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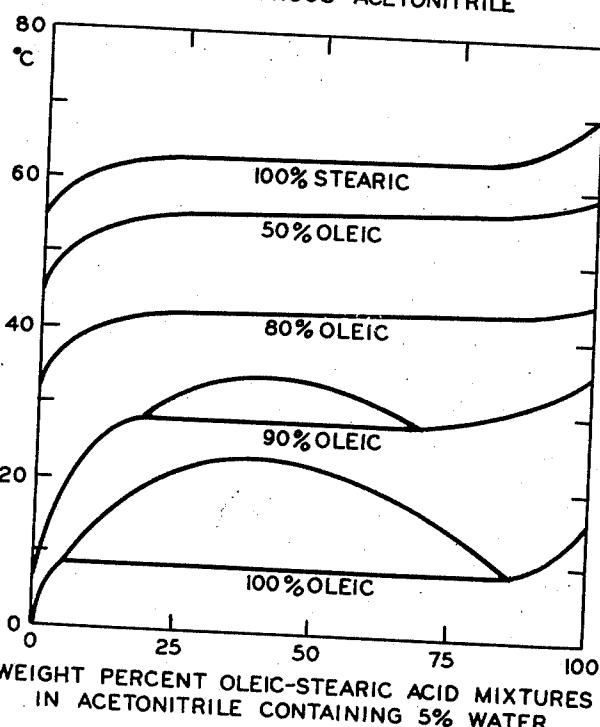
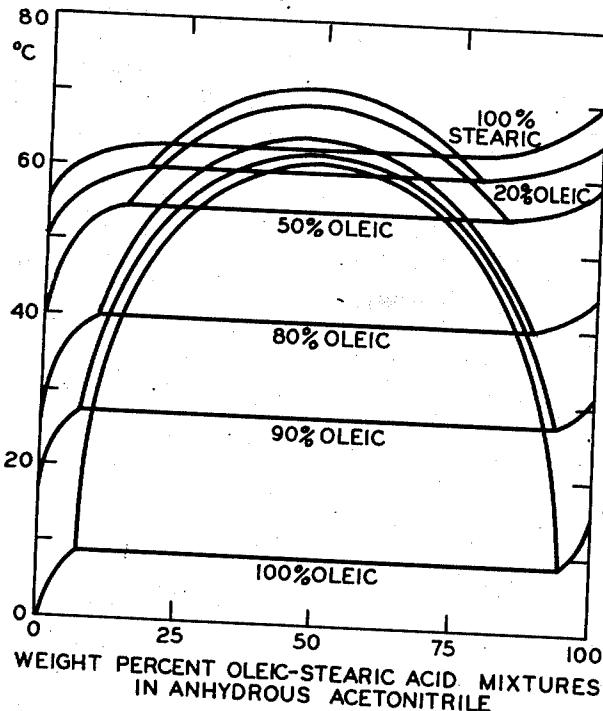
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2,705,723

