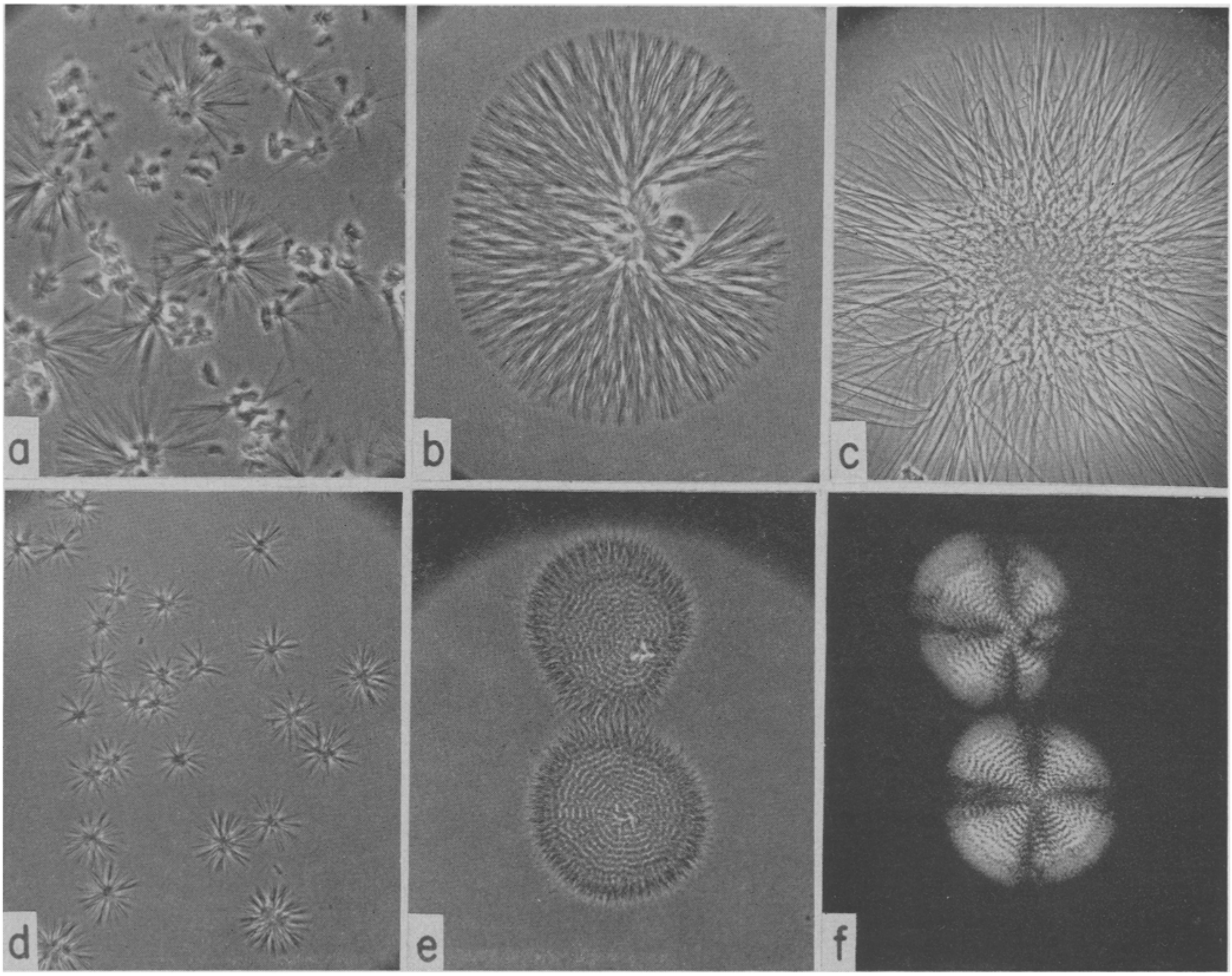

FIG. 4. Miscellaneous photomicrographs.
(a, b, and c) from lard, technique (B), 400 x magnification, phase contrast.
(d) from rearranged lard, technique (C), 100 x magnification, phase contrast.
(e) low melting di-saturated glyceride fraction from lard, technique (C), 100 x magnification, phase contrast.
(f) low melting di-saturated glyceride fraction from lard, technique (C), 100 x magnification, polarized light.

