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THE SEPARATION MECHANISM FOR THE DETERGENT FRACTIONATION OF BEEF TALLOW AND ITS RELATION TO PROCESS VARIABLES

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THE SEPARATION MECHANISM FOR THE DETERGENT FRACTIONATION OF BEEF TALLOW AND ITS RELATION TO PROCESS VARIABLES

By

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ABSTRACT

THE SEPARATION MECHANISM AND ITS RELATION TO PROCESS VARIABLES FOR THE DETERGENT FRACTIONATION OF BEEF TALLOW

By

David Allen Glassner

Aqueous or detergent fractionation is done by partially crystallizing the fat and recovering the crystals by wetting them into an aqueous solution containing a surfactant and an electrolyte. The goal of the fractionation process is to obtain fat fractions having more value than the original fat. The aqueous fractionation of tallow is studied to determine the separation mechanism and the relationship of important processing variables to the mechanism.

Detergency phenomena was found to explain the wetting of crystals from the oil to the aqueous phase, hence the term detergent fractionation. Key process variables were crystallization conditions, surfactant (sodium dodecyl sulfate) concentration, electrolyte (sodium citrate) concentration, the weight ratio of detergent solution to partially crystallized tallow and the viscosity of the dispersion. These variables were studied for the separation of beef tallow at 40 °C.

It was found that crystal surface area was proportional to the weight of surfactant required. The quantity of surfactant, not the concentration of surfactant was important. Most of the surfactant associated with the crystal surface. Too much surfactant caused emulsified olein product and too little surfactant resulted in an incomplete separation.

The electrolyte helped create an ionic solution which oriented the surfactant and allowed the crystals to be wetted into the aqueous phase. Low electrolyte concentrations resulted in incomplete separations. The optimum concentration was found over a wide range with a tendency for the formation of more emulsified olein at higher concentrations of electrolyte.

For a given crystallization procedure an optimum weight ratio of detergent solution to tallow existed. Ratios higher than the optimum resulted in the same separation but required processing a larger volume of fluid. Ratios lower than the optimum caused incomplete separations.

The rheology of the detergent solution-partially crystallized tallow dispersions was investigated with a paddle mixer viscometer. Apparent viscosities of the dispersions were measured at a rotation rate of 60 rpm. An apparent viscosity of 0.08 Pa s or less was necessary for maximum olein recovery. The apparent viscosity of the aqueous solution-olein mixture without any crystals was about 0.015 Pa s.

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NOTATION

Å, Angstroms (Table 2.3).

B, constant depending on impeller system geometry (Eqn 2.3).

°C, degrees Celsius (Section 2.1).

D , constant for a particular shape solid (Eqn 4.3).

d, Impeller diameter, m (Eqn 2.1).

g^*, acceleration of gravity, cm/s^2 (Eqn 3.1).

k', constant for a particular impeller (Eqn 2.5).

K, consistency coefficient, Pa s^n (Section 2.8).

L, mean circumference of the ring, cm (Eqn 3.1).

M, torque, N m (Eqn 2.7).

n, flow behavior index (Section 2.8).

P_o, Power number (Eqn 2.1).

p, power, N m s (Eqn 2.1).

Re, Reynolds number (Eqn 2.2).

s, apparent surface tension, dynes/cm (Eqn 3.1).

S, volume fraction solids in fluid (Eqn 4.3).

W, weight placed on ring, g (Eqn 3.1).

ρ , fluid density, kg/m (Eqn 2.1).

γ_a , shear rate, s^{-1} (Eqn 2.5).

η_r , reduced viscosity of dispersion (Eqn 4.3).

τ , shear stress, Pa (Eqn 2.6).

μ , fluid viscosity, Pa s (Eqn 2.2).

ω , rotational speed of the impeller, rad/s (Eqn 2.1).

η_a , apparent viscosity, Pa s (Section 2.8).

INTRODUCTION

Fractionation of a fat by partial crystallization produces two fractions with different properties from the original fat. The fractions have different chemical compositions, and the melting point range of each fraction is much more narrow than the original fat. The fractions separated are the liquid and solid formed by a partial crystallization of the tallow at a specific temperature. The process is most useful on a fat which exhibits a wide melting point range, a characteristic of a fat with a wide range of saturated and unsaturated fatty acids. Palm oil and beef tallow are fats commonly fractionated. Groundnut oil, partially hydrogenated soybean oil, coconut oil, rapeseed oil, hog fat, whale oil, menhaden oil and cod liver oil are some other oils that have been fractionated (Rek, 1977; Stein and Hartmann, 1957).

