# Phase Investigations of Fats. II. Systems Containing Oleic and Stearic Acids and an Organic Solvent

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## Introduction

THE solubilities of single fatty acids and their derivatives in various solvents have been determined at various temperatures by several workers (1, 2, 3). Ralston and Hoerr (4) have published data on the solubilities of binary mixtures of saturated fatty acids in benzene and acetone. Other investigators (5. 6) have reported melting and eutectic point data for binary systems of saturated and unsaturated fatty acids.

The intersolubilizing effects of mixtures of saturated, or saturated and unsaturated fatty acids or their derivatives in organic solvents have not been investigated. Information is also lacking with respect to the degree of separation which can be effected when mixtures of fatty acids are fractionally crystallized from solvents.

It has been the purpose of the investigation reported here to determine the composition of the solid and liquid phases existing in equilibrium in the ternary systems oleic acid-stearic acid- acetone, and oleic acid-stearic acid-commercial hexane, at various temperatures, and with varying amounts of the three components. Such data are essential for the analysis of fatty acid systems, and they also provide a scientific basis for predicting the degree of separation which may be obtained with any given mixture of these fatty acids when crystallized from an organic solvent. Furthermore, the application of these data to the purification of fatty materials by solvent fractionation indicates the limits of purity obtainable by present conventional methods.

## Materials

*Preparation of Oleic Acid.* Oleic acid was prepared from pecan oil by interesterification of the oil with methanol, subsequent separation and purification of the methyl oleate by the method of Wheeler and Riemenschneider (8), and conversion of the purified methyl oleate to oleic acid. The regenerated acid was crystallized from acetone which gave a product containing 99.8% of oleic acid as calculated from its iodine value (corrected to 100% oleic in the experimental work). Alkali isomerization followed by spectrophotometric examination of the product indicated that the oleic acid contained less than the spectrophotometric limit of more highly unsaturated acids.

One hundredth of 1% of hydroquinone was added to the oleic acid and the product was stored under hydrogen in a refrigerator to prevent oxidation prior to use.

*Preparation of Stearic Acid.* Stearic acid was prepared from commercial Neo-Fat by repeated crystallization from acetone. The solubility of this acid was determined after each crystallization until a constant solubility value was reached after a total of 20 crystallizations. Its melting point was 69.9°-70.1°C.

*Solvents.* The organic solvents were commercial hexane, boiling range 146°-158°F. (Skellysolve B),[2] which was used without further purification, and acetone which was purified with caustic $AgNO_3$, by the Method of Werner (9).

## Experimental

The method used for equilibration of the three-component system, oleic acid- stearic acid- organic solvent, has been described in detail in a previous article in this series (7). Briefly this method is as follows: weighed amounts of the fatty acids and solvent were equilibrated in a special apparatus (7), the liquid and solid phases separated by filtration, and the composition and proportion of each phase determined. (Corrections were made for entrained mother liquor.) That substantial equilibrium was obtained in each experiment was determined previously. It was found that the solubility of stearic acid was approximately 2% lower when approached from the cold side than when approached from the warm side. Also, that there was no appreciable difference in its solubility at holding periods of from 6 to 48 hours when approached from the cold side. The uniform procedure adopted for each experiment was that of chilling the system to about 20°C. below the holding temperature, and equilibrating overnight (a period of 16 hours).

In order to ascertain the mutual solubility of each component at various concentrations and at temperatures of 0°, —10°, —20°, —30°, and —40°C. under isobaric conditions the following ranges of concentrations were investigated: 90% oleic and 10% stearic to 0% oleic and 100% stearic acid and solvent ratios from 5:1 to 30:1 (solvent to total acids) by weight. Each original mixture yielded a solid and liquid phase when equilibrated; the composition of these phases together with the proportions of fatty acids and solvent in each phase at each temperature are summarized in Table 1. These data were plotted on triangular coordinates in the form of phase diagrams, in order to designate the phases existing in equilibrium in a heterogeneous system at any given temperature. The compositions of the solid and liquid phases of each original mixture are represented by points on the phase diagrams, and are connected by straight tie lines, each of which also passes through a point representing the original composition of the heterogeneous mixture.

From the number of heterogeneous mixtures of different oleic acid-stearic acid-solvent compositions which have been equilibrated isothermally, and the compositions of the phases plotted, curves have been drawn through the points representing liquid phase compositions, and the limiting boundary of the liquid phase at each isotherm has been outlines. Figures 1 to 10 represent these phase diagrams at each isotherm.

The liquid phase area for each isotherm has been plotted on an expanded scale as rectangular coor-

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Skellysolve B is named as part of the specification of the exact experimental conditions and does not imply that this solvent is particularly endorsed or recommended by the Department of Agriculture over other commercial hexanes having the same or similar properties.