Separation of Monoglycerides, Diglycerides, and Triglycerides by Liquid-Liquid Extraction

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MONO- AND DIGLYCERIDES possess high surface activity because of the presence of lipophilic (fatty acid) and hydrophilic (hydroxyl) groups. Consequently partial glycerides exhibit unusual and valuable properties and have found important applications in the food, paint, and plastics field. While triglycerides occur naturally as fats and oils, appreciable quantities of mono- and diglycerides are found only in fats which have become partially hydrolyzed (14). Commercial products of 40–60% monoglyceride content are made by reacting fatty acids, or triglycerides such as lard and coconut oil, with an excess of glycerol. Higher monoglyceride contents are limited by glycerine solubility but can be prepared with mutual solvents (phenol and cresol) and a large glycerol excess. Nevertheless these methods are costly, and industrial applications require complete solvent removal. Monoglycerides of about 90% purity are currently made by molecular distillation and enjoy acceptance in the baking field (9).

Selective liquid-liquid extraction has become a widely accepted means of separating chemicals and should be adaptable to mono-, di-, and triglyceride mixtures which differ in molecular weight and number of polar groups. Selective extraction of monoglycerides by ethanol-hexane mixtures (4, 6, 19) and frac-

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[1] The findings reported in this paper were included in a thesis submitted by J. A. Monick to the Graduate Division of the College of Engineering of New York University in partial fulfillment of the requirements for the degree of Doctor of Engineering Science.

[2] Presented at the fall meeting, American Oil Chemists' Society, in Philadelphia, Pa., October 10–12, 1955.

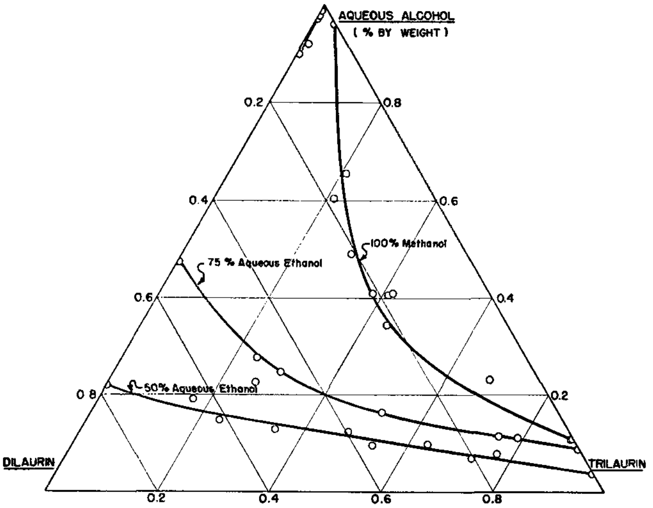


FIG. 1. Ternary-equilibrium data for dilaurin-trilaurin-aqueous alcohol systems; weight fraction at 60°C.

tional crystallization from mixed solvents (4, 11) have been previously reported. The objective of the investigation however was to obtain fundamental extraction data with a single solvent. Ternary systems containing mono- and dilaurin, and di- and trilaurin were studied with aqueous ethanol. Subsequently the investigation was extended to quaternary systems based on pure mono-, di-, and trilaurin, and then to commercial monoglycerides.

Experimental

Material Used. Crude monolaurin was prepared with fractionated methyl laurate and glycerol and was purified by crystallization from ethyl ether, using the method of Hilditch and Rigg (8). Melting point of the purified compound was 62°C., and literature values are 63.0°C. (1) and 62–63°C. (5). Monoglyceride assay by the method of Pohle *et al.* (13) was 100%.

Crude dilaurin was prepared with fractionated methyl laurate and glycerol, and part of the monolaurin content was removed by crystallization from ethyl ether. Purification was obtained by two crystallizations from heptane, and three crystallizations from ethanol. Combined glycerine content was 20.15–20.30%, and the theoretical value was 20.18%. Melting point of purified dilaurin was 55.5–55.8°C., and literature values were 56.6°C. (1) and 55°C. (7).

Crude trilaurin was prepared with fractionated methyl laurate and glycerol and initially purified by extraction with 90% aqueous ethanol from a petroleum ether solution. Final purification was by several crystallizations from 85–90% aqueous ethanol. Combined glycerine content was 14.42–14.50%, and the theoretical value was 14.42%. The melting point was 46.5°C. while the literature reported 45.6°C. (1).

