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✿ The Effects of Surfactant Concentration and Crystal Size on the Olein Yield from the Detergent Fractionation of Tallow

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The surfactant concentration, the electrolyte concentration, the detergent solution to tallow weight ratio and the crystal surface area affect the olein yield from the detergent fractionation of tallow. Three crystal sizes were produced by using various rates of cooling for the partial crystallization step. The amount of sodium dodecyl sulfate (SDS) needed to maximize olein yield was proportional to the surface area of the crystals. The olein yield of the separation increased with increasing detergent solution to tallow weight ratio and increased with increasing electrolyte concentration up to their optimum levels.

Several authors have studied the detergent fractionation of tallow (1-6). The process consists of a partial crystallization step followed by the addition of a detergent solution to form an aqueous dispersion. The dispersion is centrifuged to yield an olein fraction and a fraction with solid fat entrained in the water phase. The olein fraction recoverable from a specific tallow sample depends primarily on the crystallization temperature. The actual olein yield from the dispersion process depends on the crystal size and the amount of surfactant used (7).

For a given partially crystallized tallow, the olein yield from the centrifugation will increase as the surfactant concentration is increased from zero. The maximum in olein yield with surfactant concentration marks the point at which emulsion formation occurs. The emulsion phase has a density between those of the water and olein phases, and reduces the olein yield. At greater surfactant concentrations, olein yield is sporadic and may be only half of its maximum value. Surfactant preferentially wets the crystal surfaces until most of the solids have been enclosed by a water droplet. At this point, extra surfactant appears to be available for forming an oil-in-water emulsion. The emulsion phase entrains olein and makes the centrifugation more difficult, thereby lowering the olein yield.

The wetting of the fat crystals by the surfactant solution can be considered similar to the wetting of

fibers by detergent solutions (7). The rolling up of oil from the crystal is caused by the detergent solution preferentially wetting the solid surface. The surfactant concentration must be above the critical micelle concentration (CMC) for the detergency phenomenon to occur. Showing that surfactant levels for good dispersing solutions were above the CMC would constitute a partial confirmation of the proposed detergent mechanism. A number of solution properties change when the surfactant concentration changes through the critical micelle point (8). The surface tension of a surfactant solution exhibits a distinct dip or discontinuity near the CMC as surfactant concentration is changed and can be used to determine the CMC. Surfactant in excess of the CMC value would be available for adsorption on the crystal surface. Presumably, the amount of excess surfactant needed to completely wet all crystals should be a function of their total surface area. Surfactant molecules which do not contact and wet solids into the aqueous phase, and are not part of the micelle structures, would be available for forming an emulsion.

The two primary objectives of this study were: to obtain more evidence confirming the detergency mechanism and to develop qualitative relationships between crystal size (surface area), surfactant concentration and olein yield. This information should lead to an improved understanding of emulsion formation and might help determine operating conditions for an industrial process.

Different crystal sizes of partially crystallized tallow were produced using different time-temperature histories. The recovery of olein from products of these different procedures was studied while varying the surfactant concentration and the ratios of detergent solution to tallow weight. Separations also were made using various concentrations of electrolyte. The separation mechanism concept was reviewed using the new data.

EXPERIMENTAL METHODS

Sample preparation. Tallow was obtained in a 55-gallon

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drum, from a commercial supplier. Samples for quantitative comparisons were prepared by melting a large quantity of tallow and separating it into 200-ml aliquots. Beakers were used as crystallization and separation vessels for the process. The sample weight was 170 g of fat. All tallow samples were prepared by raising the tallow temperature to 60 C to completely melt any crystal nuclei. Tallow at this temperature was optically clear with no evidence of solid fat. This preheating temperature was used prior to all crystallizations as a reproducible method for removing crystal nuclei.

Crystallization procedures. Three crystallization procedures were used to produce partially crystallized tallows, with a final crystallization temperature of 40 C in all cases. The procedures differed in the initial cooling period for crystal nuclei initiation and in the final solids content. The number of crystal nuclei produced determined the number and size of the final crystals. The rate of cooling and temperature of the fat determine the initial triglyceride crystal type (α or β').

