# Separation of Oleic Acid and Linoleic Acid by Solvent Extraction

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## Abstract

Oleic acid and linoleic acid were separated by extraction with the solvent system *n*-heptane-dimethyl sulfoxide. The separation factor decreased with increasing concentrations of fatty acids in the dimethyl sulfoxide (DMSO) layer. At fatty concn of 0.60 and 16.02%, the separation factors of linoleic acid were found to be 2.18 and 1.28, respectively. The solvent could be removed by adding water to the extract. DMSO is very soluble in water while the fatty acids are only sparingly soluble. Thus DMSO and fatty acids are separated. A phase diagram for the system Unitol ACD-DMSO-water at 25C and 1 atm is given.


## Introduction

IT IS DIFFICULT to separate oleic acid and linoleic acid by fractional distillation since they have substantially the same volatilities. Separation by low temp crystallization and recrystallization may require temp as low as −70C to crystallize most of the acids. The present work was intended to study the fractionation of oleic acid and linoleic acid by extraction with selective solvents. The method is of potential interest because the separation may be based on the degree of unsaturation.

The liquid-liquid extraction process for the fractionation of fatty acids and fatty acid esters of glycerides have been studied by numerous investigators. Among the earlier publications are those of Freeman (2–4), Gloyer (5) and Passino (7). In their experiments, soybean oil and linseed oil were separated into portions having different iodine values by extraction with furfural, liquid propane or similar solvents. More recently Cannon et al. (1) described the countercurrent distribution of methyl esters of higher fatty acids between hydrocarbon and nitroparaffin solvents in Craig apparatus. A solvent system consisting of a petroleum ether and dimethyl sulfoxide has also been used to separate a mixture of capric, lauric, myristic, palmitic and stearic acids (8). However, such applications were mostly limited to the analytical laboratory for the separation of fatty acid mixtures before analysis.

Data concerning the distribution of oleic and linoleic acids between solvents essential to the designing of commercial extraction units are thus far not available and have to be determined experimentally.

## Experimental

Unitol ACD (Union Bag-Camp Paper Corp., Savannah, Ga.), a tall oil fatty acids mixture which contained chiefly stearic, oleic and linoleic acids, was used for the extraction. The analysis of Unitol ACD as furnished by the manufacturer is given in Table I.

In selecting the solvents, consideration was given to the degree of extraction and separation that could be accomplished, as well as the readiness and completeness with which the solvents could be removed and recovered. After careful scanning of a number of solvents, the system *n*-heptane-DMSO was selected. Both solvents used in this work were reagent grade.

A weighed quantity of Unitol ACD was mixed with *n*-heptane (n-$C_7$) and DMSO by shaking vigorously in a separatory funnel. The mixture was then allowed to separate into the extract (DMSO) and the raffinate (n-$C_7$) layers. The oleic acid and linoleic acid contents in each layer were analyzed and the equilibrium distribution data were expressed as separation factors. The separation factor was defined as

$$\text{s.f. of linoleic acid} = \frac{Y_{C_{18:2}}/Y_{C_{18:1}}}{X_{C_{18:2}}/X_{C_{18:1}}}$$

Where

X = wt fraction of a component fatty acid in the raffinate layer (solvent-free basis)
Y = wt fraction of a component fatty acid in the extract layer (solvent-free basis)
$C_{18:1}$ = oleic acid, the reference fatty acid
$C_{18:2}$ = linoleic acid.

The system Unitol ACD-DMSO-water was also in-

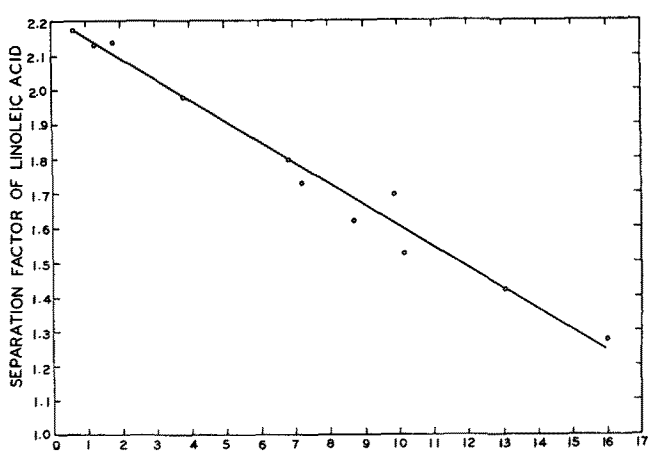


FIG. 1. Separation factors of linoleic acid.

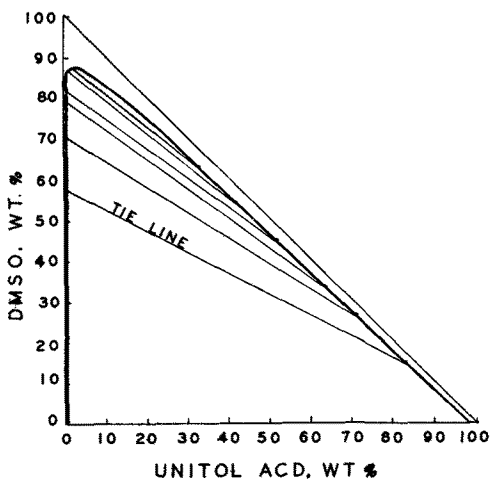


FIG. 2. Phase diagram for unitol ACD-DMSO-water at 25C and 1 atm.

vestigated to evaluate the possibility of removing the solvent by adding water to the extract. After mixing and separating the components into two layers, each layer was analyzed for DMSO, water and acids.

