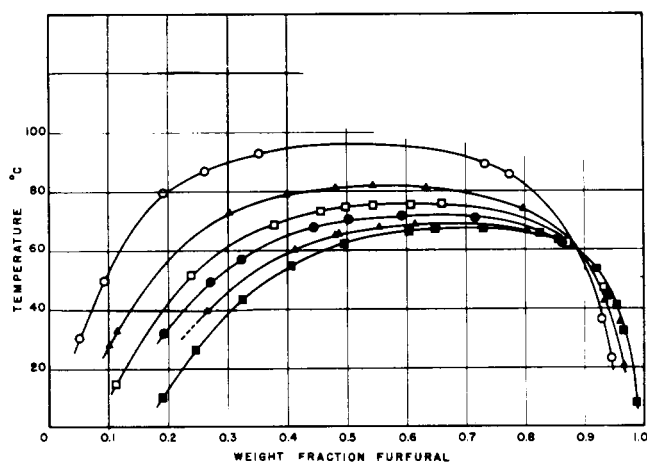Figure 1. Compositions of ternary mixtures for cloud point determinations



Figure 2. Cloud point correlation, triolein–furfural–n-heptane

O B/(B + C) = 1.000
△ B/(B + C) = 0.657
□ B/(B + C) = 0.462
● B/(B + C) = 0.308
▲ B/(B + C) = 0.150
■ B/(B + C) = 0

(B = n-heptane, C = triolein)

used in this study is a variation of the latter method. The composition of the upper phase was identified by refractive index measurement. A Bausch and Lomb Precision refractometer, accurate to $\pm 0.00003$ R.I., was used.

**Phase Equilibrium at 30° C.** The method of determining tie lines at 30° C. is explained with the aid of Figure 4. The point $E_{CA}$ represents a saturated solution of furfural in triolein at 30° C. It was prepared in the following way: Appropriate amounts of triolein and furfural were sealed into a 10-ml. glass tube so that the resulting mixture would be in the two-phase region. The tube was shaken in a bath at 40° C. to ensure supersaturation at 30° C. The tube was then transferred to a constant temperature bath at 30° $\pm 0.01°$ C. and was shaken for 20 minutes. From the experiments on cloud points, it had been found that equilibrium would be attained in a few minutes if the tube were shaken vigorously. The two phases were allowed to separate while the tube was still immersed in the 30° C. bath. The upper layer (triolein-rich phase) was the equilibrium mixture $E_{CA}$.

The equilibrium mixture $E_{BA}$ was prepared in the same way by using $n$-heptane and furfural.

The necks of these two tubes were raised above the surface of the 30° C. bath and cut open. Various amounts of each upper phase ($E_{CA}$ or $E_{CB}$) were weighed into glass tubes of approximately 2-ml. volume. Long-nose droppers were used in transferring the mixtures. The point $M$, representing such a resulting mixture, lies on the straight line connecting the two points $E_{CA}$ and $E_{BA}$, as shown in Figure 4. Ten tubes with varying proportions of $E_{CA}$ and $E_{BA}$ were prepared at one time. The sealed tubes containing mixtures $M$, etc., were then shaken in a 30° C. bath. Each mixture was allowed to attain equilibrium, the two phases were allowed to separate, and the refractive index of the

upper layer was measured at 30° C. $\pm 0.01°$ C. The refractive index of the upper layer was plotted against the weight fraction of triolein in the mixture (Figure 5). This graph gave the relationship between the location of $M$ on the line $E_{CA}E_{BA}$ and the refractive index of its upper layer.

Next, ten sealed tubes containing ternary mixtures of known composition corresponding to points in the two-phase region and nearer to the furfural phase, were prepared. Point $M'$ in Figure 4 indicates such a composition. The mixtures were brought to equilibrium at 30° C. by shaking them in the constant-temperature bath for 10 minutes. The layers were allowed to separate, and the refractive indices of the upper layers were taken at 30° C. For each of these mixtures the point on line $E_{CA}E_{BA}$ having the same upper phase refractive index was determined from Figure 5. Thus, the point $M''$ having the same upper phase refractive index as $M'$ was located. These two mixtures had identical upper phase compositions so they must be on the same tie line. A line through $M'$ and $M''$ and extended in both directions to the binodal curve is the tie line. Tie lines were constructed through each of the furfural-rich two-phase ternary mixtures. They are shown in Figure 6.

**Phase Equilibrium at Higher Temperatures.** Tie lines at higher temperatures than 30° C. could not be determined accurately by the above method because of the volatility of $n$-heptane. An alternate method, similar to one previously described (1), was employed.