No agitation was used during the nucleation or crystallization steps. Heat removal from the sample was adequate because of the small sample size. Shear seems to affect the nucleation rate (7). It might be preferable to crystallize the tallow samples using a low-shear device, such as a scraped wall heat exchanger. No such device was available in this laboratory.

In procedure #1, the tallow was cooled at an ambient temperature of 0 C for two hr. The sample nucleated rapidly and crystallized totally. The completely crystallized tallow was heated to 40 C and remained at that temperature for 16 hr to allow equilibrium to occur between the liquid and solid phases. Figure 1 shows the temperature profile for procedures #1, 2 and 3.

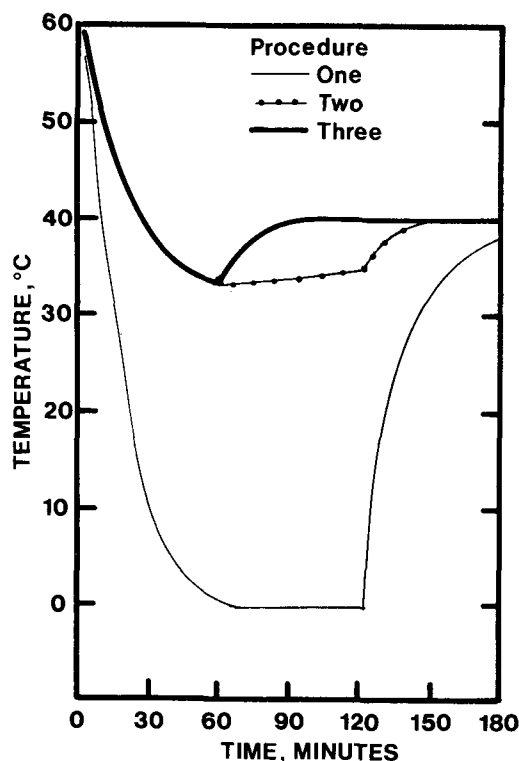


FIG. 1. Temperature programs for three crystallization procedures as a function of time.

In procedure #2, the oil was cooled at an ambient temperature of 29 C for two hr. The oil temperature dropped to 33 C before the first crystal nuclei could be observed (the solution became cloudy after one hr). Nucleation was continued for another hour at the same ambient temperature. The heat of solidification caused the tallow temperature to rise slowly as fat began to crystallize (Fig. 1). At the end of the two-hr nucleation period, the tallow temperature was 35 C. The tallow sample was placed into a 40 C temperature bath for the remaining 16 hr of crystallization.

Procedure #3 consisted of cooling the 60 C tallow at an ambient temperature of 29 C until crystal nuclei could be seen. The sample was placed into the 40 C temperature bath for the remainder of the 16-hr crystallization.

Dispersion procedure. A detergent solution to tallow weight ratio of 0.80 was used for all separations except those in which the ratio was changed intentionally. The detergent solution to tallow weight ratio was specified for each experiment. The electrolyte (sodium citrate) concentration in the detergent solution was 5.0% for all separations unless otherwise specified. The surfactant weight fraction reported was based on the aqueous phase composition. Distilled water, the electrolyte and the surfactant were mixed together thoroughly and heated to 40 C prior to mixing with the oil.

The detergent solution was added to the partially crystallized tallow by mixing with a stirring rod. Mixing was carried out until a uniform dispersion was obtained. Tests indicated that more intense mixing did not increase olein yield. The dispersion was allowed to sit for one hr before it was centrifuged at a force of 3,600 times that of gravity.

The olein was poured out of the centrifuge tubes after the centrifugation. Little of the olein adhered to the polycarbonate tubes. The yield of olein was calculated as the weight ratio of the olein collected to the original tallow.