Commercial products (glyceryl monostearate, glyceryl monococate, and lard monoglyceride) were obtained from Colgate-Palmolive Company. Washing an ethyl ether solution of the industrial preparation with 5% potassium carbonate solution and water removed glycerine, free fatty acids, and catalyst.

Absolute grain alcohol had a purity of 99.9% ethanol by volume. Absolute methanol assayed over 99.5% purity by weight.

Liquid Equilibria. Equilibrium-solubility data and tie lines were obtained at 60°C., as described by Treybal (15). Ternary-equilibrium data were plotted on an equilateral triangle, and the length of the perpendicular represented the weight fraction of a component.

Distribution of a component (A) between layers was shown, as indicated by Treybal (16), by means of a plot of its concentration in the solvent-rich phase (X_{AC}) at equilibrium against concentration of A in the B-rich phase (X_{AB}) at equilibrium. A 45° line on this plot represents a distribution coefficient of one.

Selectivity (β) is the measure of ability of a solvent preferentially to extract one component of a solution. Relationship between selectivity of C for A and distribution coefficient (m) has been defined by Treybal (17) as

$$\beta = mX_{BB}/X_{BC} = X_{AC}X_{BB}/X_{AB}X_{BC} \qquad \text{I}$$

Analysis. Monoglycerides were determined by the periodic acid method of Pohle *et al.* (13). Troy and Bell (18) have presented a method for combined glycerine content which can be used in conjunction with monoglyceride content to calculate mono-, di-, and triglyceride percentages.

Free glycerine was removed by water extraction of an ethyl acetate solution and was determined by the periodic oxidation method of Pohle *et al.* (13).

Fatty matter was removed from the extract phase of equilibrium layers by five extractions with petroleum ether after 50% dilution with water. Removal of petroleum ether on a steam bath resulted in dry solids for analysis. Weight of solids was used to determine partial-glyceride content of the extract. Raffinate solids were obtained by evaporation of solvent on a steam bath, followed by drying to constant weight in an oven at 80°C. for about 3 hrs.

Contact of monolaurin with 50 wt.-% aqueous ethanol for 1 week at 60°C. did not form any detectible ethyl esters.

Results and Discussion

Solvent Selection. The hydrogen-bonding theory of Ewell and others (2) was used as a guide for solvent selection. Hydrocarbons, such as heptane and paraffin wax, were completely miscible in all proportions with mono-, di-, and trilaurin due to the hydrocarbon nature of the long fatty-acid chain. Methanol and aqueous ethanol however formed systems of limited solubility at 60°C. (12).

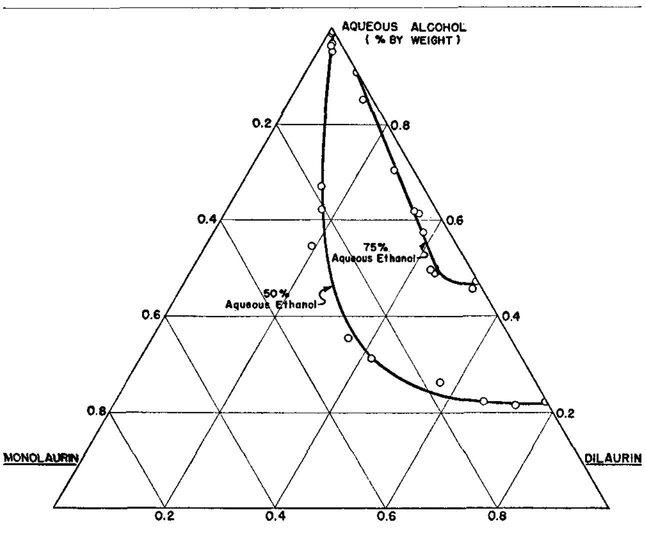
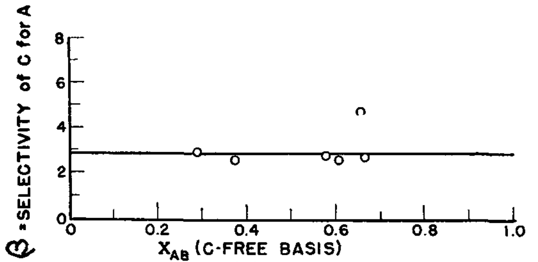
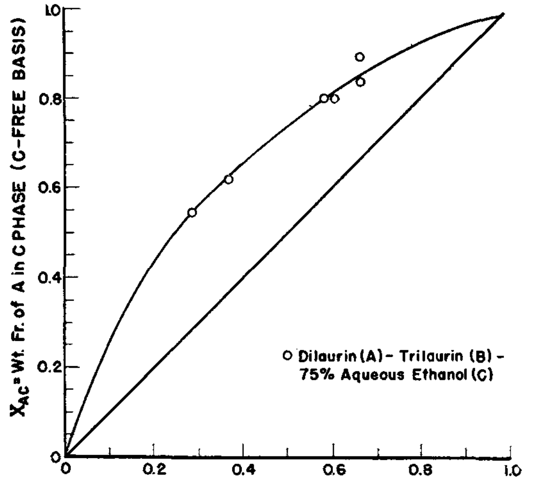