This method is explained with the aid of Figure 7. The components of a mixture corresponding to a point $M$ in the two-phase region were weighed into an $L$-shaped tube and the tube was sealed. The tube was then shaken in an oil bath maintained at the desired high temperature within $\pm 0.01°$ C. until equilibrium was attained. Care was taken
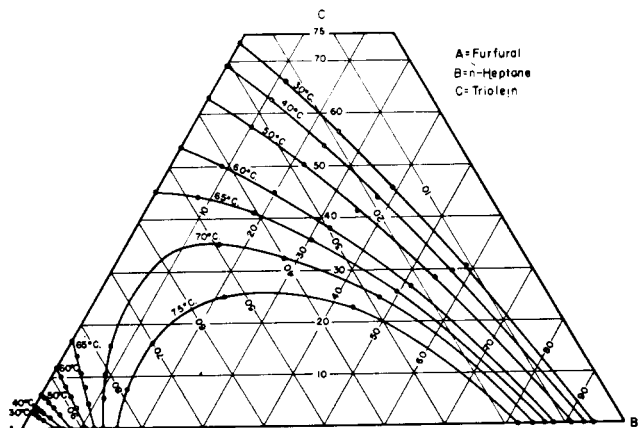


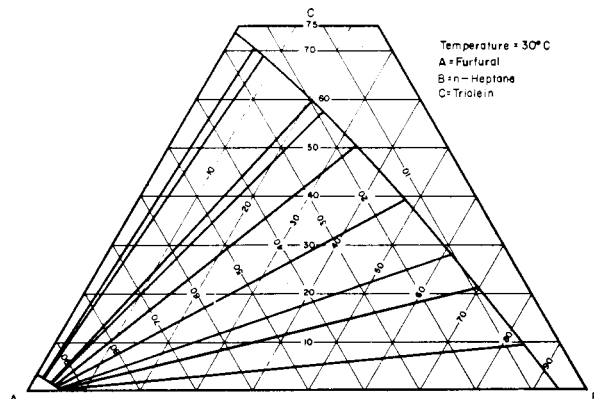Figure 3. Binodal curves, triolein–furfural–$n$-heptane



Figure 6. Phase equilibrium at 30° C., triolein–furfural–$n$-heptane
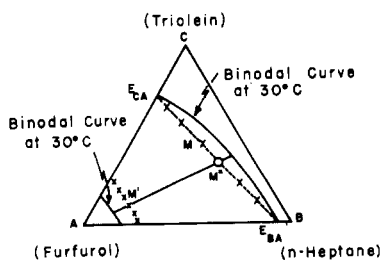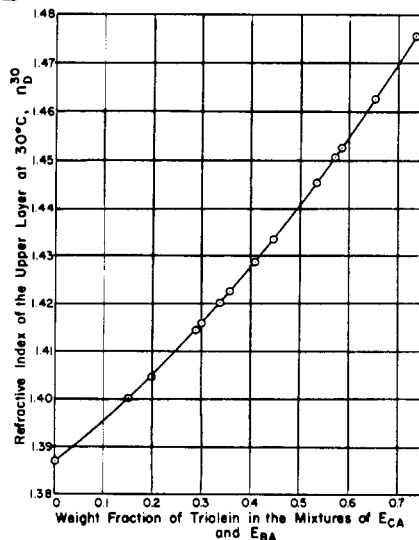


Figure 4. Construction of tie lines at 30° C.



Figure 5. Refractive index correlation for tie line determination, triolein–furfural-$n$-heptane
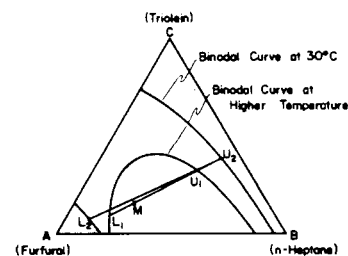