Surface tension procedure. A Cenco Tensionometer Model No. 70530 was used to obtain the surface tension measurements. The detergent solution was mixed to the desired concentration and measurements taken at 40 C. Both a platinum ring and a Teflon-coated platinum ring were used to obtain the surface tension values. The Teflon-coated ring was used to insure a zero contact angle with the material being tested (10). The surface tension values were corrected as recommended by Zuidema and Waters (11,12).

RESULTS AND DISCUSSION

Crystallization results. The temperature-time histories used for procedures #2 and #3 are much more similar to those used commercially than the temperature-time history of procedure one. The crystals produced by procedures #2 and #3 were similar to those reported for industrial processes (3,4).

The crystals produced in the crystallization step have been determined to be important to the success of a fractionation (7). To characterize the size of crystals produced by each crystallization procedure, photomicrographs were made of the crystals from each crystallization procedure. Figures 2 and 3 show representative crystals from the second and third

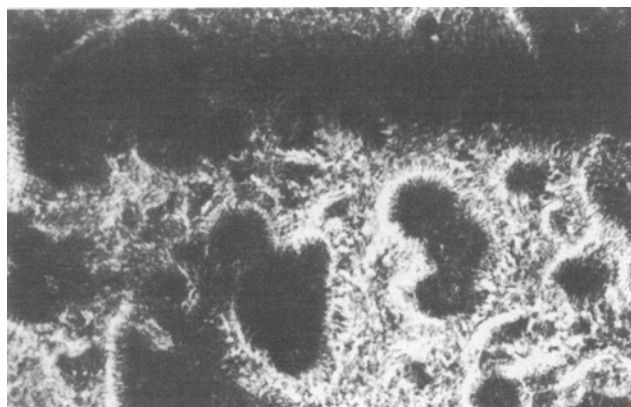


FIG. 2. Photomicrograph of crystallization procedure #2 crystals (100 \times magnification).

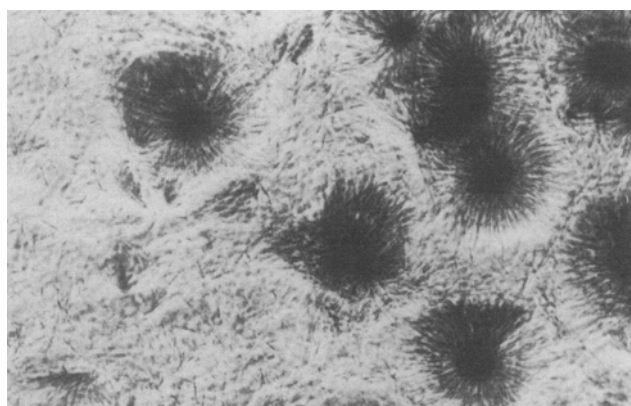


FIG. 3. Photomicrograph of crystallization procedure #3 crystals (100 \times magnification).

crystallization procedures. Satisfactory photographs were not obtained for products from crystallization procedure #1 because of the extremely small crystal size. They were not easily seen even at 2,000 times magnification. Initially, these crystals probably were unstable α type crystals. The α crystals rearrange into the next most stable form, β' , when tempered at the proper temperature (13). This information affects the crystal size very little. Because so many nuclei are produced by the rapid cooling, the crystals are extremely small.

The crystals from procedures #2 and #3 were much easier to observe. Based on the photomicrographs, the types of triglyceride being crystallized and the procedures used, procedures #2 and #3 produced β' crystals. The crystals from procedure #2 existed both as single crystals and spherulitic agglomerates of individual crystals. The crystals from procedure #3 existed primarily as spherulitic agglomerates. The average size of the crystal agglomerates from procedure #2 was 40 microns in diameter. The single crystals making up the agglomerates were assumed to be cylindrical in shape, 30 microns in length and 0.3 microns in diameter. β' crystals are usually orthorhombic and, therefore, are regular extended length polyhedrons. The features of the minor axes of the crystal could not be discerned