Tallow production in the United States for 1983 totaled 6.04 billion pounds. Of the total produced 1.22 billion pounds was edible tallow. The edible tallow produced was used for baking or frying. Tallow accounted for 14 percent of the baking and frying fat market in the U.S. (USDA ERS, 1984). Fractionation of tallow at various temperatures can result in fractions which are more useful and valuable than the original tallow (Luddy et al., 1973; Taylor et al., 1976).

Many investigators attest to the suitability of tallow fractions for use in food preparation (DeFouw et al., 1981, Holsinger et al., 1978, Kozempel et al., 1981, Luddy et al., 1973, Taylor et al., 1976, Ryan, 1985). Suitable tallow fractions can be used in shortenings, as frying media and as confectionary fats. Tallow imparts a characteristic taste to fried potatoes and is highly desired for this use (Ryan, 1982).

The object of a fractionation process is to completely separate the liquid and solid components of a partially crystallized oil. A complete liquid-solid separation maximizes the chemical composition and physical property differences of the two fractions. In the case of tallow, the crystals are called the stearin and the oil is called the olein. These terms refer to the preferential distribution of stearic and oleic acids in the triglycerides of each fraction.

The problem in any separation of crystals and oil is that the viscosity of the medium is generally too great to allow a good separation between the oil and crystals. Filtration processes require large crystals to be formed so that the crystals can be recovered from the oil-crystal mixture. A long crystallization period, 3-4 days, is required to produce the large crystals. Because of the long crystallization periods and the incomplete separation, better methods of oil-crystal separation have been developed.

1.1 Fractionation Processes

Three fat fractionation processes have been commercialized: dry, solvent and detergent (Kreulen, 1976). The dry fractionation process involves partial crystallization of the oil followed by vacuum filtration of the partially crystallized oil. The filtration yields clear oil but results in significant olein entrainment in the stearin fraction. Solvent fractionation of fats using hexane and other solvents yields fractions containing residual solvent. Process equipment must be explosion proof. Solvent recovery can be a significant portion of total process costs. In detergent fractionation, the liquid-solid separation is accomplished by mixing a detergent solution with a partially crystallized oil, preferentially wetting the crystals into the aqueous phase. Detergent fractionation has the disadvantages of emulsified olein product formation, residual electrolyte and surfactant in the fractions obtained, and additional chemical costs. The residual surfactant easily can be removed from the olein and stearin fractions by hot water washings, since the equilibrium is greatly towards the water phase. Water washing also would remove any electrolyte present.

1.2 Detergent Fractionation

The detergent fractionation of a fat consists of a crystallization and a separation step. The crystallization step is a fractional

crystallization at a specific temperature, resulting in a partially crystallized oil. A detergent solution containing a surfactant and an electrolyte is then mixed with the partially crystallized oil. The detergent solution is at the same temperature as the partially crystallized oil. Centrifugation then yields a clear liquid olein and a stearin-detergent solution layer. The stearin and detergent solution are separated by heating and recentrifuging.

Many authors have discussed the requirements for the surfactant, electrolyte and quantity of detergent solution to be used (Stein, 1968; Kreulen, 1976; Rek, 1977; Glassner, 1983; Bussey et al., 1981). The chemical quantities and concentrations reported are not consistent. The separation step of the detergent fractionation of tallow is identified as being crucial to the design of the fractionation process (Glassner, 1983).

Crystal size and surfactant concentration both affect the formation of undesireable emulsion in the detergent fractionation of tallow (Glassner, 1983). Larger crystal size causes less emulsion formation at the same surfactant concentration. Smaller crystal sizes resulted in poor separations. Higher surfactant concentrations, given the same crystal size, were found to result in more stable emulsion. Low surfactant concentration resulted in efficient wetting of the crystals into the aqueous phase and poor separation results. This research attempts to define the conditions necessary for a successful separation step.

1.3 Research Plans

The process variables for the separation step include the surfactant concentration, electrolyte concentration, aqueous volume, crystal size of the partially crystallized tallow and dispersion mixing characteristics. Since the mechanism of the separation has not been reported, the relationships between these process variables has not been established. Some of the difficulty in choosing the optimum amount of surfactant and electrolyte could be reduced if the mechanism of the separation process was better understood. Such information may help to control the formation of emulsified olein product.

The mechanism of the separation step will be linked to detergency theory to explain experimentally observed relationships. Preston (1948) and Harris (1958) described the relationship of detergency to the critical micelle concentration. The phenomenon of detergency was shown to increase greatly upon the surfactant concentration reaching the critical micelle concentration.