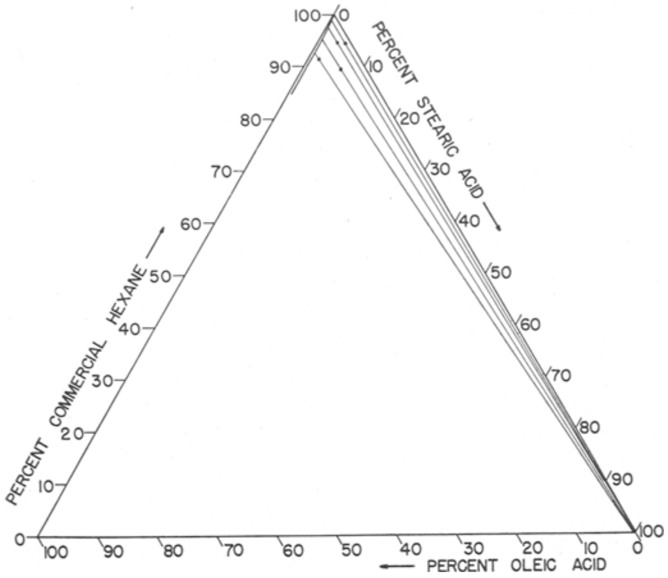

Fig. 1. Phase diagram of oleic acid-stearic acid-commercial hexane at 0°C.

dinates, using the weight per cent of oleic and stearic acids as ordinates and abscissae, respectively, the balance being solvent. The total at any point is 100%. Figures 11 and 12 represent the liquid phase areas for the various isotherms.

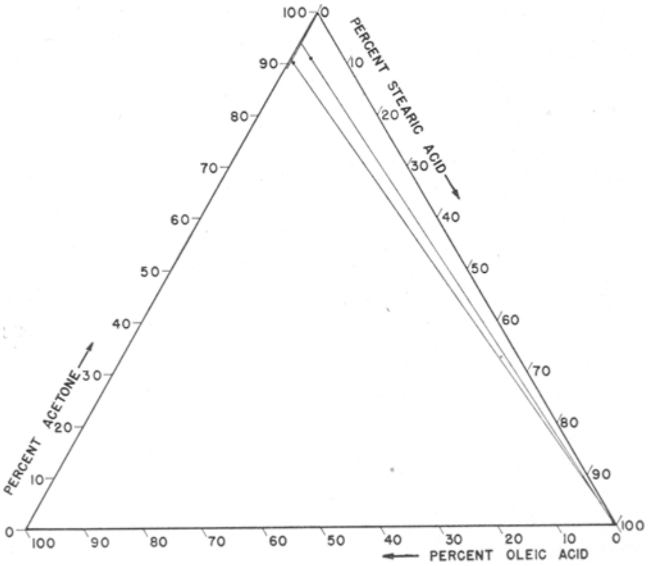

Fig. 2. Phase diagram of oleic acid-stearic acid-acetone at 0°C.

## Discussion of Results

(a) *Effect of Different Fatty Acid Ratios.* At 0°C. the solubility of stearic acid was found to average 0.038 g./100 g. in commercial hexane and 0.103 g./100 g. in acetone. These solubilities differ significantly from the values of 0.024 g./100 g. and 0.219 g./100 g. in these respective solvents reported by Foreman and Brown (3). Increasing amounts of oleic acid in the original mixtures, up to approximately 30 to 35% of the weight of total acids, considerably increased the solubility of stearic acid at 0°C., the effect being greater in commercial hexane than in acetone solutions. Further addition of oleic acid had less effect on the stearic acid solubility, merely enriching the homogenous or liquid phase with respect to oleic acid which is soluble in both solvents at all practical concentrations. However, at all temperatures employed, including 0°C., there was a tendency for some oleic acid to be precipitated along with stearic acid (possibly in the form of mixed crystals), being especially evident in solutions of commercial hexane.

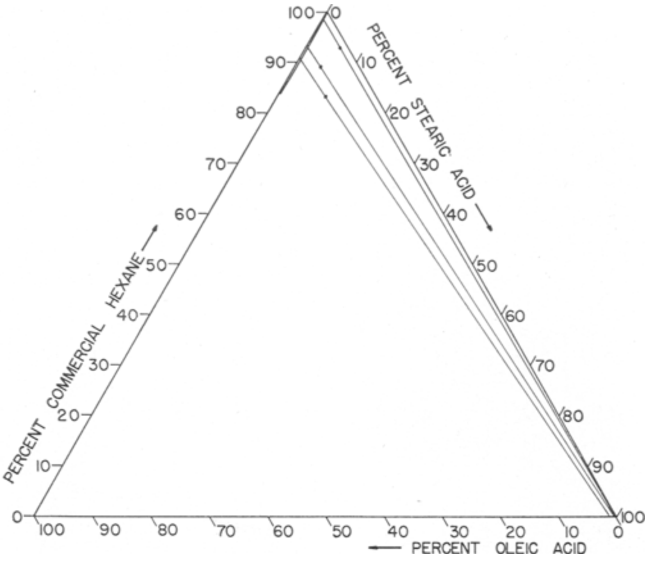

Fig. 3. Phase diagram of oleic acid-stearic acid-commercial hexane at —10°C.