The fatty acids were considered as a whole to be a single component for convenience, since practically all the acids separated in one layer, which also contained some DMSO and water. The other layer consisted mostly of DMSO and water, with only a small amt of acids.

In actual continuous countercurrent extraction, the water in the solvent should be removed before the solvent is recycled because the presence of water will greatly reduce the solubility of fatty acids. It is recommended that the water remaining in the solvent should not be more than 2%.

In determining the separation factors of linoleic acid, all experiments were carried out at room temp, since temp appeared to have little effect on the separation factor in this particular system studied.

*Analytical Methods.* The fatty acids were analyzed directly by gas-liquid chromatography on an F&M chromatograph. The chromatographic column was packed with LAC-3R-728 (diethylene glycol succinate polymer) treated with phosphoric acid (6). It seemed that the solvents present did not interfere with the determination. Therefore, the samples were analyzed without solvent removal.

For the system Unitol ACD-DMSO-water, the acids were analyzed by titration with alcoholic potassium hydroxide and the water by the Karl-Fischer method. The water contents in both layers were added up. The results agreed with the total amt of water originally present, within experimental error. The DMSO was, therefore, obtained by difference.

*Experimental Results.* Separation factors of linoleic acid were correlated as the function of the concn of acids and the results were shown in Figure 1. The equilibrium distribution curve and the tie lines for the system Unitol ACD-DMSO-water were given in Figure 2.

TABLE I

Analysis of Unitol ACD

| | |
|---|---|
| Fatty acids, % | 98.8 |
| Rosin acids, % | 0.6 |
| Unsaponifiables, % | 0.6 |
| Acid no. | 199 |
| Saponification no. | 200 |
| Color | 4 |
| Saturated acids, % | 2.4 |
| Iodine no. | 132 |
| Titer, °C | 0.4 |
| GLC analysis[a] | |
| Oleic acid, % | 56.6 |
| Linoleic acid, % | 39.0 |
| Stearic acid, % | 2.6 |
| Others, % | 1.8 |

[a] GLC analysis was done at the author's laboratory.

*Discussion.* The separation factor of linoleic acid decreases with increasing acid concn in the DMSO layer. In designing equipment for extraction an optimum condition should be chosen, considering both the selectivity and the capacity.

If operating conditions are chosen such that the average separation factor of linoleic acid is 1.7, a minimum of twelve theoretical plates will be required to obtain a 95% oleic acid fraction at one end and a 95% linoleic acid at the other.

## Conclusions

The experimental data presented here indicate that oleic acid and linoleic acid can be separated by extraction with selective solvents. As extraction possesses many favorable engineering aspects as a unit operation, the process warrants further consideration from an economic standpoint.

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# Report of the Instrumental Techniques Committee, AOCS, 1963-1964[1]

AT ITS INAUGURAL meeting, the Instrumental Techniques Committee agreed that each of its Subcommittees would meet during each Annual Convention of the Society to discuss progress and to consider plans for the coming year. These independent meetings of the Subcommittees are to be followed by a meeting of the entire Committee where objectives of each Subcommittee would be reviewed, and any activities involving more than one Subcommittee would be discussed. At each Fall Convention of the Society only a single meeting of the entire Instrumental Techniques Committee, to consider progress and plans of each Subcommittee, is to be scheduled.

Accordingly, during the past year the Instrumental Techniques Committee held two meetings. The first of these was in the Marquette Suite A of the Radisson Hotel in Minneapolis, Minn., on Tuesday, Oct. 1, 1963, during the 37th Fall Meeting of the Society. The second meeting was held, following earlier meetings of the Subcommittees, on Wednesday, April 22, 1964, in the Red Oak Room of the Roosevelt Hotel, during the 55th Annual Meeting of the Society.

[1] Report of collaborative work of the USDA, ARS, S. Utiliz. Res. Dev. Div.; E. Utiliza. Res. Devel. Div.; Dep. of Health, Education, and Welfare, FDA; Hormel Institute; and the following companies: Anderson, Clayton & Company; Archer-Daniels-Midland Company; Arizona Chemical Company; Carnation Company; Colgate-Palmolive Company; Darling & Company; Procter & Gamble Company; Provincial Traders Pty., Limited; and A. E. Staley Mfg. Company.

## Color Subcommittee

As described in the last report (*1*), the Color Subcommittee had been considering two problems: (1) specifications and methods for surface color by reflectance techniques; and (2) possible revisions of present methods for color evaluation either by the subjective tintometer method (Cc 13b–45) or the objective spectrophotometric method (Cc 13c-50) to provide for the measurement of very light-colored oils if trading rules are modified. At a meeting of the Color Subcommittee held in Atlanta, Georgia on April 22, 1963, during the 54th Annual Meeting of the Society (1), it was decided that before any further experimental effort was devoted to the project on surface color by reflectance