At the critical micelle concentration, many solution properties undergo easily detectable changes. One of the properties, the surface tension, is quickly and easily measured (Adamson, 1982). The surface tension of a surfactant solution exhibits a distinct dip, or a discontinuity in a surface tension versus surfactant concentration plot at the critical micelle concentration. The

change in the surface tension allows the determination of the critical micelle concentration for a particular surfactant or detergent solution. The surface tension measurements along with emulsification tests will be used to determine the surfactant distribution between crystal surface and the aqueous solution.

The crystal size dependence of the process will be investigated. Various crystal sizes will be made by using different rates of cooling and different intermediate temperatures during the crystallization step. The recovery of olein from different crystals sizes will be studied as a function of surfactant and electrolyte concentration and detergent solution to tallow weight ratio. The separation mechanism will then be reviewed using the new data.

The effect of detergent solution to tallow weight ratio on the olein yield may be related to the rheological properties of the dispersion. Viscosity effects will be studied using a paddle mixer viscometer. The effect of various detergent solution volumes will be related to the rheology of the dispersion. The desired information is the rheology of the tallow-detergent solution dispersion as a function of the detergent solution to tallow weight ratio. The effect of the apparent viscosity on the olein yield is to be correlated directly.

The results of this research should help establish upper and lower bounds on processing conditions to allow process design and control

to be done. The relationship between the crystals formed in the crystallization step and the process variables include the effect of crystal size on the required detergent strength, the type of crystallization process required and the volume of detergent solution required for an optimum separation. Research of the separation mechanism is the first step in the process. The results obtained in this research may sometimes be qualitative because of limitations in measurement and scale-up of results from small, batch laboratory experiments to industrial size operations.

LITERATURE REVIEW

2.1 Chemistry of Tallow and other Triglycerides

Tallow is made up of a collection of triglycerides. A triglyceride is a glycerol molecule esterified to three fatty acids. The fatty acid composition of the triglycerides determines the properties of the fat or oil. The fatty acid composition of natural fats like tallow, varies depending on geographic location and feed characteristics. Table 2.1 shows some of the variations in tallow fatty acid composition that have been observed. The composition differences cause small differences in the melting point and iodine value of the fat. The crystallization properties at a specific temperature may vary greatly.

The melting point of fats is a function of the fatty acid composition and position on the glycerol molecule. The melting point of a triglyceride is directly controlled by the melting point of the fatty acids it contains. The fatty acids may be either saturated or unsaturated. The melting point of the unsaturated fatty acids can be 70 °C higher than the melting point of a saturated fatty acid. The chain length of the saturated or unsaturated fatty acid also affects its melting point. The longer the fatty acid chain the higher the melting point for the fatty acid.

Table 2.1

TALLOW FATTY ACID COMPOSITION

Data source		(1)	(2)	(3)
Fatty acid common name				Mole Fraction
Myristic acid	C14:0	.044	.036	.02-.08
Myristoleic acid	C14:1	.016	.014	.004-.006
Palmitic acid	C16:0	.267	.241	.24-.37
Palmitoleic acid	C16:1	.050	.066	.019-.027
Stearic acid	C18:0	.139	.137	.140-.290
Oleic acid	C18:1	.417	.501	.400-.500
Linoleic acid	C18:2	.023	----	.010-.050
Linolenic acid	C18:3	.003	.004	--------

1 Luddy et al., 1973

2 Bussey et al., 1981

3 Swern et al., 1979

Mixed triglycerides, containing a number of different fatty acids, minimize the effect of the differing melting points of the fatty acid components on the whole fat. Predicting the melting range of a group of triglycerides based on the fatty acid composition is not possible. A fat with a wide variety of fatty acids, for example tallow, has a melting range of 10 to 45 °C. A fat without a great variety of fatty acids, such as cocoa butter, has a narrow melting point range of 6-8 °C.

The mixed nature of the triglycerides combined with the random distribution of the fatty acids means that a fat like tallow with eight main fatty acids has over a hundred different triglycerides. This makes the melting and crystallization of fats complicated. Replication of crystallization processes is difficult as exact duplications of time-temperature conditions are necessary.

2.2 Fractionation Processes

There are three methods of fractionation which have industrial importance (Braae, 1976). The methods are based on cooling the fat to a temperature where the high-melting components crystallize while the low-melting ones remain in liquid form.

The oldest method consists of a slow cooling of the fat in small shallow tanks to an appropriate temperature at which the fat is kept for 3-4 days during crystals formation (Braae, 1976). For instance, tallow might be crystallized at 25-30 °C. It is

important that the crystallization is extremely slow so that large crystals are formed. Large crystal agglomerates, larger than 100 micron diameter, are recoverable by filtration.