FIG. 2. Ternary-equilibrium data for monolaurin-dilaurin-aqueous ethanol systems; weight fraction at 60°C.

Ternary-Equilibrium Data. Ternary-equilibrium data at 60°C. were obtained for mono- and dilaurin, and di- and trilaurin with aqueous alcohol as a solvent. In Figure 1 data are presented for the system dilaurin (A)-trilaurin (B)-aqueous alcohol (C), where the solvent polarity was varied by using 50 and 75 wt.-% ethanol, and 100% methanol. Decreasing the polarity of the solvent (by reducing the water content) caused a shrinking of the boundary curve. Type 2 systems for aqueous ethanol became Type 1 for methanol. Figure 2 shows data for the system monolaurin (A)-dilaurin (B)-aqueous ethanol (C), where Type 1 diagrams were obtained with 50 and 75 wt.-% aqueous ethanol. In Figures 3 and 4 are shown equilibrium distribution data in the form of curves similar to isobaric vapor-liquid-equilibria, and selectivity data (β) are plotted against the same abscissa. Selectivity values of 2.8 for dilaurin from trilaurin were obtained with 50 and 75 wt.-% aqueous ethanol. In Figure 4 it is seen that the use of 50% aqueous ethanol resulted in selectivities which varied from 4 to 1 (at the plait point) for monolaurin.



(b) SELECTIVITY

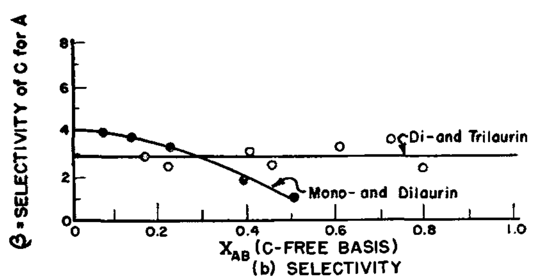


(a) DISTRIBUTION

Fig. 3. Distribution and selectivity diagrams for dilaurin-trilaurin-75% aqueous ethanol; weight fraction at 60°C.

Quaternary-Equilibrium Data. Equilibrium studies were made with three commercial monoglycerides and three synthetic mono-, di-, and trilaurin mixtures, using 50 wt.-% aqueous ethanol. Figure 5 presents data that show the more favorable monoglyceride distribution and solvent selectivity when di- and triglyceride were combined as one component.

Agreement between commercial monoglycerides and synthetic mixtures of mono-, di-, and trilaurin for selectivity data was good. A tendency towards a plait point was noticed for the synthetic mixture.



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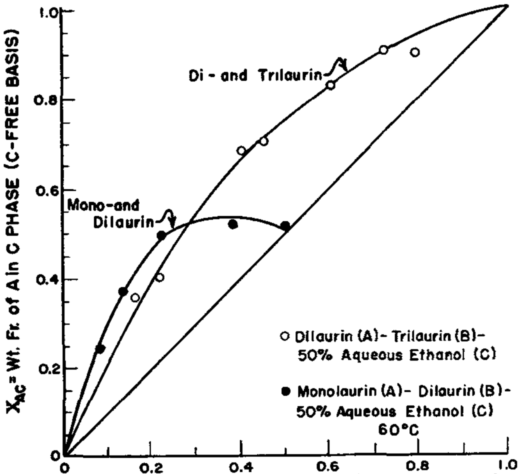


(a) DISTRIBUTION

Fig. 4. Distribution and selectivity diagrams for dilaurin-trilaurin-50% aqueous ethanol, and monolaurin-dilaurin-50% aqueous ethanol; weight fraction at 60°C.