TABLE 1

Crystal Sizes Produced by Procedures #2 and #3

Item	Procedure #2	Procedure #3
Crystal shape	Cylindrical	Cylindrical
Average crystal diameter	$0.3 \times 10^{-6}\text{m}$	$0.6 \times 10^{-6}\text{m}$
Average crystal length	$30 \times 10^{-6}\text{m}$	$50 \times 10^{-6}\text{m}$
Average diameter of spherulites	$50 \times 10^{-6}\text{m}$	$80 \times 10^{-6}\text{m}$
Average crystal volume	$2.1 \times 10^{-18}\text{m}^3$	$14 \times 10^{-18}\text{m}^3$
Average crystal surface area	$28 \times 10^{-12}\text{m}^2$	$95 \times 10^{-12}\text{m}^2$
Average surface area/volume	$13 \times 10^6\text{m}^{-1}$	$6.8 \times 10^6\text{m}^{-1}$

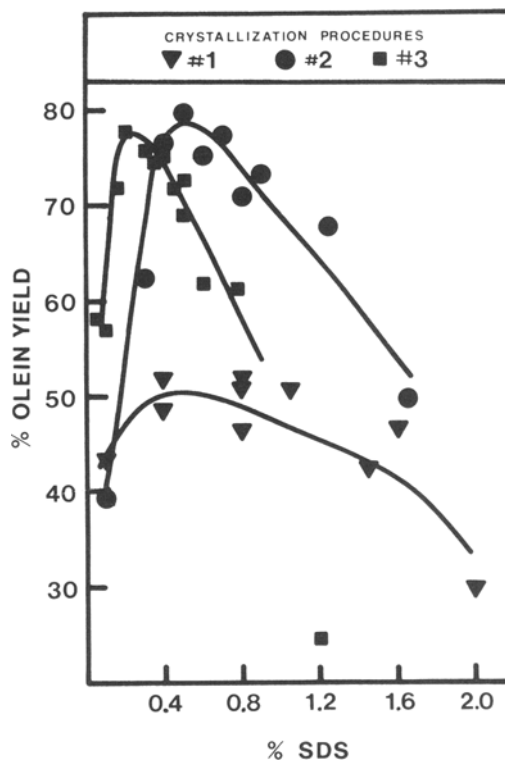


FIG. 4. Percentage olein yield versus percentage sodium dodecyl sulfate in the detergent solution for three different crystallization procedures. Dispersion performed at 40 C.

under the microscope. The assumption of a cylindrical crystal simplified surface area and volume calculations. The single crystals were estimated to make up about 20% of the crystal mass in the procedure #2 crystallization. The average size of the procedure #3 spherulites was 60 to 80 microns in diameter. The individual crystals making up the spherulitic crystals appeared to be cylindrical and had an average length of 50 microns and an average diameter of about 0.6 microns. The single crystal sizes were determined from higher magnification photographs. Table 1 summarizes the dimensions of the crystals from procedures #2 and #3.

Separation results. Figure 4 shows the olein yield vs. wt% SDS for all three crystallization procedures. Table 2 shows the olein fatty acid compositions for olein from each crystallization procedure. The crystallization time-temperature history had a large effect on the separation

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TABLE 2
Fatty Acid Composition of Olein from each Crystallization Procedure

Common Name	Crystallization Procedure		
	One	Two	Three
Myristic acid	3.3%	3.1%	3.1%
Palmitic acid	24.5	24.3	24.4
Palmitoleic acid	4.6	4.7	4.7
Stearic acid	17.8	17.8	17.9
Oleic acid	45.3	45.8	45.6
Linoleic acid	2.1	2.6	2.7
Others	1.4	1.7	1.6

results. Crystallization procedure #1 had a maximum olein yield of 51 wt%. This maximum occurred in a broad SDS concentration range of 0.4 to 1.1 wt%. The reason for the broad range of surfactant concentrations giving the same olein yields was related to the crystallization procedure and to the type of crystals present. The yield of olein with practically no surfactant was very close to the best yield of olein obtained. However, these olein yields are too low for the procedure to be useful industrially. The low yield can be attributed to the fine structure of the crystals. The packed fine crystals probably trapped components which were liquids at 40 C. Therefore, the olein yield was reduced.