After the crystallization is complete, the viscous grainy mass is put into canvas press cloths, which are stacked in presses of the plate type and the liquid oil is pressed out of the crystals (Braae, 1976). This is a labor intensive process and has been largely replaced by more efficient methods. The more efficient methods use larger crystallization tanks and the separation is accomplished by vacuum band filters. Careful crystallization is still necessary to produce crystals which can be filtered.

The filtration can be made more easily if the fat is mixed with a suitable solvent before it is crystallized (Braae, 1976). The solvent should not prevent crystallization from occuring. Suitable solvents include hexane, isopropyl alcohol and acetone. The solvent will lower the liquid phase viscosity making the physical separation of oil from crystals easy to accomplish. The crystallization in solvent tends to be selective compared to other crystallizations. This means the two fractions obtained have the greatest possible chemical composition difference. The fractionation plants are quite complicated and costly to run because of the solvent processing requirements.

A third fractionation method is based on a method for separating fat crystals and oil first described by Fratelli Lanza in 1905.

The partially crystallized fat is mixed with an aqueous solution containing a surfactant. The surface active component of the aqueous solution allows the crystals to be freed from the oil and wetted into the aqueous solution. The oil can then be easily recovered from the aqueous-crystal mixture by centrifugation.

2.3 Aqueous Fractionation

Aqueous fractionation has been discussed by many authors. Because certain aspects of the process mechanism have not been defined the results of the various authors can present a confusing array of information. Table 2.2 has been prepared to help organize the various findings which are discussed in the following paragraphs.

Stein and Hartmann (1957) describe a process for the separation of various high molecular organic compound mixtures found in vegetable, fish and animal fats. They describe several ways of obtaining a liquid-solid fat mixture suitable for dispersion with an aqueous solution containing a surface active material. The liquid-solid fat mixture is dispersed with an aqueous solution containing a surface active material. The result is an oil-in-water emulsion or dispersion. The dispersion is then centrifuged to yield the liquid product directly. The solid portion is recovered as a liquid after heating the aqueous-solid mixture and centrifuging.

Table 2.2

Aqueous Fractionation Process Variable Recommendations

Research Author	Surfactant & Quantity	Electrolyte & Quantity	Aqueous Quantity	Crystal Size & Type
	weight percent of aqueous solution	weight percent of aqueous solution	weight ratio of aqueous soln to fat	
Stein & Hartmann (1957)	.05 to 5.0% fatty alcohol sulfates 10 to 28 Carbons	—	0.5 to 5.0	—
Stein (1968)	0.2 to 0.5% fatty alcohol sulfate	1-2% magnesium sulfate	1.0-2.0 aqueous to fat by volume	—
Haraldsson (1974)	—	—	—	beta or betaprime crystals desirable
Poot et al. (1975)	—	—	—	0.1-3.0 micron crystals cause separation problems
Rek (1977)	sodium decyl sulfate 0.3%	2.5-5.0% many mono-valent cation salts	0.2-0.8	—
Bussey et al. (1981)	sodium dodecyl sulfate 0.6%	0.7-4.0% sodium sulfate	3.5	—
Glassner (1983)	surfactant quantity = f(crystal size)	—	—	—

Stein and Hartmann (1957) comment briefly on the role of the surfactant in the separation. They state that the surface active material reduces the interfacial tension between the organic material and the aqueous medium. The amount of surface active agent to be used is said to depend on the surfactant properties. Concentrations of 0.05 to 5% based on the weight of the aqueous medium are sufficient for good results. The last two statements apply to a range of fatty alcohol sulfates, containing 10 to 28 carbons in the carbon chain.

Stein and Hartmann (1957) mention that properties of the aqueous solution can be influenced by adding electrolytes which are inert to the other components of the dispersion. Any electrolyte is suitable as long as it does not form substantially insoluble precipitates with the surface active material. Electrolytes help to stabilize the hydrophilic portion of the surfactant molecules in the water phase. The preferable concentration for the electrolytes are not stated. The amount of the aqueous solution to be used ranges from 0.5 to 5.0 parts by weight of aqueous solution for each part by weight organic material.

In addition to the desirable wetting action of the surfactant solution, the aqueous solution can exhibit emulsifying power which can cause difficulty in the subsequent separation (Stein and Hartmann, 1957). To combat this problem "protective colloids" are recommended. Addition of the protective colloids reduces the

amount of surface active material required and thereby reduces the emulsifying power of the aqueous solution.