SEPARATION OF OLEIC ACID FROM STEARIC AND PALMITIC ACIDS

Filed April 21, 1951

2 Sheets-Sheet 1



WEIGHT PERCENT OLEIC-STEARIC ACID MIXTURES  
IN ACETONITRILE CONTAINING 5% WATER

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April 5, 1955

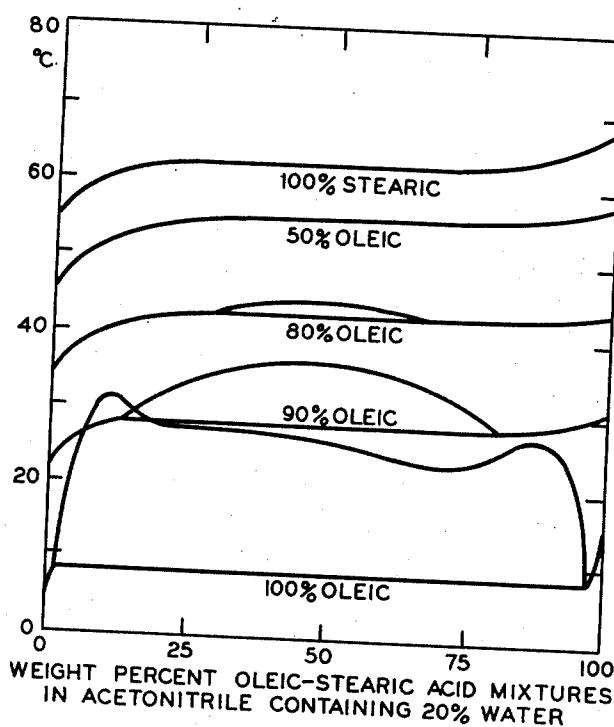
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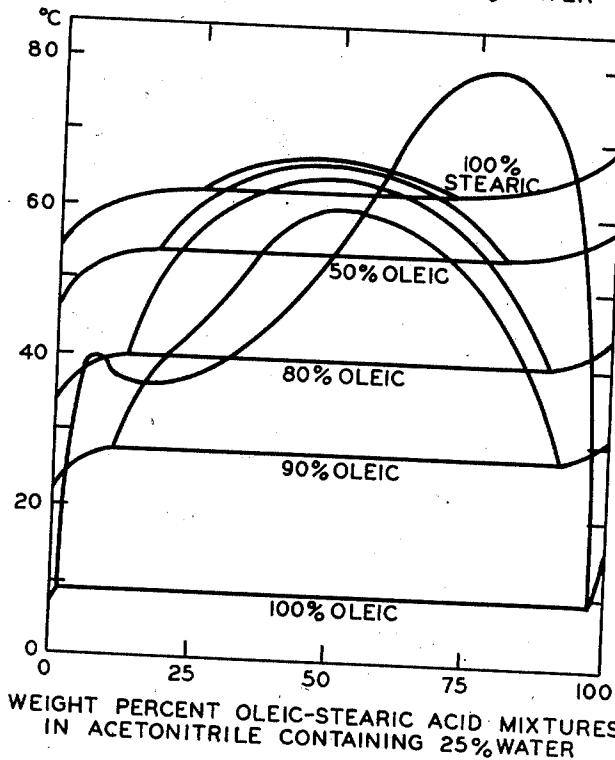
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2 Sheets-Sheet 2



WEIGHT PERCENT OLEIC-STEARIC ACID MIXTURES

IN ACETONITRILE CONTAINING 20% WATER



WEIGHT PERCENT OLEIC-STEARIC ACID MIXTURES  
IN ACETONITRILE CONTAINING 25% WATER

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2,705,723

## SEPARATION OF OLEIC ACID FROM STEARIC AND PALMITIC ACIDS

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Application April 21, 1951, Serial No. 222,252

7 Claims. (Cl. 260—419)

My invention relates to the separation of oleic from stearic and palmitic acids, and more particularly to the separation of these fatty acids by solvent crystallization.

Most of the common fats and oils are composed mainly of triglycerides of oleic, stearic, and palmitic acids. The free fatty acids are readily obtained from these fats and oils by subjecting the fatty materials to acid hydrolysis in the presence of naphthalene sulfonic acid, and then separating the glycerin from the fatty acids. Thus, there are available a variety of commercial mixtures of free fatty acids, which are substantially composed of oleic, stearic, and palmitic acids.

Oleic acid is unsaturated and contains 18 carbon atoms, while stearic and palmitic acids are saturated and respectively contain 18 and 16 carbon atoms. In the common mixtures of the free fatty acids stearic and palmitic acids are found in roughly equal amounts. The total amount of these saturated fatty acids varies from about 20 to 50% by weight to the total amount of fatty acids present. In other words, the unsaturated oleic acid is generally present in larger amounts than the saturated fatty acids.

Since oleic acid due to its unsaturation has differing properties and therefore different common uses from the saturated fatty acids, it is desired to separate oleic acid from stearic and palmitic acids. It has been found to be very difficult to produce a clean separation on a commercial basis by fractionation of the mixtures of the free fatty acids. Solvent extraction methods have also been found to be of little value. At the present time, the separation is carried out by two solvent crystallization processes, in one of which acetone is employed as the solvent and in the other of which methanol is employed.