Prediction of Data. It was noted that all components of the quaternary system monolaurin (A)–dilaurin (B)–trilaurin (C)–solvent (D) were studied as two ternary systems with a common solvent. Other investigators in the field of solvent extraction have tried to obtain quaternary data from ternary systems. When β_{AB} represents selectivity of solvent (D) for monolaurin in the system monolaurin (A)–dilaurin (B)–solvent (D), and β_{BC} is used for the system dilaurin (B)–trilaurin (C)–solvent (D), the equation of Lawrence (10) would be shown as

$$\beta_{AC} = \beta_{AB}\,\beta_{BC} \qquad \text{II}$$

Equation III is now proposed for selectivity in quaternary systems as follows:

$$\beta_{ABC} = \beta_{AB}\,[1 + X_C/(X_B + X_C)\ (\beta_{BC} - 1)] \qquad \text{III}$$

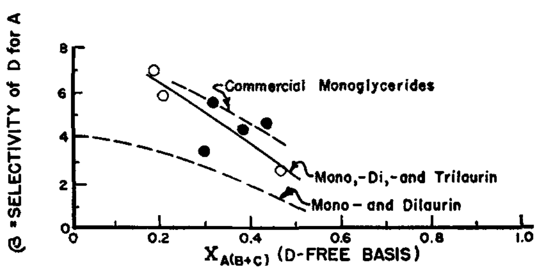
where $X_C/(X_B + X_C)$ represents weight fraction of trilaurin based on the di- and trilaurin content. When dilaurin is zero, Equation III simplifies to Equation II.

Application of Equation III is shown in the following example:

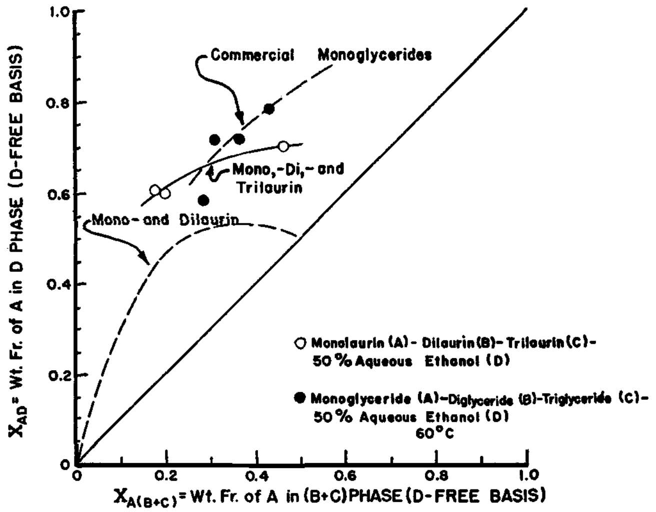
When the weight fraction of monolaurin (A) in the di- and trilaurin (B + C) layer is 0.466 in Figure 5, selectivity (β_{ABC}) of 50 wt.-% aqueous ethanol (D) for monolaurin (A) is 2.7.

When data were used from ternary-selectivity plots, Figure 4, β_{AB} equalled 1.5 for a monolaurin weight fraction of 0.466 in the dilaurin or (B) layer. Trilaurin weight fraction in the feed (di- and trilaurin basis) was as follows:

$$0.165/(0.230 + 0.164) \text{ or } 0.416$$



(b) SELECTIVITY



(a) DISTRIBUTION

FIG. 5. Distribution and selectivity diagram for quaternary systems; weight fraction at 60°C.

Substitution in Equation III results in

$$\beta_{ABC} = 1.5\ [1 + (0.416)\ (2.8\text{–}1)] = 2.6$$

Experimental values for β were 2.7, 5.9, and 7.0 while corresponding calculated results were 2.6, 4.9, and 6.7. Therefore ternary data for two adjacent systems with a common solvent were used to predict quaternary data with a reasonable degree of accuracy.