The term "protective colloids" refers to any inorganic or organic substances capable of increasing the viscosity of the aqueous phase (Stein and Hartmann, 1957). Examples of inorganic protective colloids are swelling clays, microcrystalline silica and other materials which will remain suspended in colloidal form in water or only settle slowly. Organic protective colloids include glue, gelatin, pectins, polyglycol ethers, polyacrylates, cellulose glycolates and methyl celluloses. The concentration of the protective colloids recommended ranges from 0.1 to 7.0 percent by weight of the aqueous solution.

The optimum quantity of the surface active material, the liquid organic compounds, the electrolytes and the protective colloids and the fineness of comminution may be determined by preliminary tests (Stein and Hartmann, 1957). Variation of the operating conditions during processing of the material to be separated can be used to control liquid and solid product compositions. Some of these operating conditions are rate of cooling, final separation temperature and the original mixture of raw materials.

In a later publication, Stein (1968) recommends a 1-2% concentration of inorganic salt in the aqueous solution. The preferred salt was magnesium sulfate. The optimum surfactant concentration was 0.2-0.5% of a fatty alcohol sulfate. The

recommended aqueous solution to organic phase ratio was 1:1-2:1 by volume. These optimums were for the separation of oleic and stearic fatty acids.

Stein (1968) found that mixing the dispersion with a small amount of the aqueous solution containing all the surfactant and electrolyte, and then diluting the dispersion with water to the final aqueous to fatty acid ratio was advantageous.

Poot et al. (1975) found that extremely small crystals of fat presented serious problems for fractionation by the aqueous method. Crystal sizes of 0.1-3.0 microns in length made high demands on the dispersion technique, the wetting ability of the detergent and on the separation by centrifugation.

A necessary condition for a successful fractionation using the aqueous dispersion technique is formation of crystals of the proper type (Haraldsson, 1974). The actual size of the crystals is of minor importance. Haraldsson (1974) did state that 25-50 micron crystals are large enough. If the oil is cooled too rapidly, amorphous crystals of the alpha type are formed. Slower cooling creates beta or betaprime crystals which are easily wetted by the aqueous solution. The alpha crystals are not properly wetted and oil recovery is not good. For fats such as palm oil, tallow and lard the necessary crystallization time is 4-6 hours.

Rek (1977) states that the process, although simple, is complicated by speed of crystallization, form of crystals, occlusion of oil in the crystals and inexplicable and unpredictable effects. The author does not define the effects. The problems are said to be more severe at low temperatures and when small crystals are formed.

Rek (1977) found that use of an oil-soluble surface-active agent in addition to the water soluble surface active agent improves the olein yield. The preferred oil-soluble surface active agents are unsaturated monoglycerides of twelve to twenty-eight carbon unsaturated fatty acids. The desired water soluble surfactant is sodium decyl sulfate. The concentrations of both surfactants depends on the particular surface active agents, the mixture of triglycerides and the aqueous system used. The oil soluble surfactant is preferably added to the mixture of triglycerides but addition to the aqueous solution is suitable. It should be noted that some oil soluble surfactants are naturally occurring in crude fats.

Rek (1977) found that the water soluble surface active agent, preferably sodium decyl sulfate, should be present in a concentration of at least 0.3% based on the triglyceride mixture weight. The inorganic salt concentration in the aqueous solution should be between 2.5 to 5.0% by weight of the aqueous solution. The volume ratio of water to triglyceride mixture should be between 0.2 to 0.8:1.

Bussey et al. (1981) fractionated tallow and state that the optimum surfactant, sodium dodecyl sulfate, concentration to be 0.6% by weight of the tallow. The optimum volume of water to tallow is stated to be 3.5:1. Bussey et al. recommend adding the surfactant directly to the partially crystallized tallow and find this increases olein yield.

During the fractionation of tallow, the size of the triglyceride crystals and the concentration of the surface active agent are important (Glassner, 1983). The olein yield increases as the surfactant concentration increases. The olein yield reaches a maximum and increasing the surfactant concentration above the level needed for the maximum olein yield results in the formation of an emulsion, which makes recovery of the olein fraction by centrifugation difficult. The size of crystals formed effects the amount of surfactant required for a successful fractionation.

2.4 Crystal Morphology

Polymorphism is the existence of two or more crystalline modifications for the same substance. Triglycerides exhibit multiple crystal packings and this was first demonstrated using x-ray diffraction by Clarkson and Malkin (1934).

The monoacid saturated triglycerides or mixtures of only a few saturated triglycerides exhibit three polymorphs described by their x-ray short spacings (See Table 2.3).