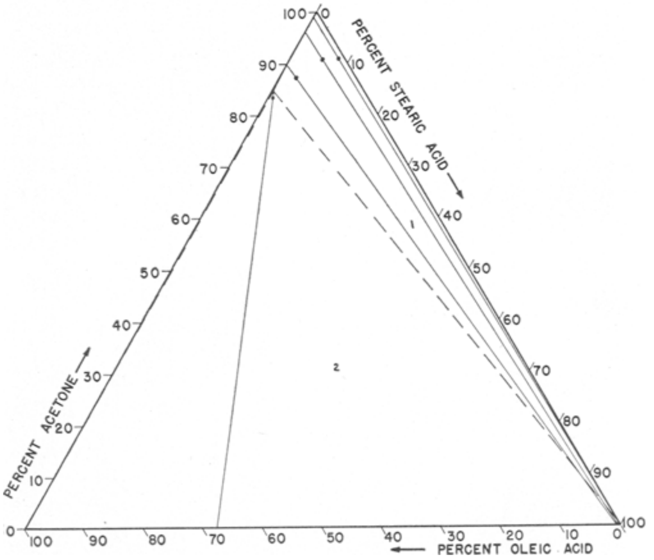

Fig. 4. Phase diagram of oleic acid-stearic acid-acetone at —10°C.

No attempt was made to obtain data with solvent-acid ratios less than 5 to 1 by weight as separations became impractical at lower ratios, owing to increased filtration difficulties and entrainment of filtrate, in the precipitate fraction. Therefore, the liquid phases at 0°C. do not become saturated with oleic acid under the conditions imposed but probably would be saturated at a solvent-acids ratio of 1 to 1 or less in commercial hexane, and at an even lower ratio in acetone. Figures 1 and 2 represent the 0°C. isotherms.

The effect of oleic acid on the solubility of stearic acid is not as pronounced at —10°C. as at 0°C. (Figures 3 and 4). A gradual increase in the solubility of

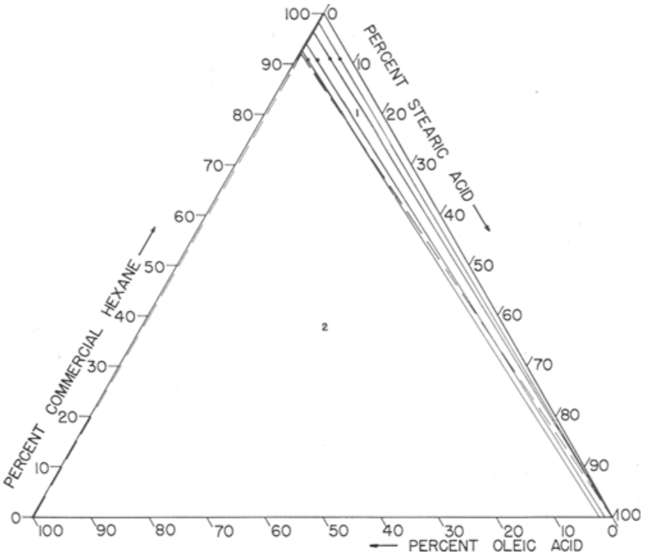

FIG. 5. Phase diagram of oleic acid-stearic acid-commercial hexane at —20°C.

stearic acid, with additions of oleic acid, was noted in the solutions of commercial hexane, oleic acid having a greater effect up to a concentration of 5 to 10% of the total acids in the mixture. In acetone solutions at —10°C. oleic acid had but slight effect on the solubility of stearic acid. With the latter solvent the acetone-oleic acid ratio must be in excess of 5:1 by weight to prevent precipitation of oleic acid from the liquid phase.

If the oleic acid-acetone ratio is not in excess of 5:1, the liquid phase becomes saturated with both acids. As the proportion of oleic acid in the original mixtures was further increased, a mixture was reached in which the small amount of stearic acid present was completely soluble. Points representing the liquid phase compositions then moved toward the oleic acid apex, forming a closed surface (Figure 12).

The dashed lines on Figure 4 and subsequent figures, drawn from the point of liquid phase saturation

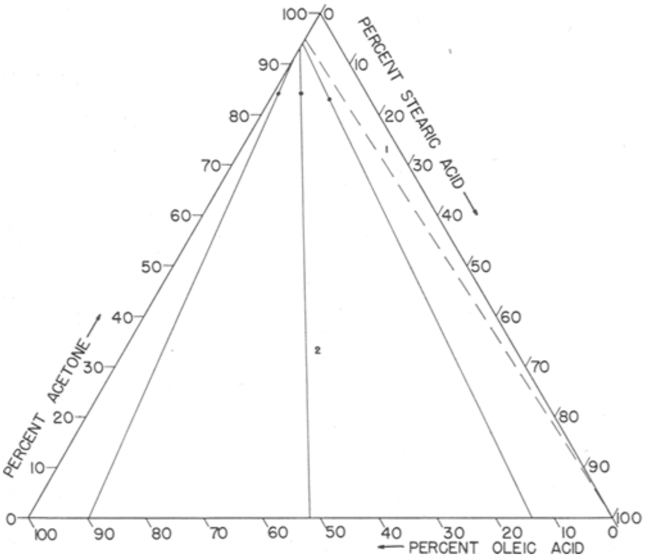

FIG. 6. Phase diagram of oleic acid-stearic acid-acetone at —20°C.