The olein yield reached a maximum of 79 wt% for crystallization procedure #2. This maximum occurred at an SDS concentration of 0.50 wt%. At concentrations above 0.50 wt% SDS, olein yield was reduced by emulsion formation. At SDS concentrations below 0.30 wt%, the olein yield was lowered due to ineffective wetting of the crystals into the aqueous phase.

The olein yield peaked at 78 wt% for the crystallization procedure #3 separations. The maximum yield occurred at an SDS concentration of 0.20 wt%. At concentrations of surfactant above 0.20 wt%, olein yield was reduced by emulsion formation. At SDS concentrations below 0.15 wt% the olein yield was lowered because of inefficient wetting of the crystals.

The maximum yields from crystallization procedures #2 and #3 were essentially the same. The difference in the SDS concentrations between procedures #2 and #3 at the maximum olein yield was not due to a difference in the amount of olein present. The crystal mass was almost identical for the two cases based on the maximum yield of olein. The stearin fractions in both cases had no yellow color, which indicates they were free of olein. At an olein yield of 75 wt%, the yellow color could be seen easily in the stearin fraction of both procedures. The calculated total surface areas for the crystals from procedures #2 and #3 show that procedure #2 produced crystals with 1.9 times as much surface area per crystal volume as procedure #3 (Table 1). The optimum SDS levels for procedures #2 and #3 differed by a factor of 2.5, based on the weight of surfactant required. The ratio of calculated surface areas (1.9) for

procedures #2 and #3 differed by about the same factor as the difference in the required weight of SDS (2.5). Crystal surface area may be the parameter determining the amount of surfactant required for a successful fractionation.

The detergency mechanism suggests that the surfactant should be adsorbed on the crystal surfaces. Experiments were performed to determine where the SDS was distributed after the dispersion step. The method of Moore and Kolbesen (14) was tried. The analysis was not successful on the partly refined and commercially available tallow, because it contained either a minor component or an emulsifier that solubilizes methylene blue into chloroform (15). However, experiments were conducted to determine how much SDS in solution was required to emulsify pure olein. It was found that a concentration of 0.05 wt.% SDS, with an electrolyte concentration of 5.0%, would emulsify completely all the olein present. The aqueous and olein mixture was centrifuged to see whether normal processing broke the emulsion; it was found that it did not. In order to prevent emulsion formation, very little surfactant should be left in the aqueous solution after the dispersion step. Almost all the SDS should be at the crystal surface or in micelles. In cases where too much surfactant was used, the surfactant completely coated the crystal surface, and the excess surfactant caused emulsified olein. It is possible that the low amount of mixing during the dispersion step in this study reduced the amount of emulsification occurring at SDS concentrations greater than those needed to coat all the crystals.

The role of the electrolyte, sodium citrate, in the separation step was investigated by using various electrolyte concentrations for the separation step while holding other variables constant. The results are shown in Figure 5. The olein yield increased as a function of the electrolyte concentration until an electrolyte concentration of 5.0% was reached. The olein yield neither increased nor decreased above the 5.0% electrolyte concentration, but at concentrations above 8.0% increased amounts of emulsified olein were noted.

Increasing the electrolyte, sodium citrate concentration, increased the ionic strength of the detergent solution. This allowed the surfactant sodium dodecyl sulfate, to be aligned around the surface of the crystals. The surfactant has a hydrocarbon end and a charged sulfate end. Calculations show (See Table 3) that the surfactant molecules had the necessary spatial dimensions to have been in contact with the crystal surface. The SDS molecules could be aligned either perpendicularly or at some angle less than 90° to the crystal surface. The hydrocarbon end was in contact with the crystal while the charged, sulfate end was hydrated by the ionic solution. The charged layer surrounding the crystals allowed them to wet into the aqueous phase. If the electrolyte or surfactant concentration was too low, the crystals were not wetted into the aqueous phase completely. If the surfactant concentration was too low, there were insufficient surfactant molecules to coat the crystals. If the electrolyte concentration was too low, the surfactant molecules could not be aligned properly.