Figure 7. Construction of tie lines at higher temperatures

not to contaminate the upper chamber. The two layers were allowed to separate as shown in Figure 8a. The compositions of the upper layer $U_1$, and the lower layer $L_1$, are indicated on the high temperature binodal curve of Figure 7. The upper chamber of the $L$-shaped tube was raised out of the oil bath and cooled with a cloth immersed in ice water. This cooling produced a suction which pulled part of the upper layer, $U_1$, into the upper chamber (Figure 8b). The solution was kept below the oil level at all times so that no phase separation would occur due to cooling. None of the lower layer was sucked into the upper chamber. The tube was then turned over (Figure 8c), removed from the bath, and cooled. It was broken apart at the constriction and the upper chamber containing part of the upper layer was sealed again. This sealed tube was shaken in the 30° C. constant-temperature bath until it reached a new equilibrium. The two layers were allowed to separate (Figure 8d) and the refractive index of this new upper layer; $U_2$ was measured. The point along line $E_{CA}E_{BA}$ having the same upper phase refractive index (30° C.) was determined from Figure 5. A 30° C. tie line was constructed through this point. The intersection of this tie line and the higher temperature binodal curve determined the original upper-phase composition, $U_1$. A line through $U_1$ and $M$ and extended to $L_1$ on the higher temperature binodal curve was, then, the higher temperature tie line. Tie lines were obtained in this way at 50° C. and 70° C. They are shown in Figures 9 and 10, respectively. Tie line data at the three temperatures are listed in Table I.

**Binary Constants.** Binary constants for the systems furfural-$n$-heptane and triolein-furfural were calculated from the appropriate binary data and the Scatchard-Hamer Equation (*3, 7*). This equation was chosen because of the relatively large molecular volume of triolein. The constants are plotted as functions of the reciprocal of absolute temperature in Figures 11 and 12. The corresponding heats of

solution at infinite dilution were calculated from the slopes of these curves and the following equation:

$$\frac{dA}{d(1/T)} = \frac{\Delta H_i'}{2.303R}$$

The results of the calculations are:

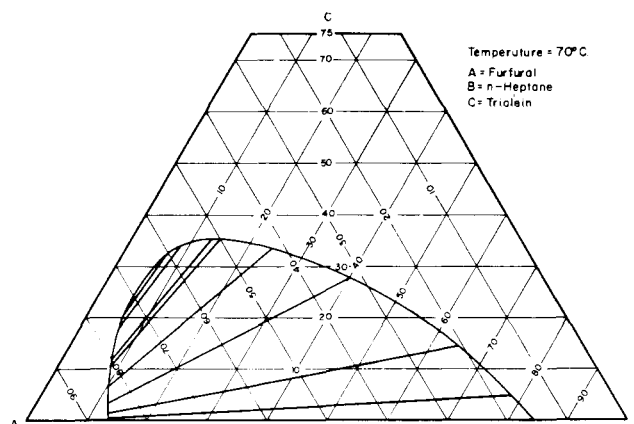| System | $\Delta H_i'$ Cal./Gram Mole |
|---|---|
| Furfural in $n$-heptane | 4060 |
| $n$-Heptane in furfural | 3510 |
| Triolein in furfural | 8370 |
| Furfural in triolein | 930 |



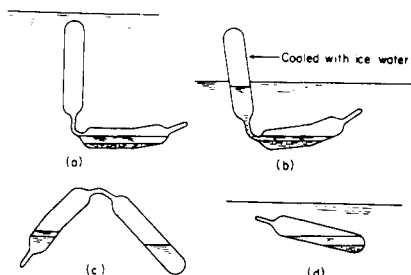Figure 10. Phase equilibrium at 70° C., triolein–furfural–$n$-heptane



Figure 8. Technique used in tie line determination at higher temperatures
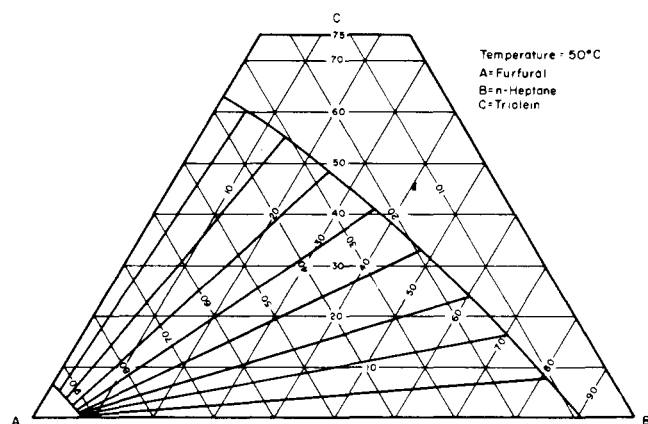