TABLE 1

Compositions of the Original Oleic Acid-Stearic Acid-Solvent Mixtures and Phases Present at Equilibrium [a]

| Temp. °C. | Original mixture | | | Liquid phase | | | Solid phase | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | By difference | | By calculation | |
| | Stearic acid | Oleic acid | Solvent | Stearic acid | Oleic acid | Solvent | Stearic acid | Oleic acid | Stearic acid | Oleic acid |
| | | | | | Commercial Hexane | | | | | |
| 0 | 1.684 | 6.852 | 91.464 | 0.311 | 6.906 | 92.783 | 96.91 | 3.09 | 98.01 | 1.99 |
| | 3.181 | 4.887 | 91.932 | 0.278 | 4.997 | 94.725 | 98.72 | 1.28 | 98.72 | 1.28 |
| | 3.209 | 2.150 | 94.639 | 0.204 | 2.194 | 97.602 | 99.20 | 0.80 | 99.30 | 0.70 |
| | 4.658 | 0.816 | 94.526 | 0.133 | 0.884 | 99.023 | 99.77 | 0.23 | 99.76 | 0.24 |
| | 4.671 | 4.144 | 91.184 | 0.261 | 4.277 | 95.457 | 98.67 | 1.33 | 99.26 | 0.74 |
| | 6.313 | 4.223 | 89.464 | 0.253 | 4.476 | 95.271 | 99.65 | 0.35 | 99.53 | 0.47 |
| —10 | 0.720 | 6.500 | 92.780 | 0.215 | 6.513 | 93.272 | 95.95 | 4.05 | ........ | ........ |
| | 8.311 | 8.542 | 83.146 | 0.251 | 9.195 | 90.553 | 98.79 | 1.21 | ........ | ........ |
| | 6.044 | 1.083 | 92.873 | 0.066 | 1.102 | 98.832 | 99.22 | 0.78 | 99.60 | 0.40 |
| —20 | 0.0 | 9.253 | 90.747 | 0.0 | 9.054 | 90.946 | 0.0 | 100.00 | ........ | ........ |
| | 2.132 | 7.091 | 90.776 | 0.121 | 7.179 | 92.700 | 97.35 | 2.65 | 97.89 | 2.11 |
| | 3.543 | 5.691 | 90.766 | 0.108 | 5.849 | 94.043 | 98.77 | 1.23 | 99.75 | 0.25 |
| | 5.841 | 3.225 | 90.934 | 0.068 | 3.528 | 96.404 | 100.00 | ........ | ........ | ........ |
| | 7.569 | 1.507 | 90.924 | 0.048 | 1.570 | 98.382 | 99.25 | 0.75 | 99.88 | 0.12 |
| —30 | 2.802 | 0.906 | 96.293 | 0.018 | 0.870 | 99.112 | 97.92 | 2.08 | 97.44 | 2.56 |
| | 0.0 | 5.305 | 94.695 | 0.0 | 1.938 | 98.062 | 0.0 | 100.00 | ........ | ........ |
| | 5.478 | 4.100 | 90.424 | 0.034 | 2.009 | 97.957 | 70.81 | 29.19 | 70.78 | 29.22 |
| | 5.520 | 1.580 | 92.900 | 0.036 | 1.615 | 98.349 | 99.01 | 0.99 | ........ | ........ |
| —40 | 0.152 | 2.754 | 97.094 | 0.030 [b] | 0.373 | 99.597 | 1.78 | 98.22 | 5.50 | 94.50 |
| | 0.561 | 2.179 | 97.260 | 0.033 | 0.483 | 99.483 | 23.61 | 76.39 | 24.60 | 75.40 |
| | 2.705 | 2.624 | 94.671 | 0.035 | 0.455 | 99.511 | 54.94 | 45.06 | 55.41 | 44.59 |
| | | | | | Acetone | | | | | |
| 0 | 3.594 | 5.561 | 90.845 | 0.265 | 5.753 | 93.982 | 100.00 | 0.0 | ........ | ........ |
| | 0.920 | 8.951 | 90.129 | 0.315 | 9.006 | 90.679 | 100.00 | 0.0 | ........ | ........ |
| | 2.214 | 0.0 | 97.786 | 0.103 | ........ | 99.897 | 100.00 | 0.0 | ........ | ........ |
| —10 | 2.668 | 6.524 | 90.808 | 0.136 | 6.516 | 93.348 | 93.20 | 6.80 | 99.29 | 0.71 |
| | 5.419 | 3.610 | 90.971 | 0.124 | 3.811 | 96.065 | 100.00 | 0.0 | 100.00 | 0.0 |
| | 2.016 | 19.753 | 78.753 | 0.172 | 14.927 | 84.901 | 25.64 | 74.36 | ........ | ........ |
| —20 | 1.300 | 0.0 | 98.700 | 0.038 | ........ | 99.962 | 100.00 | 0.0 | ........ | ........ |
| | 4.767 | 11.213 | 84.020 | 0.107 | 6.920 | 92.973 | 48.32 | 51.68 | ........ | ........ |
| | 0.879 | 14.984 | 84.138 | 0.117 | 8.825 | 91.058 | 10.14 | 89.86 | ........ | ........ |
| | 10.058 | 6.972 | 82.970 | 0.095 | 6.082 | 93.823 | 86.31 | 13.69 | ........ | ........ |
| —30 | 0.950 | 0.0 | 99.050 | 0.0 | ........ | 100.00 | 100.00 | 0.0 | ........ | ........ |
| | 2.707 | 2.991 | 94.303 | 0.014 | 2.035 | 97.951 | 72.31 | 27.69 | 73.71 | 26.29 |
| | 2.061 | 2.111 | 95.828 | 0.005 | 2.132 | 97.863 | 98.90 | 1.10 | 99.33 | 0.67 |
| —40 | 0.402 | 3.290 | 96.309 | 0.015 [b] | 0.879 | 99.107 | 13.72 | 86.28 | ........ | ........ |
| | 1.954 | 2.776 | 95.270 | 0.010 | 0.885 | 99.106 | 50.24 | 49.76 | ........ | ........ |