Both the acetone and the methanol solvent crystallization processes for the separation of oleic acid from stearic acids suffer from serious disadvantages. The fatty acids are highly soluble in both acetone and methanol, and have very steep solubility curves in both solvents. Therefore, in carrying out these processes it is necessary to heat and then refrigerate large volumes of solvent, which are costly operations because of the spread in temperatures required to produce the separation. Furthermore, the separation is not as efficient as might be desired since the oleic acid begins to crystallize at the low temperatures necessary to complete the crystallization of the stearic and palmitic acids. In fact, it has been found impossible to obtain 90% or better separation between the saturated and unsaturated components of the fatty acids on a commercial scale with only one crystallization. At present, if the saturated and unsaturated acids are desired in better than 90% purity, they must be subjected to recrystallization. Therefore, a need has long been felt for better crystallization solvents for use in separating the fatty acids.

I have now discovered that acetonitrile has unexpectedly superior properties as a solvent for use in separating oleic acid from stearic and palmitic acids. Specifically, I have discovered that these fatty acids are all of limited solubility in acetonitrile, and that these acids have very flat solubility curves separated by a relatively wide temperature range. These properties of acetonitrile mean that only a relatively small volume of solvent need be employed for separating a given quantity of the fatty acids, and that the separation can be carried out over a narrow temperature range. Furthermore, cooling of the solvent by refrigeration to crystallize the stearic and palmitic acids is not required since this crystallization occurs at or above ordinary room temperature.

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In spite of these desirable properties of acetonitrile, it is probably not a commercially practical solvent. This is true because oleic acid is not completely miscible with acetonitrile in the desired commercial operating range of from 10 to 50% by weight of fatty acids in the crystallizing solution. When operating at fatty acid concentrations above 50%, the acetonitrile is actually dissolved in the fatty acids, and therefore the bulk of the crystallizing saturated acids will entrain portions of the solvent as well as absorbing quantities of the oleic acid. This results in a relatively poor separation between the saturated and unsaturated fatty acids, and the entrained solvent must be removed from the product. On the other hand at concentrations below about 10%, the volume of the solvent required greatly increases the cost of the separation. This is due to having to heat the larger volumes of solvent, and also to the larger equipment required.

When as little as 20% by weight of the fatty acids is 20 oleic acid, a two phase system will exist between about 10% and 80% concentrations of the fatty acids in the acetonitrile. As the percentage of oleic acid is increased, the two phase region exists over wider concentration ranges, until when the fatty acid mixture contains 90% 25 oleic acid the two phase region extends from concentrations of about 5% to 95%. One of these phases, which will normally be the top layer, consists of a relatively dilute solution of the fatty acids in the acetonitrile, while the other phase or bottom layer consists of a concentrated 30 solution of the fatty acids in the acetonitrile. In fact, in the bottom layer, the acetonitrile is actually dissolved in the fatty acids. Crystallization of the stearic and palmitic acids from the two phase system results in a 35 much poorer separation between the saturated and unsaturated acids than is obtained when the solution is homogenous. Most of the saturated fatty acids are in the concentrated bottom layer which causes them to entrain portions of the solvent and to adsorb quantities of the oleic acid while crystallizing. An even more serious 40 disadvantage of carrying out the crystallization from the two phase system is that the crystals of the saturated acids collect at the bottom of the bottom layer. Thus, in order to separate the crystallized material it is necessary to filter the concentrated bottom layer, which is an 45 extremely difficult operation.

Therefore, the problem is presented as to how to increase the solubility of oleic acid in acetonitrile to such a point that oleic acid and acetonitrile will be completely miscible at all concentrations over temperature ranges 50 within which substantially all of the stearic and palmitic acids can be crystallized. In other words, it is desired to selectively increase the solubility of oleic acid without increasing the solubility of stearic and palmitic acids, and also without altering the desirable characteristics of the solubility curves of these acids, as discussed above.