Figure 9. Phase equilibrium at 50° C., triolein–furfural–$n$-heptane

Table I. Equilibrium Compositions
Triolein-furfural-$n$-heptane

| Furfural-Rich Phase, wt. % | | | $n$-Heptane-Rich Phase, wt. % | | |
|---|---|---|---|---|---|
| Triolein | Furfural | $n$-Heptane | Triolein | Furfural | $n$-Heptane |
| | | 30° C. | | | |
| 0 | 0.942 | 0.058 | 0 | 0.052 | 0.948 |
| 0.001 | 0.942 | 0.057 | 0.095 | 0.067 | 0.838 |
| 0.002 | 0.943 | 0.055 | 0.213 | 0.089 | 0.698 |
| 0.003 | 0.944 | 0.053 | 0.281 | 0.104 | 0.615 |
| 0.005 | 0.945 | 0.050 | 0.392 | 0.131 | 0.477 |
| 0.008 | 0.947 | 0.045 | 0.502 | 0.165 | 0.333 |
| 0.011 | 0.950 | 0.039 | 0.558 | 0.184 | 0.258 |
| 0.012 | 0.951 | 0.037 | 0.571 | 0.189 | 0.240 |
| 0.013 | 0.952 | 0.035 | 0.594 | 0.198 | 0.208 |
| 0.022 | 0.958 | 0.020 | 0.687 | 0.236 | 0.077 |
| 0.024 | 0.960 | 0.016 | 0.703 | 0.245 | 0.052 |
| 0.032 | 0.968 | 0 | 0.736 | 0.264 | 0 |
| | | 50° C. | | | |
| 0 | 0.919 | 0.081 | 0 | 0.089 | 0.911 |
| 0.001 | 0.920 | 0.079 | 0.078 | 0.108 | 0.814 |
| 0.004 | 0.920 | 0.076 | 0.165 | 0.131 | 0.704 |
| 0.006 | 0.920 | 0.074 | 0.239 | 0.155 | 0.606 |
| 0.008 | 0.921 | 0.071 | 0.331 | 0.191 | 0.478 |
| 0.013 | 0.922 | 0.065 | 0.409 | 0.229 | 0.362 |
| 0.021 | 0.923 | 0.056 | 0.484 | 0.267 | 0.249 |
| 0.035 | 0.925 | 0.040 | 0.550 | 0.307 | 0.143 |
| 0.053 | 0.930 | 0.017 | 0.603 | 0.346 | 0.051 |
| 0.066 | 0.934 | 0 | 0.630 | 0.370 | 0 |
| | | 70° C. | | | |
| 0 | 0.863 | 0.137 | 0 | 0.153 | 0.847 |
| 0.004 | 0.863 | 0.133 | 0.050 | 0.166 | 0.784 |
| 0.013 | 0.857 | 0.130 | 0.146 | 0.205 | 0.649 |
| 0.033 | 0.848 | 0.119 | 0.280 | 0.318 | 0.402 |
| 0.069 | 0.829 | 0.102 | 0.336 | 0.421 | 0.243 |
| 0.100 | 0.810 | 0.090 | 0.353 | 0.500 | 0.147 |
| 0.118 | 0.800 | 0.082 | 0.354 | 0.512 | 0.134 |
| 0.180 | 0.755 | 0.065 | 0.341 | 0.571 | 0.088 |
| 0.210 | 0.730 | 0.060 | 0.320 | 0.607 | 0.073 |
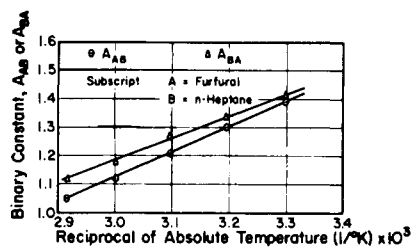
Figure 11. Binary constants,
furfural–n-heptane



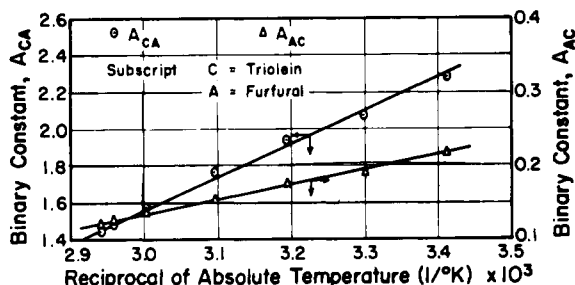Figure 12. Binary constants, triolein–furfural

## TRILINOLEIN–FURFURAL–n-HEPTANE

The system trilinoelin–furfural–n-heptane was studied as a continuation of the investigation. Binodal curves were obtained over the range 30° C. to 75° C. Tie lines were obtained at 30° C., 50° C., and 70° C.

**Materials.** The source and preparation of furfural and n-heptane have been described. Trilinolein (Hormel Institute) was used without further purification. The purity was estimated to be greater than 98%. The refractive index, $n_D^{30}$, was 1.47608 [literature value $n_D^{50} = 1.4683$, $n_D^{40} = 1.4719$, corresponding to $n_D^{30} = 1.4755$ (6)].