[a] Compositions are expressed in weight (gram)-per cent of total solution.
[b] These values are slightly high.

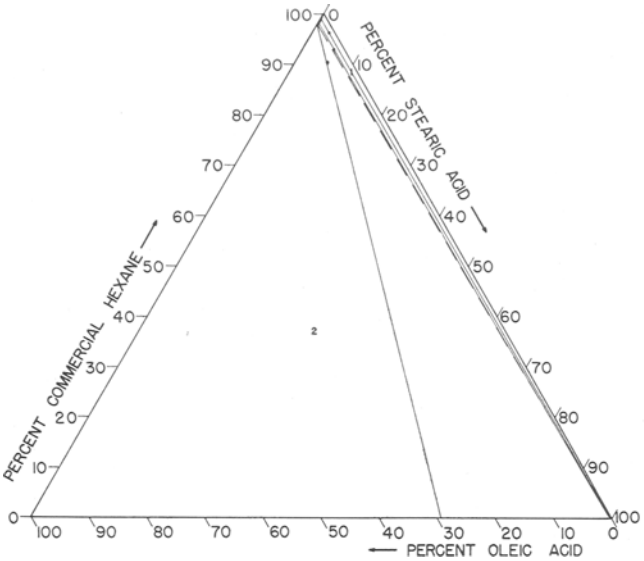

Fig. 7. Phase diagram of oleic acid-stearic acid-commercial hexane at —30°C.

with both acids to the apex of both stearic and oleic acids, give the limits of the fields designated as "1" and "2" on these figures. Original mixtures within field "1" will, at equilibrium, result in solution or liquid phase plus stearic acid since up to the saturation point the liquid phase was saturated only with respect to this acid. Field "2" limits those original mixtures which will yield saturated liquid phases, with stearic and oleic acids in the solid phases. The narrow field at the extreme left of Figure 4, between the dashed line and the border of the triangle, contains those original mixtures which will yield liquid phases saturated with oleic acid, but not with stearic acid. The solid phases from such mixtures will be oleic acid.

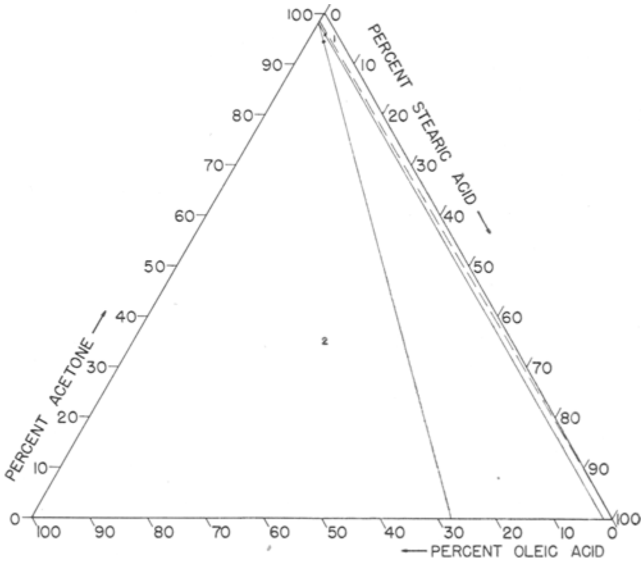

Fig. 8. Phase diagram of oleic acid-stearic acid-acetone at —30°C.

On a solvent-free basis the liquid phases contained 96 to 98% of oleic acid with commercial hexane as the solvent compared to 98 to 99% oleic acid with acetone as the solvent.

At —20°C. oleic acid separated from solution at relatively high ratios of solvent to fatty acids. In commercial hexane a ratio of less than 12 g. of oleic acid per 100 g. solvent in the original mixture resulted in the absence of oleic acid in the solid phase after equilibration, except for a small amount as mixed crystals. Similarly, a ratio of about 8 g. of oleic acid per 100 g. of acetone retained the oleic acid in the liquid phase.