Table 2.3

X-ray Short Spacings

Crystal Type	Short Spacings
alpha	4.1 Å
betaprime	3.80 Å, 4.20 Å
beta	4.6 Å

(Chapman, 1962)

For a natural mixture of mixed fatty acid triglycerides three polymorphs may not be observed (Hoerr, 1960). Some exhibit only the lower melting forms such as alpha and betaprime. Only two polymorphs are formed because the mixed triglycerides can not pack together closely enough to transform to the beta form, the most closely packed triglyceride form. Fats crystallized initially in the alpha or betaprime form will transform in the sequence, alpha to betaprime to beta, until the most stable form for the fat is attained. If close packing cannot be achieved, the betaprime form may be the most stable for a mixed triglyceride.

The beta form crystals have triclinic packed chains, the betaprime crystals have orthorhombic packed chains and the alpha form crystals have hexagonal packed chains (Chapman, 1962). The triglyceride packing structure is shown in Figure 2.1. The end view of the triglycerides in Figure 2.1 would show one of the three patterns mentioned above, thus defining the crystal type.

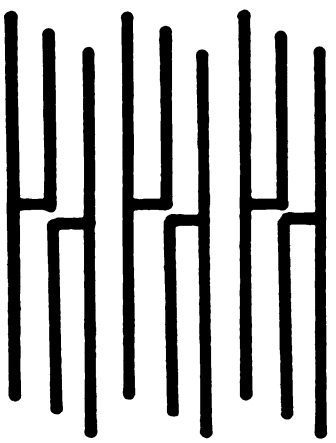


Figure 2.1 Triglyceride Chain Packing Diagram.

The rate of cooling determines the crystalline type initially formed. Slow cooling will produce the more stable crystal polymorphs, beta or betaprime (Hoerr, 1960). Fast cooling will likely result in alpha type crystal packing. If the alpha crystals are tempered at the correct temperature the alpha crystals will transform to the most stable form, beta or betaprime.

Hoerr (1960) also proposed that each crystalline type has features that can distinguish it from other crystal types when viewed using a microscope. Microscope investigations are not too definitive because a variety of crystal habits may occur for one crystal form (Chapman, 1962). Alpha form crystals are fragile, transparent platelets with a characteristic size of about five microns. Betaprime crystals are tiny needles of one micron in length. The beta crystals are large needles up to fifty microns in length or longer. They form clumps up to one millimeter in diameter. The type of fat was not stated. The sizes described by Hoerr (1960) depend on the temperature driving force and on the type of fat being crystallized.

2.5 Detergency Theory

Detergency is defined as the process of cleaning the surfaces of a solid material by means of a liquid bath involving a physicochemical action other than simple solution (Neiditch, 1972). The displacement of an oil-water interface by a water-fiber interface by an aqueous solution containing electrolyte and

surfactant is a detergency phenomenon (Schott, 1972). Detergency is the sum of a variety of phenomena, including electrostatic forces, interfacial potentials, and ion activities of both surfactants and builder electrolytes (Goette, 1949).

Surfactants are characterized by their absorption at all types of interfaces (Lange, 1972). The cleansing action of surfactants is due to their absorption at the interfaces involved. The mechanical, electrical and chemical properties of the interfaces are all altered by the surfactant absorption. The degree of absorption depends on the type and concentration of the surfactant, the presence of other materials in solution, the solution temperature and the absorbent properties.

The absorption of a surfactant strongly increases as the surfactant concentration is increased until the critical micelle concentration is reached (Lange, 1972). Micelles are aggregates of surfactant molecules. They form in solutions at concentrations above the critical micelle concentration (CMC) (Neiditch, 1972). Since the concentration of individual surfactant molecules in the aqueous phase is virtually constant above the CMC, the surfactant is at essentially its optimum for many applications such as wetting.

Electrolytes have been shown to reduce the concentration of surfactant needed to reach the CMC. The addition of electrolytes to a surfactant solution causes the property changes characteristic

of reaching the CMC to occur at lower surfactant concentrations than if the electrolytes were not in the solution (Harris, 1958).

The work of Adam (1937) showed that oily soil was removed from fiber surfaces by wash water through a mechanism of preferential wetting. Kling (1949) called the mechanism exchange wetting, because the oil-fiber interface exchanged to become a water-fiber interface.