**Solubility Measurements (Binodal Curves).** Binodal curves at various temperatures for the ternary system furfural–n-heptane–trilinolein were determined by measuring cloud point temperatures of mixtures and correlating the results. The procedure has been described. Plots of temperature vs. weight fraction furfural with the ratio of n-heptane to trilinolein plus n-heptane as the parameter are shown in Figure 13. Binodal curves at selected temperatures are shown in Figure 14.

**Phase Equilibrium–Tie Lines.** Tie lines were determined at 30° C., 50° C., and 70° C. in the manner previously described. The refractive index vs. composition correlation, paralleling that in Figure 5, is shown in Figure 15. Tie lines are shown in Figures 16, 17, and 18. Tie line data are listed in Table II.

**Binary Constants.** Binary constants for the system trilinolein–furfural were calculated from the appropriate binary data and the Scatchard-Hamer Equation. The constants are plotted as functions of the reciprocal of the absolute temperature in Figure 19. The corresponding heats of solution at infinite dilution are:

| System | $\Delta H_i'$ Cal./Gram Mole |
|---|---|
| Trilinolein in furfural | 9630 |
| Furfural in trilinolein | 730 |

**Separation of Triolein and Trilinolein.** A number of interesting, although speculative, calculations may be made on the basis of triolein–furfural–n-heptane and trilinolein–furfural–n-heptane ternary data. The distribution coefficient of triolein between n-heptane-rich and furfural-rich phases, respectively, is 12 at 70° C. when solute

concentrations are dilute. The corresponding figure for trilinolein is 6. The distribution coefficient is defined here as the ratio of the solute to nonsolute weight ratio in the one phase to the solute to nonsolute weight ratio in the conjugate phase. These distribution coefficients should hold when both solutes are present provided concentrations are sufficiently dilute. The selectivity of the furfural-rich phase for trilinolein is, then, 2.0.

The separation of an equiweight mixture of triolein and trilinolein into a 90 wt. % triolein and 10 wt. % trilinolein mixture and a 10 wt. % triolein 90 wt. % trilinolein mixture (both on a solvent-free basis) by continuous countercurrent extraction with furfural and n-heptane is calculated (5) to require 12 theoretical stages. The system would be center-fed and the solvents would enter at opposite ends. In making this calculation it is assumed that the solute concentrations are so dilute that distribution ratios are 6 and 12, respectively, throughout the system and that the ratio of solvents in each phase is the same as in the respective saturated two-solvent mixtures throughout the system. Relatively large quantities of solvents are required, on the basis of 2 wt. % solute in the furfural-rich phase being the highest concentration permissible and each solvent saturated with the other solvent before entering the system, 120 lb. of furfural saturated with n-heptane, and 14 lb. of n-heptane saturated with furfural would be required for extracting one lb. of feed.
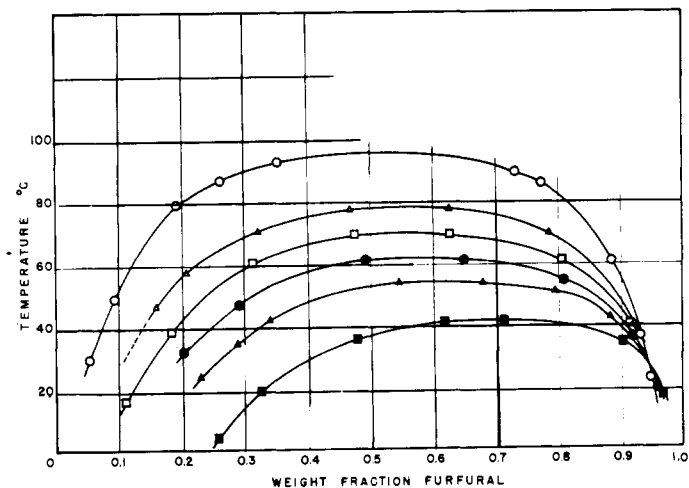


Figure 13. Cloud point correlation,
trilinolein–furfural–n-heptane

O   B/(B + C') = 1.000
△   B/(B + C') = 0.706
□   B/(B + C') = 0.557
●   B/(B + C') = 0.400
▲   B/(B + C') = 0.256
■   B/(B + C') = 0