Figure 6 shows the results of experiments conducted using various ratios of detergent solution to tallow

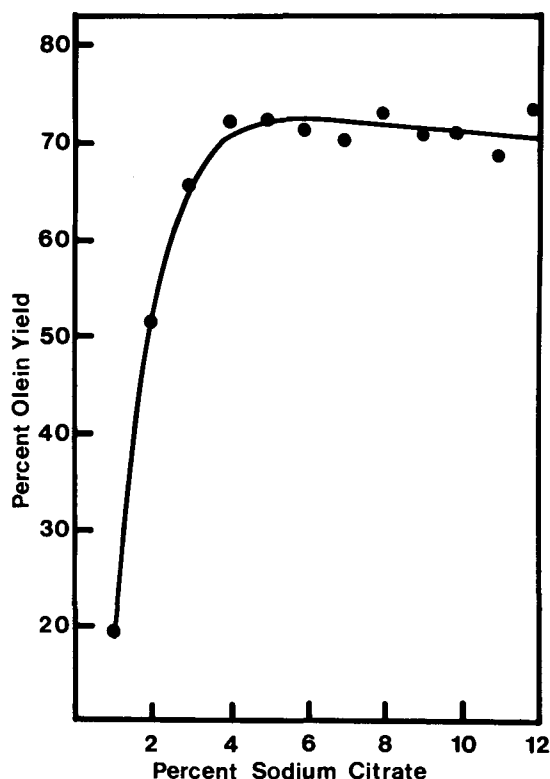


FIG. 5. Olein yield as a function of the electrolyte concentration in the aqueous solution at 40 C. The tallow weight was 170 g/sample. The sodium dodecyl sulfate weight was 0.45 g. The detergent solution to tallow weight ratio was 0.93.

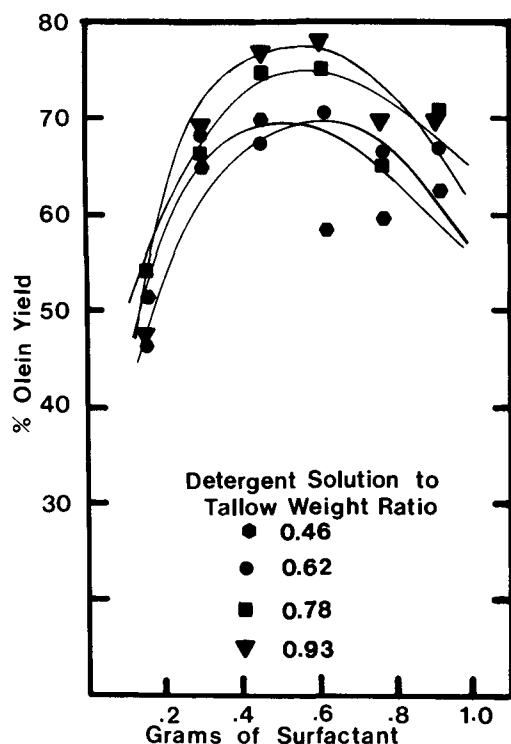


FIG. 6. Percent olein yield as a function of the surfactant, sodium dodecyl sulfate, weight. The tallow weight was 170 g/sample. The detergent solution to tallow weight ratios were 0.46, 0.62, 0.78 and 0.93. Five percent sodium citrate was present in each detergent solution.