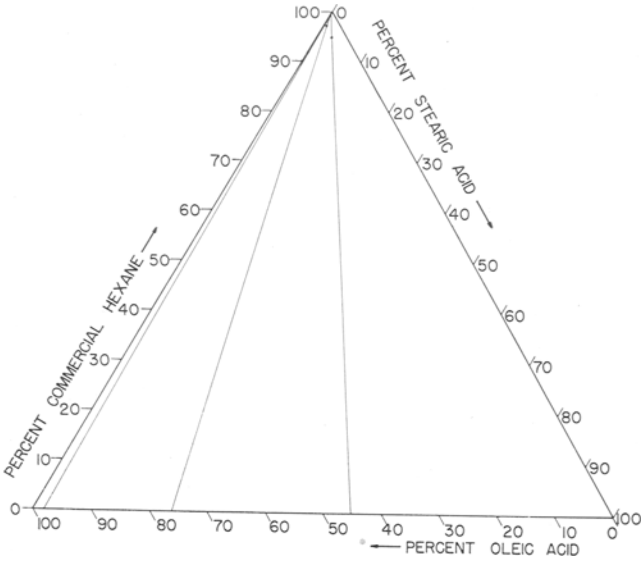

Fig. 9. Phase diagram of oleic acid-stearic acid-commercial hexane at —40°C.

When present in excess of 12 g./100 g. of commercial hexane and 8 g./100 g. of acetone appreciable quantities of oleic acid, together with stearic acid, were present in the solid phase. At these acid-solvent ratios, the liquid phases became saturated with both acids and remained constant in composition until as the original mixtures increased in oleic acid, concentrations were reached at which the small amount of stearic acid present became completely soluble, appearing entirely in the liquid phase. Boundaries of the liquid phase then moved toward the oleic acid

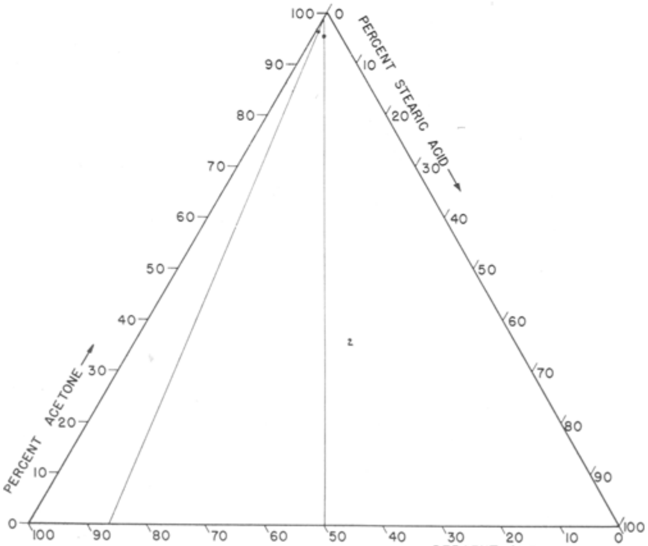

Fig. 10. Phase diagram of oleic acid-stearic acid-acetone at —40°C.

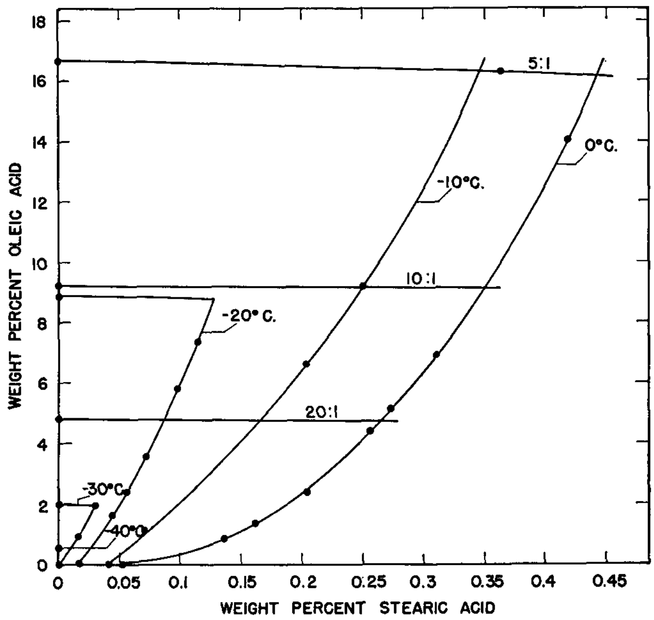

FIG. 11. Liquid phase compositions of the system oleic acid-stearic acid-commercial hexane at various temperatures and acid-solvent ratios.

apex, forming closed areas (Figures 11 and 12). Acetone exhibits a greater dissociating effect on the oleic acid-stearic acid mixtures than does commercial hexane.

Field "1" appears with the commercial hexane systems at this isotherm (Figure 5). That all of the tie lines are not contained within this field is due to oleic acid entrainment, mentioned previously. Field "3" is extremely narrow.

The acetone systems at —20°C. indicated the diminishing effect of oleic acid on stearic acid solubility, as exhibited by a narrowing of Field "1," Figure 6. Field "3" is almost removed. Thus closed areas, representing liquid phase compositions, are found in both systems for this isotherm.