Adam and Stevenson (1953) and Moillet et al. (1961) gave the following description of the preferential wetting or rolling-up mechanism. A fiber partly covered by a film of oil was immersed in a dilute aqueous surfactant solution, which did not completely displace the oil. A state of equilibrium resulted. The oil and the aqueous solution both remained in contact with the fiber. The surfactant molecules were adsorbed at the fiber-water and oil-water interfaces in a monolayer film. The film of surfactant molecules being adsorbed at the fiber surface displaced the oil because the surfactant adhered to the fiber surface more strongly than did the oil.

As the concentration of surfactant increases, the oil rolls up until it no longer is in contact with the fiber (Adam, 1937). The oil droplets are now surrounded by an aqueous phase. The surfactant is adsorbed at the oil-water interface helping to stabilize the oil-in-water emulsion (Adam and Stevenson, 1953).

If a smooth film of oil completely covers a fiber surface, an aqueous solution can not break through the oil to wet the fiber surface (Schott, 1972). A point at which the three surfaces meet is necessary to roll-up the oil. If a contact point for the three phases is established, the displacement of the oil-fiber interface by the aqueous-fiber interface can occur.

The mechanical force exerted upon the particles in the cleansing process may be important in connection with the influence of the particle size (Lange, 1972). It is well established that solid particulate soil can not be completely removed by a surfactant solution without mechanical action. This can be explained by the necessity of detergent solution contact with the fiber. Contact of the detergent solution with the fiber is necessary for wetting the fiber.

2.6 Critical Micelle Concentration

In surfactant solutions, aggregations of molecules form over a narrow concentration range called the critical micelle concentration (Harris, 1958). The shape of micelles is first pictured by McBain (1913). Hartley (1936) proposes another configuration for the orientation of micelles. Many other shapes have since been proposed and all have valid supporting evidence (Harris, 1958). The chemical structure of the compound being investigated may be a controlling factor.

In addition to shape, the size of the micelles is important (Harris, 1958). For low molecular weight compounds as few as ten molecules are associated while in other cases they exceed a hundred. Studies have shown that within a homologous series of surfactants the number of molecules associating is definite and increases with increasing hydrophobe chain length. A micelle molecular weight can vary from 4,000 to 40,000.

The most effective surfactants generally have the lowest CMC while having longer, optimum hydrophobe structure. Consequently a comparison of surfactants can be made on this basis, but of even greater importance is the measurement of the effect of builder electrolytes upon surfactant CMC. These generally lower the initial CMC remarkably (Harris, 1958).

2.7 Surface Tension Measurement

Measurement of either surface or interfacial tension are time-consuming but relatively effective methods for determining CMC (Harris, 1958). A method widely used involves the determination of the force to detach a ring or loop of wire from the surface of a liquid (Adamson, 1984). Table 2.4 lists other possible methods.

One of the difficulties with the DuNouy (1919) method lies in adequate temperature control, but apparatus for this purpose can be constructed. At elevated temperatures, evaporation is also a difficulty, but again this can be corrected (Harris, 1958).

Table 2.4

Methods of Surface Tension Measurement

1. Capillary Rise
2. Maximum Bubble Pressure
3. Drop Weight
4. Ring
5. Wilhelmy Slide
6. Pendant Drop
7. Sessile Drop or Bubble

The method is capable of good precision. The tensiometer makes use of a torsion wire and is commonly used for determining the detachment force. Harkins and Jordan (1930) worked out an empirical correction factor to use for correcting the detachment force to the true surface tension. The detailed theory of the method has been determined by Freud and Freud (1930). The calculated correction factors agree with the empirical factors to within 0.25%.

The method is quite accurate if sources of error are avoided (Adamson, 1982). The dry weight of the ring should be used for calibration purposes. The ring must be kept horizontal to avoid measurement errors. An angle of 1° causes an error of 0.5% and a deviation of 2.1° causes an error of 1.6%. The surface of the fluid must not be disturbed as the detachment point is approached. Flaming of the ring before measurements removes grease and other contaminants from the ring. The fluid vessel is best if it can be overflowed to remove surface contaminants.

A zero or near zero contact angle is required or the recorded results will be low (Adamson, 1982). This was found to be the case with surfactant solutions. A teflon coated or polyethylene ring may be used to keep the contact angle at zero (Krynitsky and Garrett, 1963).

2.8 Dispersion Rheology

Due to the wide variation in recommended detergent solution quantities of previous investigators the dispersion rheology may be important (See Table 2.2). Previous results of this author revealed a separation dependence on the crystal size. Since the solid properties affect the dispersion rheology the crystal properties may be critical.

A paddle mixer viscometer will be used for the dispersion rheology experiments. The paddle mixer is the choice for two reasons (Steffe and Ford, 1985). First, wall effects due to slip are minimized with the mixer or impeller type sensor. The second reason is that mechanical degradation of the sample during instrument loading is less for the paddle sensor system than the concentric cylinder systems.