It is therefore an object of my invention to develop a commercially feasible crystallization process for the separation of oleic acid from stearic and palmitic acids in which acetonitrile is employed as a solvent. More 60 specifically, it is an object of my invention to provide a means for modifying the solvent properties of acetonitrile to selectively increase the solubility of an oleic acid over stearic and palmitic acids. It is also an object of my invention to increase the temperature range within which oleic acid and acetonitrile are completely miscible at all concentrations. Further objects and advantages will appear as the specification proceeds.

I have discovered that the solubility of oleic acid in acetonitrile can be greatly increased without affecting the solubility of stearic and palmitic acids therein by adding a minor proportion of water to the acetonitrile. More specifically, I have discovered that the separation of oleic acid from stearic acid can be remarkably improved by having present in the solvent from 3% to 25% of water to the combined weight of the acetonitrile and water, and preferably between 5 and 20% by weight of water. This is a completely unexpected result. All of the fatty acids are insoluble in water, and it is well-known that the addition of water to other solvents for the fatty acids, and specifically for oleic, stearic, and palmitic acids, decreases the solubility of fatty acids in

the solvent. It is therefore my belief that I have discovered a unique phenomenon in that the presence of certain critical amounts of water in acetonitrile increases the solubility of oleic acid therein. The effect of adding water to acetonitrile is also remarkable in that the solubility of palmitic and stearic acids therein are not appreciably changed. My investigations have led me to believe that this phenomenon may be specific to systems of oleic, stearic, and palmitic acids in aqueous acetonitrile.

My invention is illustrated in the accompanying drawings, in which—

Figure 1 shows the solubility of stearic and oleic acids and mixtures thereof in anhydrous acetonitrile; Fig. 2, the solubility curves of the fatty acids of Fig. 1 when the acetonitrile contains 5% by weight of water; Fig. 3, the solubility curves of the same fatty acids when the acetonitrile contains 20% water by weight and Fig. 4, the solubility curves of the same materials when the acetonitrile contains 25% water by weight.

Looking first at the phase diagram of Fig. 1, it can be seen that pure stearic acid in anhydrous acetonitrile possesses a simple solubility curve consisting of a highly desirable broad flat region terminating in a quite abrupt change of slope at lower concentration. Oleic acid, on the other hand, exists over a wide concentration range (approximately 5 to 95%) as a heterogeneous system consisting of two immiscible liquids. This diagram also shows that as little as 20% oleic acid in stearic acid produces this two phase region over the concentration range of the fatty acids in the solvent at which it would be desired to carry out the crystallization process. Such a system, as discussed above is undesirable in solvent crystallization operations in that it necessitates working at relatively great dilutions or results in inefficient separations at the higher concentrations.

Fig. 2 illustrates the unusual phenomenon resulting from the addition of as little as 5% water by weight to the acetonitrile. This diagram shows that when the oleic acid is present in the fatty acid mixture in concentrations of not over 80%, that the oleic acid is completely miscible at all concentrations down to temperatures below that at which the stearic acid crystallizes out of the solution. The improvement in the solubility of oleic acid in acetonitrile becomes appreciable when about 3% water by weight is present in the solvent. As the concentration of water increases from 3 to 5%, the solubility of the oleic acid increases rapidly until the condition is reached illustrated in Fig. 2. At water concentrations in the solvent between 5% and 20% the solubility of the oleic acid remains practically constant. At water concentrations of about 20%, the system begins to revert to solubility conditions similar to those in anhydrous acetonitrile. The beginning of this reversion is illustrated in Fig. 3 in which the solubility curves of oleic and stearic acid mixtures are shown for acetonitrile containing 20% water. Between 20 and 25% water concentrations in the solvent, the solubility of oleic acid decreases until at concentrations of 25% as illustrated in Fig. 4, the presence of the water becomes of little value in modifying the system to improve the separation of the acids.