TABLE 3

Calculation of Crystal Surface Area per Surfactant Molecule

	Procedure #2	Procedure #3
Crystal surface area	$28 \times 10^{-12} \text{m}^2$	$95 \times 10^{-12} \text{m}^2$
Crystal weight	$1.89 \times 10^{-12} \text{g}$	$1.26 \times 10^{-11} \text{g}$
Number of crystals/200 ml aliquot	1.8×10^{13}	2.7×10^{12}
Total surface area	500 m^2	260 m^2
Optimum gmoles SDS/200 ml aliquot	1.73×10^{-3}	6.93×10^{-4}
gmoles SDS/ m^2 area	3.5×10^{-6}	2.7×10^{-6}
Crystal surface area per molecule SDS	47	61
Perpendicular area of SDS molecule		3.1 A^2
Parallel area of SDS molecule		54 A^2

weight and various surfactant weights. Detergent solution to tallow weight ratios of 0.46, 0.62, 0.78 and 0.93 were used to fractionate tallow samples weighing about 170 g each. The results are plotted using the weight of surfactant as the x-axis value. If the surface area was important in determining the amount of surfactant required, all ratios of detergent solution to tallow used should give a maximum olein yield at almost the same weight of surfactant. The results of these experiments coincided closely with those expected. The maximum olein yield was at 0.6 g SDS for the 0.62, 0.78 and 0.93 aqueous to tallow ratios. The maximum yield for the 0.46 ratio was at 0.45 g SDS. The olein yield for the 0.62, 0.78 and 0.93 ratios at a surfactant weight of 0.45 g was very close to the olein yield for those ratios at 0.60 g surfactant. These results supported the conclusion that the surface area of the crystals determined the required amount of surfactant.

Detergency theory requires the surfactant concentration to be above the CMC (9). Surface tension was measured to determine the critical micelle concentration for SDS solutions with and without electrolyte added. Figure 7 shows the surface tension measurements for two electrolyte concentrations as functions of SDS concentration. One case was with the 5.0 wt% sodium citrate in solution and one case was with no electrolyte in solution. The CMC for the solution containing surfactant only occurred at approximately 0.1 wt% at the test temperature of 40 C. The CMC for the surfactant and electrolyte solution was at 0.01 wt%. This shows that the concentration of surfactant required for detergency action was very low. This means that most of the surfactant can be at the crystal surface as the surface area theory requires.

Another interesting feature of the results shown in Figure 6 was that the amount of detergent solution used had a great effect on the olein yield achieved. The olein yield was still rising at the maximum ratio of detergent solution to tallow weight used. The maximum olein yields were 78.0%, 75.3%, 70.6% and 70.1% at aqueous to tallow ratios of 0.93, 0.78, 0.63 and 0.46, respectively. This effect might be related to the dispersion viscosity.

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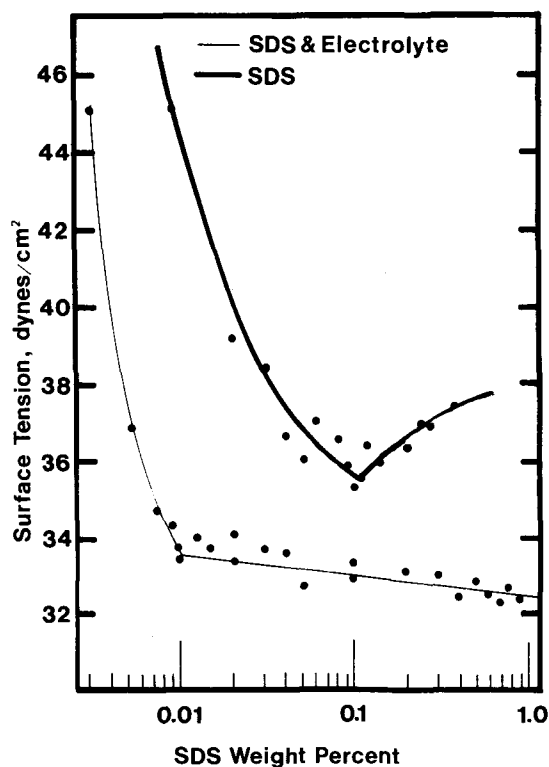


FIG. 7. Surface tension of aqueous solutions as a function of the surfactant concentration at 40 C. One curve represents a solution that contains only surfactant, and the second curve represents a solution containing 5.0% sodium citrate in addition to the SDS.

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