The phase diagrams corresponding to —30°C. and —40°C. give definite closed areas for the liquid phases with both solvents, except at highly impractical solvent to acid ratios. The liquid phases at —30°C. range in composition up to 2.0% of oleic acid and from 0.0 to 0.03% of stearic acid in commercial hexane solutions (Figure 11); from 2 to 3% of oleic acid and from 0.0 to 0.02% of stearic acid in acetone (Figure 12). Field "2" has increased in both systems, further diminishing Field "1" (Figures 7 and 8).

At —40°C. the liquid phases were found to contain only about 0.01% of stearic acid, with either solvent. However, the solubility of oleic acid was very low, amounting to about 0.36 to 0.54% in commercial hexane, and about 0.9% in acetone (Figures 11 and 12). Stearic acid alone is practically insoluble in either solvent at these temperatures; its presence in the liquid phase may be attributed entirely to the solubilizing effect of oleic acid. Oleic acid in commercial hexane at —30°C. solubilizes approximately 3 to 4% of its own weight of stearic acid while at —40°C. it solubilizes about 7 to 8% of stearic acid. This apparent gain in the solubility of stearic acid results solely from the fact that at both —30°C. and —40°C. the liquid phases have reached a minimum compositional value of about 0.01 to 0.03% of stearic acid, while the solubility of oleic acid at —40°C. is much less than at —30°C. The acetone solutions behave in similar manner.

Since the amount of fatty acids in the liquid phases would greatly diminish with further reduction of temperature, no lower isothermal conditions were investigated.

(b) *Effect of Different Solvent Ratios.* Commercial hexane was added in increasing amounts to the oleic-stearic acids mixtures to determine its effects on the composition of the liquid phases. At those isotherms at which most of the oleic acid is in solution (0°C. and —10°C.), increasing the solvent over that present in the original mixture naturally does not increase the amount of oleic acid in the liquid phase but does increase the amount of stearic acid in this phase. The net effect is to enrich the liquid phase with respect to stearic acid and therefore to lower the percentage concentration of oleic acid as the solvent ratio is increased. However, two original mixtures having identical ratios of the two fatty acids, but varying in amount of solvent, will both have liquid phase compositions represented by points lying on the same liquid boundary curve of the phase diagram. For example, two commercial hexane solutions having the same ratio of acids but having solvent ratios of 8.5:1 and 17.7:1, respectively, were equilibrated at 0°C. The Wijs iodine values of the filtrate acids were 89.8 for the former and 82.1 for the latter. The higher iodine value denotes a greater ratio of oleic to stearic acid in the filtrate acids from the mixture with the lower solvent ratio. When the compositions of the liquid phases are plotted, both lie on the boundary representing the liquid phase compositions established by other determinations at this isotherm, with the composition of the liquid phase of the mixture having the higher solvent ratio lying closer to the solvent apex. Acetone solutions exhibit a similar behavior.

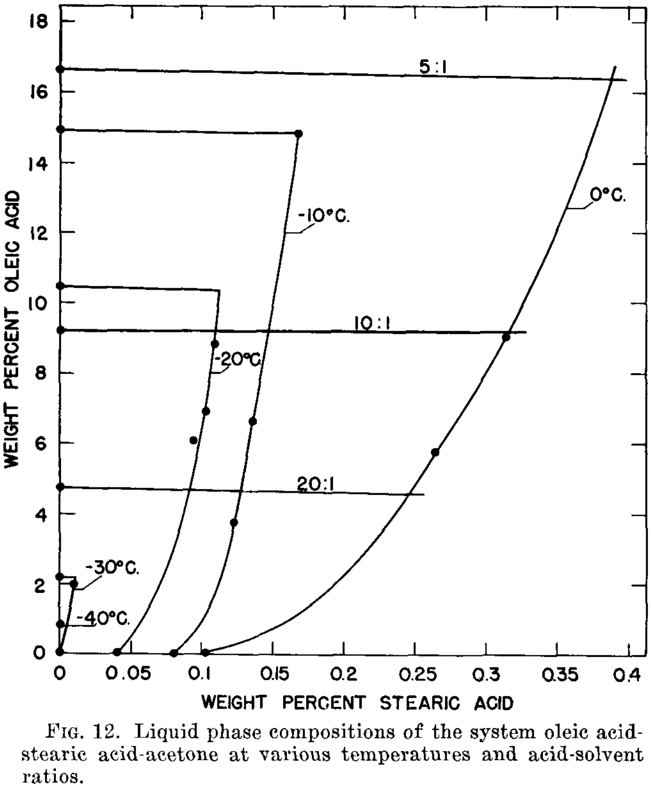

FIG. 12. Liquid phase compositions of the system oleic acid-stearic acid-acetone at various temperatures and acid-solvent ratios.