The selectivity of aqueous ethanol as a solvent for monoglyceride as shown on Figure 5 was seen to correlate to some extent with a commercial partial glyceride, and a mono-, di-, and trilaurin mixture. Since the commercial products contained unsaturated compounds and fatty acid chain lengths varied from 8 to 18 carbons, it was concluded that structural differences among mono-, di-, and triglycerides are the controlling factors in liquid-liquid extraction with polar solvents.

Extraction of Monoglycerides. Continuous countercurrent extraction was studied in a 1-in. Pyrex glass pipe, 24 in. long. Stainless steel disks and rotors were set up to make four agitated sections, which were alternated with glass-wool packed calming chambers. Vessels, flow lines, and the extractor were wrapped with resistance wire to maintain a temperature of 60°C. in the column during operation.

Flow rates were controlled by regulation of stop cocks and the use of calibrated feed vessels. Interface between raffinate and extract phase was maintained just above the solvent intake, and glass-wool packing in this section gave calming. Outflow streams were collected in tared flasked and weighed.

The glyceride feed stream was a commercial glyceryl monostearate of 42.4% monoglyceride content, and free of glycerine, soap, and fatty acids. A 40% solution of ethanol in water (instead of 50%) was used as the solvent to improve density difference and give faster phase separation. Agitation was very mild because slight increases in speed beyond 45 r.p.m. gave emulsions which interfered with extraction. Separation of fat particles in all calming sections was very slow.

Feed composition of 42.4% monoglyceride resulted in an extract monoglyceride content of 58.1%, and a raffinate composition of 39.3%. Comparison with data in Figure 5 indicated that the column was equivalent to 0.6 of the theoretical stage. (These data are based on the assumption that distribution will be substantially the same as for 50% aqueous ethanol.) The column had four stages, and an over-all stage efficiency of 15%.

Chilling of the extract to 0°C. allowed a 96.6% recovery of fatty material from the extract phase.

A batch-extraction process flow for monoglyceride is presented in Figure 7. Free glycerine can be substantially extracted by a 20% sodium sulfate solution (18). Gentle contacting with aqueous ethanol forms an extract which can be chilled in a scraped-wall cooler, and a raffinate which is further extracted. The extract precipitate is removed by filtration, melted, and then stripped of solvent. Solvent from filtration and stripping steps is recycled to the solvent feed tank. Final filtrate is stripped and returned to the monoglyceride reactor.

A continuous countercurrent extraction process for monoglycerides is presented in Figure 8. An initial pass with 20% sodium sulfate solution removes glycerine while a second pass with aqueous ethanol ex-

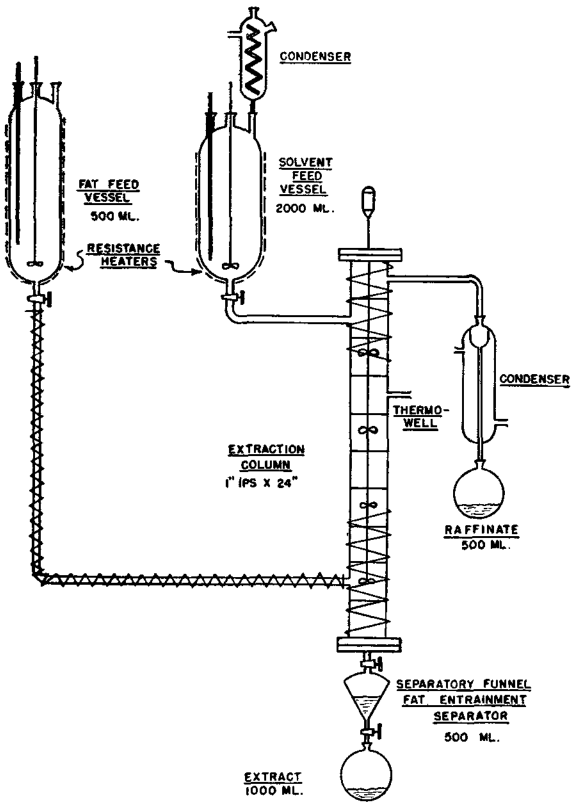


FIG. 6. Laboratory apparatus used for continuous extraction of monoglycerides.