As illustrated in Figs. 1 through 4, the presence of water in the acetonitrile has practically no effect on the solubility of stearic acid. Palmitic acid has been found to have substantially identical solubility curves to that of stearic acid in anhydrous and aqueous acetonitrile, the curve for pure palmitic acid lying a few degrees lower than that for pure stearic acid. When stearic acid and palmitic acid are both present in the solution, for all practical purposes their solubility curves are merged into one curve which has the same shape as the curves for stearic acid and mixtures of stearic and oleic acid, but lies about 1 to 2° lower in general. Therefore, the phase diagrams shown in Figs. 1 to 4 can be taken as accurate for systems containing mixtures of oleic and stearic acid, mixtures of oleic and palmitic acid, and mixtures of oleic, stearic and palmitic acids.

In general, our solvent crystallization process employing a solvent composed of acetonitrile and from 3 to 25% by weight of water and preferably 5 to 20% by weight of water, can be carried out according to well-known procedures for similar solvent crystallization processes. The fatty acids are first dissolved in the aqueous acetonitrile by slightly elevating the temperature of the sol-

vent. As shown by the accompanying diagram, an elevation of the temperature of the solvent to 60° C. will be adequate in practically all cases when separating commercially available fatty acid mixtures to bring all of the fatty acids into an homogenous solution. The exact temperature elevation necessary for varying mixtures of the fatty acids can easily be determined by consulting the phase diagrams.

After an homogenous solution has been produced by elevation of the temperature of the solvent, the solvent is cooled to produce crystallization of the saturated fatty acids. Since it is not necessary to cool the solution below about 30° C., refrigeration is not required to cool the solution and the cooling can be carried out by exposure of the solution to room temperature. However, other cooling means can be employed if it is desired to more accurately control the cooling temperatures. After the crystallization has been completed, the crystallized fatty acids can then be removed by filtration or other equivalent separating processes. As will be apparent from the phase diagrams, it is important that the solution not be cooled to such a point that the solubility of the oleic acid remaining in the solvent is so decreased as to produce a two phase system. I have found that if the filtration is carried out at temperatures at which the filtrate contains two immiscible liquid systems, that some of the oleic acid will be pushed out of solution and entrapped in the precipitate by adsorption, thus decreasing the purity of the product. I have also discovered that the optimum lower temperature in the cooling step and in the filtration step is preferably not over 5° C. above the temperature at which the material in the filtrate forms into immiscible liquid systems. Since my method of solvent crystallization when correctly carried out results in a 90% or better separation between the saturated and unsaturated acids, the filtrate will consist of oleic acid in excess of 90%. As illustrated in Figs. 2 and 3, when operating with between 5 and 20% water in the solvent and at fatty acid concentrations in the solvent of greater than 10%, the filtrate can be expected to begin to contain immiscible layers at temperatures between 30° C. and 40° C. I have found, as indicated above, that when the lower cooling temperature and the filtration temperature is more than 5° above the temperature at which the immiscible systems begin to form, that a greater proportion of the saturated acids will be left in the filtrate, and thereby decrease the cleanliness of the separation. In practical operation of my process, I have found that the preferred lower cooling temperatures and filtration temperatures are between about 34 to 36° C., and that excellent results are obtained when a temperature of 35° C. is employed. The exact minimum temperature for a given concentration of oleic acid in the filtrate can easily be determined experimentally or by consulting the phase diagrams.

After the separation of the crystallized saturated fatty acids, the oleic acid can easily be recovered from the filtrate by sending the filtrate to a steam heated stripping still in which the solvent is removed. The oleic acid recovered from this operation is found to be of high grade and purity when the prior crystallization and filtration steps have been carried out according to our preferred method.

If desired, the stearic and palmitic acids can be separated by well-known procedures, such as fractionation, etc.