(B = n-heptane, C' = trilinolein)
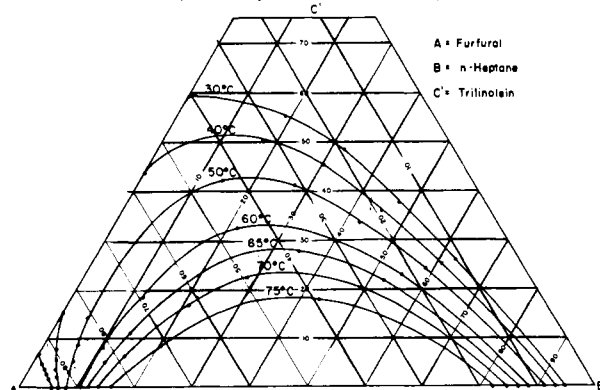


A = Furfural
B = n-Heptane
C = Trilinolein

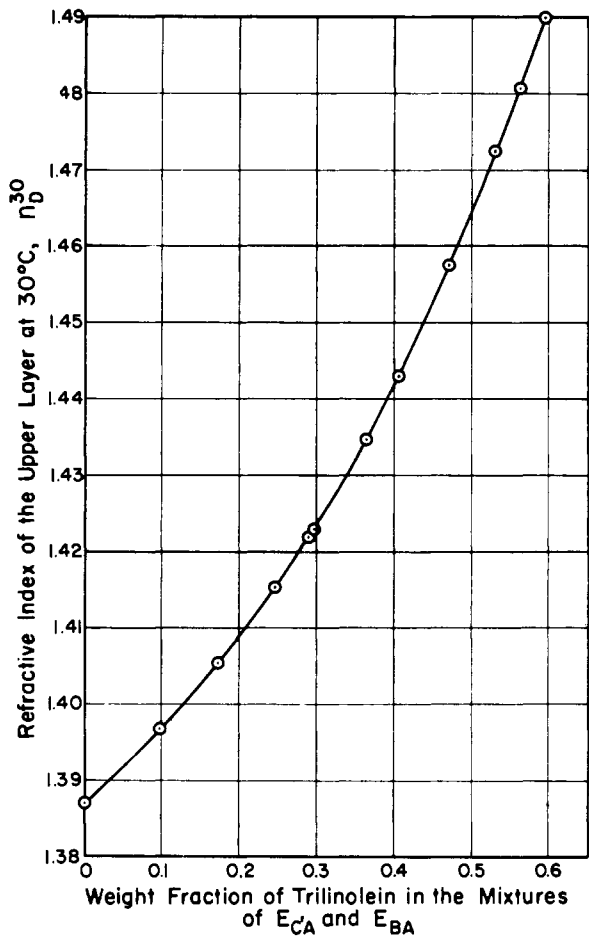Figure 14. Binodal curves, trilinolein–furfural–n-heptane

Figure 15. Refractive index correlation for tie line determination, trilinolein–furfural–$n$-heptane
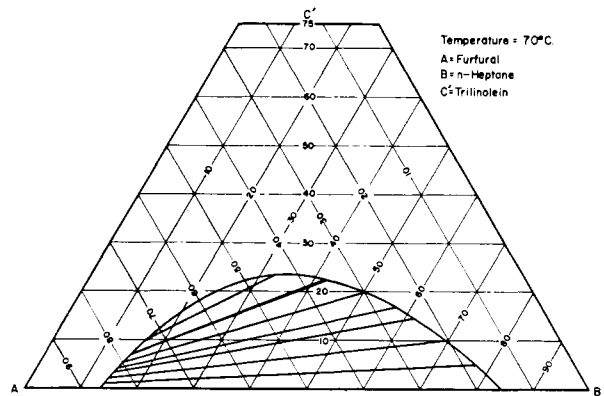


Figure 18. Phase equilibrium at 70° C., trilinolein–furfural–$n$-heptane
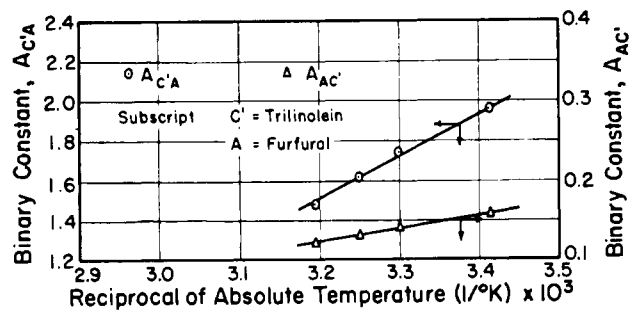