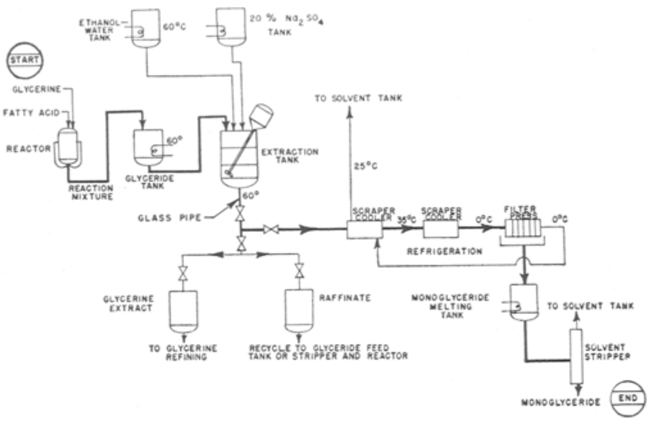


Fig. 7. Batch extraction process for monoglycerides.

tracts monoglyceride. This extract is then treated in the same manner as for the batch process. Solvent and raffinate are recycled, and final raffinate goes back into the monoglyceride reactor.

Both flowsheets indicate heat economy which can be obtained by recycling cooled and filtered extract countercurrently in the hot-extract heat exchanger.

Summary

Ternary-equilibrium data were obtained at 60°C. for mono- and dilaurin, and di- and trilaurin with aqueous alcohols. Distribution between phases and solvent selectivity are shown graphically. Variation of solvent polarity by water addition caused a shift in the phase boundary curve so that either Type 1 or Type 2 diagrams could be obtained.

Pure mono-, di-, and trilaurin mixtures, and commercial monoglycerides were studied as quaternary systems for monoglyceride distribution with 50 wt.-% aqueous ethanol. Pure and commercial systems showed similar distribution tendencies even with differences in molecular weight and degree of unsaturation.

Solvent selectivity data (β) for quaternary systems were predicted from ternary systems studied with a common solvent.

Aqueous ethanol will separate mixtures of mono-, di-, and triglycerides by selective liquid-liquid extraction; however the literature favors more complex systems based on two immiscible solvents.

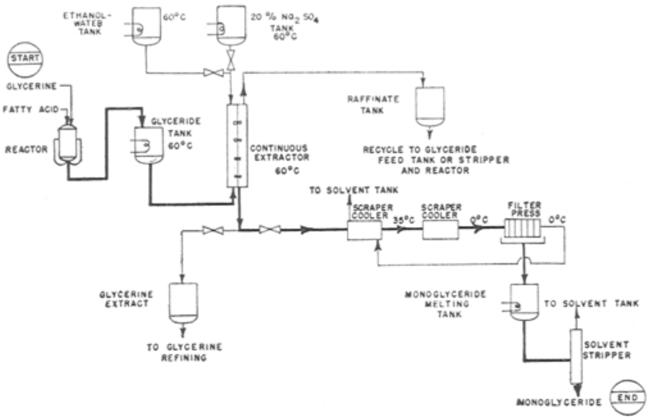


Fig. 8. Continuous countercurrent extraction for monoglycerides.

Continuous countercurrent extraction of commercial monoglycerides by 40% aqueous ethanol solution in a four-stage agitated column gave a 15% over-all stage efficiency. Cooling the extract to 0°C. precipitated 96.6% of the extract solids.

Flow diagrams were prepared for batch and continuous extraction processes.

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Molecular Distillation of Some Indian Vegetable Oils

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Several reports indicate that fractionation of the triglyceride constituents of fatty oils by molecular distillation is poor compared to what is achieved by chromatography or low temperature crystallization. The advantage however of molecular distillation consists in the ease of separation of the unsaponifiable portion and free fatty acids from the bulk of the fatty material. These are found to be concentrated in the first few fractions. Oils molecularly distilled by previous investigators include those from fish (9), linseed (4), corn and soybean (13), cottonseed (14), menhaden (4), castor (4), sesame (6, 21), crude soybean (3), peanut (1), carrot (8), palm and fish liver (19), shark liver (10, 11), whale liver (15, 18), and rice (17, 22).

Rawlings (13), who carried out molecular distillation of soybean and corn oils, reported that the first two fractions were acidic, highly colored, and odoriferous while the major portion was pale and odorless. Riemenschneider *et al.* (14) also found that in the case of cottonseed oil most of the unsaponifiable matter was concentrated in the first fraction.

Patel and Sreenivasan (11) reported a thirty-fold concentration of vitamin A from Indian shark liver