My process can be applied to a wide variety of fatty materials. However, I prefer to utilize as starting materials mixtures of free fatty acids containing not over 80% oleic acid in combination with stearic and palmitic acids. Among the fatty acid mixtures which meet these specifications are: Palm oil (50% oleic—50% palmitic-stearic), tallow (50% oleic—50% palmitic-stearic), lard (65% oleic—35% stearic-palmitic), cottonseed oil (75% oleic—25% palmitic-stearic), and peanut oil (80% oleic—20% palmitic-stearic). In order to better illustrate my process I wish to set forth the following illustrative examples:

#### Example I

80 One part of a fatty acid mixture consisting of 47% stearic acid and 53% oleic acid was dissolved in 9 parts of solvent consisting of 90% acetonitrile and 10% water at about 40° C. After cooling the solution to 31° C., the solid matter which precipitated was separated from the solution by filtration at 31° C. This precipitate was

separated from the solution by filtration at 31° C. This precipitate amounted to 49% of the original fatty acid mixture and consisted of 97% stearic acid and 3% oleic acid. The residue obtained by evaporating the solvent from the filtrate amounted to 51% of the original fatty acid mixture and consisted of 96% oleic acid and 4% stearic acid.

*Example II*

One part of a fatty-acid mixture containing 55% stearic acid and 45% oleic acid was dissolved in two parts of solvent consisting of 80% acetonitrile and 20% water at about 55° C. This solution was cooled to 35° C. and the solid matter which precipitated was separated from the solution by filtration at 35° C. The precipitate amounted to 54% of the original fatty-acid mixture and consisted of 98% stearic acid and 2% oleic acid. The residue obtained by evaporation of the solvent from the filtrate amounted to 46% of the original fatty-acid mixture and consisted of 96% oleic acid and 4% stearic acid.

*Example III*

One part of a regular commercial tallow fatty-acid feedstock consisting of 45% saturated fatty acids (essentially palmitic and stearic acids in the ratio 60:40) and 55% unsaturated acids (essentially oleic acid) was dissolved in two parts of solvent consisting of 80% acetonitrile and 20% water at 45° C. The solution was cooled to 35° C. and filtered at this temperature. The solid material which precipitated amounted to 40% of the original feedstock and consisted of 96% saturated acids and 4% unsaturated acids. The residue obtained by evaporation of the solvent from the filtrate amounted to 60% of the original feedstock and consisted of 92% unsaturated acids and 8% saturated acids.

*Example IV*

One part of the tallow acid feedstock of Example III was dissolved in three parts of solvent consisting of 95% acetonitrile and 5% water at 45° C. This solution was cooled to 35° C. and the solid matter which precipitated was removed by filtration at this temperature. This precipitate amounted to 43% of the original feedstock and consisted of 98.5% saturated acids and 1.5% unsaturated acids. The residue obtained by evaporation of the solvent from the filtrate amounted to 57% of the original feedstock and consisted of 95% unsaturated acids and 5% saturated acids.

*Example V*

One part of the tallow acid feedstock of Example III was dissolved in two parts of solvent consisting of 95% acetonitrile and 5% water at 45° C. This solution was cooled to 35° C. and the solid matter which precipitated was removed by filtration at this temperature. This precipitate amounted to 40% of the original feedstock and consisted of 96% saturated acids and 4% unsaturated acids. The residue obtained by evaporation of the solvent from the filtrate amounted to 60% of the original feedstock and consisted of 92% unsaturated acids and 8% saturated acids.

As pointed out above, it is important to have the lower cooling temperatures and the filtration temperature of the solvent not over 5° above the temperature at which the filtrate begins to contain immiscible layers, and preferably at a temperature just above the temperature at which the material in the filtrate forms an immiscible liquid system. In other words, the separation obtained becomes progressively sharper up to the temperature at which the immiscible systems begin to form in the filtrate. The criticalness of these temperatures is illustrated by the following example in which the separation of Example II was carried out at a higher filtration temperature.

*Example VI*

One part of a fatty acid mixture containing 54% stearic acid and 46% oleic acid was dissolved in 2 parts of solvent consisting of 80% acetonitrile and 20% water at about 50° C. This solution was cooled to 40° C. and the solid matter which precipitated was separated from the solution by filtration at 40° C. The precipitate amounted to 45% of the original fatty acid mixture and consisted of 90% stearic acid and 10% oleic acid. The residue obtained by evaporation of the solvent from the filtrate amounted to 55% of the original fatty acid mix-

ture and consisted of 77% oleic acid and 23% stearic acid.