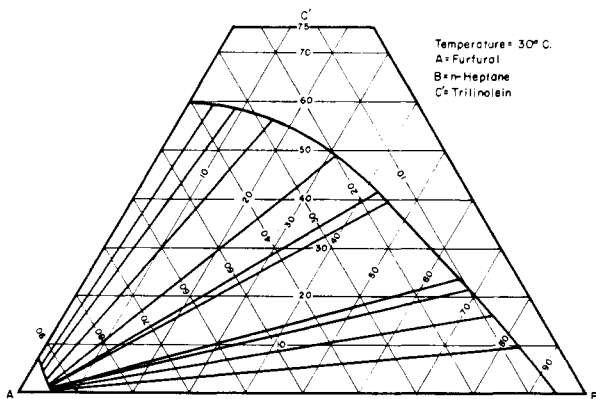Figure 19. Binary constants, trilinolein–furfural



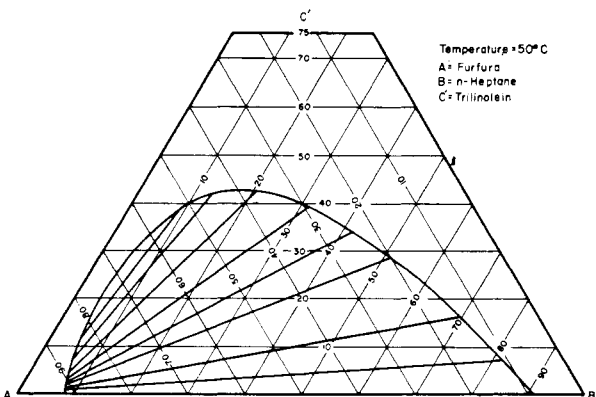Figure 16. Phase equilibrium at 30° C., trilinolein–furfural–$n$-heptane



Figure 17. Phase equilibrium at 50° C., trilinolein–furfural–$n$-heptane

Table II. Equilibrium Composition
Trilinolein-furfural-$n$-heptane

| Furfural-Rich Layer, Wt. % | | | $n$-Heptane-Rich Layer, Wt. % | | |
|---|---|---|---|---|---|
| Trilinolein | Furfural | $n$-Heptane | Trilinolein | Furfural | $n$-Heptane |
| 30° C. | | | | | |
| 0 | 0.942 | 0.058 | 0 | 0.052 | 0.948 |
| 0.002 | 0.942 | 0.056 | 0.095 | 0.069 | 0.836 |
| 0.003 | 0.942 | 0.055 | 0.162 | 0.084 | 0.754 |
| 0.005 | 0.942 | 0.053 | 0.214 | 0.097 | 0.689 |
| 0.006 | 0.942 | 0.052 | 0.237 | 0.104 | 0.659 |
| 0.009 | 0.942 | 0.049 | 0.395 | 0.153 | 0.452 |
| 0.010 | 0.942 | 0.048 | 0.416 | 0.161 | 0.423 |
| 0.013 | 0.941 | 0.046 | 0.490 | 0.198 | 0.312 |
| 0.023 | 0.940 | 0.037 | 0.562 | 0.273 | 0.165 |
| 0.040 | 0.938 | 0.022 | 0.585 | 0.329 | 0.086 |
| 0.053 | 0.936 | 0.011 | 0.593 | 0.363 | 0.044 |
| 0.069 | 0.931 | 0 | 0.596 | 0.404 | 0 |
| 50° C. | | | | | |
| 0 | 0.919 | 0.081 | 0 | 0.089 | 0.911 |
| 0.005 | 0.914 | 0.081 | 0.075 | 0.107 | 0.818 |
| 0.009 | 0.912 | 0.079 | 0.165 | 0.138 | 0.697 |
| 0.016 | 0.908 | 0.076 | 0.288 | 0.197 | 0.515 |
| 0.020 | 0.905 | 0.075 | 0.343 | 0.239 | 0.418 |
| 0.027 | 0.900 | 0.073 | 0.395 | 0.289 | 0.316 |
| 0.042 | 0.890 | 0.068 | 0.427 | 0.365 | 0.208 |
| 0.067 | 0.870 | 0.063 | 0.419 | 0.451 | 0.130 |
| 0.115 | 0.837 | 0.048 | 0.390 | 0.521 | 0.089 |
| 70° C. | | | | | |
| 0 | 0.863 | 0.137 | 0 | 0.153 | 0.847 |
| 0.009 | 0.853 | 0.138 | 0.050 | 0.176 | 0.774 |
| 0.019 | 0.841 | 0.140 | 0.099 | 0.203 | 0.698 |
| 0.032 | 0.826 | 0.142 | 0.146 | 0.237 | 0.617 |
| 0.040 | 0.814 | 0.146 | 0.168 | 0.258 | 0.574 |
| 0.052 | 0.800 | 0.148 | 0.198 | 0.296 | 0.506 |
| 0.067 | 0.780 | 0.153 | 0.223 | 0.349 | 0.428 |
| 0.069 | 0.776 | 0.155 | 0.225 | 0.352 | 0.423 |
| 0.098 | 0.738 | 0.164 | 0.236 | 0.435 | 0.329 |