On Figures 11 and 12, boundary lines have been constructed representing acid-solvent ratios of 5:1, 10:1, and 20:1. At a constant solvent ratio, sufficiently high to prevent oleic acid precipitation, and with increasing proportions of oleic to stearic acid, the solubility of stearic acid increased until the amount of this acid in the original mixture was completely soluble. The liquid phase was then saturated with neither component acid; this resulted in the absence of a solid phase. If the acid-solvent ratio was then decreased, the liquid phase became saturated with stearic acid until sufficient oleic acid was added to again cause complete solubility. It thus becomes evident that low solvent-to-acid ratios permit only small amounts of stearic acid in the liquid phase. For example, assume a constant acid-to-commercial hexane ratio of 20:1, at 0°C. At the complete-solubility point of stearic acid the liquid phase will contain about 94.6% oleic acid on a solvent-free basis. If the acid-solvent ratio is decreased to 5:1, the liquid phase at the point of complete stearic acid solubility contains about 97.5% oleic acid on the same basis.

At the lower temperatures (—30°C. and —40°C.) solubility of both the oleic and stearic acids is proportional to the amount of solvent present because oleic acid is not completely soluble in either solvent at these temperatures.

## Significance of Results

On the basis of the data presented above it is apparent that oleic and stearic acids are both more soluble in acetone than in commercial hexane at any given temperature. However, the solubility of stearic acid is not increased as much by the presence of oleic acid in acetone as by its presence in commercial hexane. Thus, the intersolubilizing effect of one fatty acid on another is influenced by the type of solvent in the acid-solvent system. Also, appreciably greater quantities of oleic acid are removed from the liquid phase at higher temperatures in acetone than in commercial hexane, oleic acid appearing in the solid phase at —10°C. in acetone solutions, and at —20°C. in commercial hexane solutions. Therefore, with commercial hexane as the solvent, lower temperatures are required to effect the same degree of separation as is the case with acetone at any given temperature.

The phase diagrams reproduced in Figures 1 to 10 do not trace the course of crystallization from a completely liquid state but are more concerned with the temperature at which fractional crystallization of the liquid and solid fatty acids occurs. Particular attention has been given to the composition of the liquid phases existing at the temperatures employed.

From the family of curves obtained with the phase diagrams it is possible to predict the degree of separation obtainable in any mixture of oleic and stearic acids, with either acetone or commercial hexane as the solvent, if it is known that a condition of equilibrium exists in the system. Since all possible proportions of these three components which will give the same liquid and solid compositions lie on the same tie line, it is necessary only to know the composition of an original mixture, locate this compositional point on a tie line, and read off the compositions of the phases which will be present at equilibrium at that particular temperature. Interpolation between the tie lines is possible for any given system which may not lie on any tie line as constructed.

By use of the diagrams as constructed in Figures 11 and 12, the results which can be expected from any acid-solvent ratio, at any constant temperature, can be determined. Also, the purity of the oleic acid in any of the liquid phases can be calculated. Likewise, the liquid phase resulting from changing temperature at constant solvent ratio can be calculated.

It had been noted in these three-component systems that stearic acid persists in the liquid phase even at temperatures low enough to precipitate most of the oleic acid which is present in the solution. This fact can be used in conjunction with the conventional procedure in the preparation of purified oleic acid. By repeatedly crystallizing a product of about 98% purity from one of these solvents at —30° or —40°C. and discarding the filtrate, which will contain soluble stearic acid and a small amount of oleic acid, the precipitate fraction will become enriched in oleic acid. For example, a sample of oleic acid having an iodine value of 88.9 (98.9% oleic acid) was treated in the above manner to obtain a product with an iodine value of 89.8 (99.9% oleic acid).

## Summary

1. The ternary systems oleic acid-stearic acid-commercial hexane and oleic acid-stearic acid-acetone containing varying amounts of the three components have been equilibrated at 0°C., —10°C., —20°C., —30°C., and —40°C.
2. From compositional data of the liquid and solid phases in equilibrium at each isotherm, ternary phase diagrams have been constructed. From these diagrams it is possible to predict the degree of separation which can be obtained with any given mixture of oleic and stearic acids, using either acetone or commercial hexane as solvent.
3. With practical solvent ratios the phase diagrams at —20° C., —30° C., and —40° C., exhibit closed areas representing liquid phase composition. The liquid phase boundaries have been established for each isotherm investigated.
4. The intersolubilizing effect of oleic acid on stearic acid, greater in commercial hexane than in acetone, and the possible formation of mixed crystals of oleic and stearic acid have been noted.
5. Oleic acid of high purity can be obtained as one of the practical applications of these data.

### REFERENCES

1. Ralston, A. W., and Hoerr, C. W., J. Org. Chem., *7*, 546-555 (1942).
2. Hoerr, C. W., and Ralston, A. W., *ibid.*, *9*, 329-337 (1944).
3. Foreman, H. D., and Brown, J. B., Oil & Soap, *21*, 183-187 (1944).
4. Ralston, A. W., and Hoerr, C. W., J. Org. Chem., *10*, 170-174 (1945).
5. Smith, J. C., J. Chem. Soc., *1939*, 974-980.
6. Stewart, H. W., and Wheeler, D. H., Oil & Soap, *18*, 69-71 (1941).
7. Bailey, A. E., Singleton, W. S., and Feuge, R. O., Oil & Soap, *23*, 201-204 (1946).
8. Wheeler, D. H., and Riemenschneider, R. W., Oil & Soap, *16*, 207-209 (1939).
9. Werner, E. A., Analyst, *58*, 335-337 (1933).