Although my invention has been described in connection with certain specific embodiments, it will be apparent that modifications and changes can be made without departing from the spirit and scope of my invention.

I claim:

1. In a solvent crystallization process for separating oleic acid from stearic and palmitic acids wherein a mixture of said fatty acids is dissolved in acetonitrile at a slightly elevated temperature and then the solution is cooled until crystallization of the stearic and palmitic acids occur, the improvement comprising having present in said solution from 3 to 25% by weight of water to the total weight of the water and acetonitrile during said cooling step to selectively increase the solubility of the oleic acid in the acetonitrile and thereby greatly increase the temperature range within which oleic acid and acetonitrile are completely miscible at all concentrations.
2. In a solvent crystallization process for separating oleic acid from stearic acid wherein a mixture of said fatty acids is dissolved in acetonitrile at a slightly elevated temperature and then the solution is cooled until crystallization of the stearic acid occurs, the improvement comprising having present in said solution from 3 to 25% by weight of water to the total weight of the water and acetonitrile during said cooling step to selectively increase the solubility of the oleic acid in the acetonitrile and thereby greatly increase the temperature range within which oleic acid and acetonitrile are completely miscible at all concentrations.
3. In a solvent crystallization process for separating oleic acid from stearic and palmitic acids wherein a mixture of said fatty acids is dissolved in acetonitrile at a slightly elevated temperature and then the solution is cooled until crystallization of the stearic and palmitic acids occur, the improvement comprising having present in said solution from 5 to 20% by weight of water to the total weight of the water and acetonitrile during said cooling step to selectively increase the solubility of the oleic acid in the acetonitrile and thereby greatly increase the temperature range within which oleic acid and acetonitrile are completely miscible at all concentrations.
4. In a solvent crystallization process for separating oleic acid from stearic acid wherein a mixture of said fatty acids is dissolved in acetonitrile at a slightly elevated temperature and then the solution is cooled until crystallization of the stearic acid occurs, the improvement comprising having present in said solution from 5 to 20% by weight of water to the total weight of the water and acetonitrile during said cooling step to selectively increase the solubility of the oleic acid in the acetonitrile and thereby greatly increase the temperature range within which oleic acid and acetonitrile are completely miscible at all concentrations.
5. In a solvent crystallization process for separating oleic acid from stearic and palmitic acids, the steps of dissolving a fatty acid mixture containing oleic, stearic, and palmitic acids in aqueous acetonitrile containing from 3 to 25% water by heating said solvent until an homogenous solution is produced, cooling the solution to a temperature at which the stearic and palmitic acids crystallize out of solution, said cooling temperature being above but not over 5° C. above the temperature at which the oleic acid and solvent separate into two immiscible layers, and filtering the solution to remove the crystallized stearic and palmitic acids at a temperature above but not over 5° C. above the temperature at which the filtrate begins to contain two immiscible portions.
6. In a solvent crystallization process for separating oleic acid from stearic and palmitic acids, the steps of dissolving a fatty acid mixture containing oleic, stearic, and palmitic acids in aqueous acetonitrile containing from 5 to 20% water by heating said solvent until an homogenous solution is produced, cooling the solution to a temperature at which the stearic and palmitic acids crystallize out of solution, said cooling temperature being above but not over 5° C. above the temperature at which the oleic acid and solvent separate into two immiscible layers, and filtering the solution to remove the crystallized stearic and palmitic acids at a temperature above but not over 5° C. above the temperature at which the filtrate begins to contain two immiscible portions.
7. In a solvent crystallization process for separation of oleic acid from stearic and palmitic acids, the steps com-

prising dissolving from 10 to 50% by weight of a mixture containing oleic, stearic, and palmitic acids in aqueous acetonitrile containing from 5 to 20% water by weight by heating said solvent, said fatty acid mixture containing less than about 80% oleic acid by weight, cooling said solution to a temperature between about 34 to 36° C. to crystallize said stearic and palmitic acids, and filtering said solution to remove the crystallized mixture at a temperature between about 34 and 36° C.

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