## SEPARATION OF MIXED TRIGLYCERIDES

Triglycerides tend to be attracted by polar solvents according to the degree of unsaturation. It was assumed that the selectivity of the furfural-rich phase, as compared with the $n$-heptane-rich phase, for triolein, trilinolein, and the related mixed triglycerides, is geometrically proportional to the number of unsaturated carbon linkages in the molecule. The .distribution coefficient for dioleolinolein between the $n$-heptane-rich phase and the furfural-rich phase would be 9.5 at 70° C. in dilute solutions. The corresponding figure for dilinoleo-olein would be 7.5. The selectivity of the furfural-rich phase for the latter would be 1.26 in dilute solutions.

The separation of an equiweight mixture of dioleolinolein and dilinoleo-olein into one mixture containing 90 wt. % of the former and 10 wt. % of the latter and another mixture containing 10 wt. % of the former and 90 wt. % of the latter is calculated to require 37 theoretical stages or about three times as many as for the similar separation of triolein and trilinolein. The amounts of solvents would be 340 lb. of furfural saturated with $n$-heptane and 40 lb. of $n$-heptane saturated with furfural for one lb. of feed. These quantities are about three times those for the separation of triolein and trilinolein.

**Separation of Triolein and Trilinolein in the Presence of Mixed Triglycerides.** A mixture of triglycerides in which the acid groups are oleic acid and linoleic acid in equal amounts and in which these groups are randomly distributed between the molecules (2) would consist .of 17% triolein, 33% dioleolinolein, 33% dilinoleo-olein, and 17%

trilinolein. Since the molecular weights of oleic acid and linoleic acid are nearly the same, this relation is true for both a weight basis and a molar basis. On assumptions previously made, the same separation of triolein and trilinoelin is calculated to require 12 theoretical stages, or the same number as before. The one product stream would contain 31 wt. % triolein, 46 wt. % dioleolinolein, 20 wt. % dilinoleo-olein, and 3 wt. % trilinolein, and the other product stream would contain 3 wt. % triolein, 20 wt. % dioleolinolein, 46 wt. % dilinoleo-olein and 31 wt. % trilinolein. Both compositions are on a solvent-free basis. The amounts of solvents required would be 420 lb. of furfural saturated with $n$-heptane and 50 lb. of $n$-heptane saturated with furfural per lb. of triolein and trilinolein in the feed.

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# Vapor-Liquid Equilibria for the Methanol–Toluene System

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Vapor-liquid equilibrium data have been determined at one atmosphere pressure for the methanol–toluene system using a modified Altsheler still. A thermodynamic evaluation proved the data to be consistent. A minimum boiling azeotrope is formed at 0.885 mole fraction methanol and a temperature of 63.6° C. Refractive index–concentration data have also been determined for this binary system.

MIXTURES OF METHYL ALCOHOL and toluene are used in chemical processing. Because these solvents are frequently recovered or repurified by distillation, columns designed for this operation require a knowledge of the binary vapor-liquid equilibria.

A review of the literature indicates only one set of vapor-liquid equilibrium data for this binary system (2). In an attempt to duplicate and extend the data of Benedict and coworkers, a somewhat different set of values were obtained and are reported in this investigation.

The data were obtained at one atmosphere pressure and were found to deviate considerably from liquid phase ideality. A minimum boiling azeotrope is formed by this binary system at 0.885 mole fraction methanol and at a temperature of 63.6° C. A thermodynamic evaluation proved the data to be consistent. The experimental results are given in Table I and the temperature—composition

and $x$-$y$ curves are shown in Figures 1 and 2, respectively. The activity coefficient—composition curves are shown in Figure 3. The refractive index—concentration data experimentally determined and used in the analytical procedure are listed in Table II.

## EXPERIMENTAL

**Materials.** Both materials were of analytical reagent grade. The toluene had a quoted boiling point range of 110.4–110.7° C., but the equilibrium boiling point was experimentally determined in the apparatus of this investigation to be 110.6° C. Prior to use the methanol was distilled over calcium oxide and its boiling point was found to be 64.6° C., the accepted literature value. The refractive indices ($n_D^{25}$) of the methanol and toluene were found to be 1.32691 and 1.49428 at 25° C., respectively. These values