Rao (1975) and Metzner and Otto (1957) have studied the application of mixer viscometry to food products. Power consumption in a mixing vessel for a Newtonian fluid can be expressed in terms of a power number,

$$P_o = (p/d^5\omega^3\rho), \qquad (2.1)$$

and a mixing Reynolds number,

$$Re = (d^2\omega\rho/\mu) \qquad (2.2)$$

as

$$P_o = B/Re \qquad (2.3)$$

or

$$p/d^5\omega^3\rho = B\mu/d^2\omega\rho \qquad (2.4)$$

Equation (2.4) can be used for power law fluids if the fluid viscosity, μ, is replaced by an apparent viscosity, η_a, evaluated at an average rate of shear, γ_a, which is defined as

$$\gamma_a = k'\omega \qquad (2.5)$$

Equation (2.5) is valid for a particular impeller if a plot of log $(p/K\omega^{n+1}d^3)$ versus (1-n) is a straight line having slope equal to -log k' (Rieger and Novak, 1973). K and n are the consistency coefficient and flow behavior index used to describe the power law fluid expressed in terms of the shear stress and shear rate as

$$\tau = K(\gamma_a)^n \qquad (2.6)$$

When using the mixer viscometry technique, the flow behavior index is calculated as the slope of the log (torque) versus log (impeller speed) curve. The consistency coefficient is calculated as

$$K_x = (M_x(\omega k')^{n_\gamma} K_y)/(M_y(\omega k')^{n_x}) \qquad (2.7)$$

where x and y are subscripts referring to the test fluid and a standard (fluid with known properties), respectively.

Equation (2.7) is a ratio of equation (2.6) for two different fluids. The torque, M, is equal to the shear stress times a constant; the constant is equal for both fluids. The shear rate, $\omega k'$, and the consistency coefficient and consistency index are the same as in equation 2.6.

The mixer viscometer constant, k', can be determined by using several different fluids and evaluating K and n for them using standard rheological techniques. Solutions of hydroxypropyl

methylcellulose, guar gum and corn syrup were evaluated. A plot of log $(p/k\omega^{n+1}d^3)$ versus (1-n) was made. The result was a straight line with slope equal -log k', from which the slope k' was determined to be 4.46 (Steffe and Ford, 1985)

EXPERIMENTAL METHODS AND EQUIPMENT

3.1 Tallow Sample Preparation

Tallow was obtained from a commercial supplier in a 55 gallon drum. 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.

3.2 Crystal Preparation Methods

Three crystallization procedures were used to produce crystals for the separation step. The goal of these procedures was to prepare three different sizes of crystals. The final crystallization temperature was 40 °C in all cases. The procedures differed during the initial cooling period. During this period crystal nucleii were produced. The crystal nucleii produced determine the number and size of the final crystals. The speed of cooling determined the initial triglyceride crystal type. Due to the small size of the samples crystallized, agitation was not necessary for adequate heat transfer.

Crystallization procedure one, a partial melting process, was begun by raising the tallow temperature to 60 °C to completely melting the tallow. The tallow was then put in a freezer which quickly

brought the tallow temperature to 0 °C in under fifteen minutes. The tallow was rapidly nucleated and crystallized totally during this period. The tallow was kept in the freezer for a total of two hours. The crystallized tallow was then put into a 40 °C temperature bath. The crystallized tallow rose to 40 °C with some of the tallow melting as the temperature rose. The tallow remained in the temperature bath for 16 hours which allowed equilibrium to occur between the liquid oil and solid crystals. The total crystallization time was 18 hours. Figure 3.1 shows the temperature profile for the three crystallization procedures.

In procedure two the tallow was heated first to 60 °C and then cooled at an ambient temperature of 29 °C for two hours. During this two hour period the oil cooled to about 33 °C before the first crystal nuclei began to form. The heat of solidification caused the tallow temperature to slowly rise after the tallow began to crystallize. The cooling to 33 °C took one hour. During the second hour crystallization generated heat which caused the tallow temperature to rise to 35 °C. The tallow sample was put into the 40 °C temperature bath for the remaining 16 hours of the crystallization time.

Crystallization procedure three was begun by melting the tallow sample completely by raising the tallow temperature to 60 °C. The tallow was then cooled at an ambient temperature of 29 °C until crystal nucleii were seen. The initial cooling took 1 hour, then the nucleii appeared. The temperature of the tallow was 33-34 °C

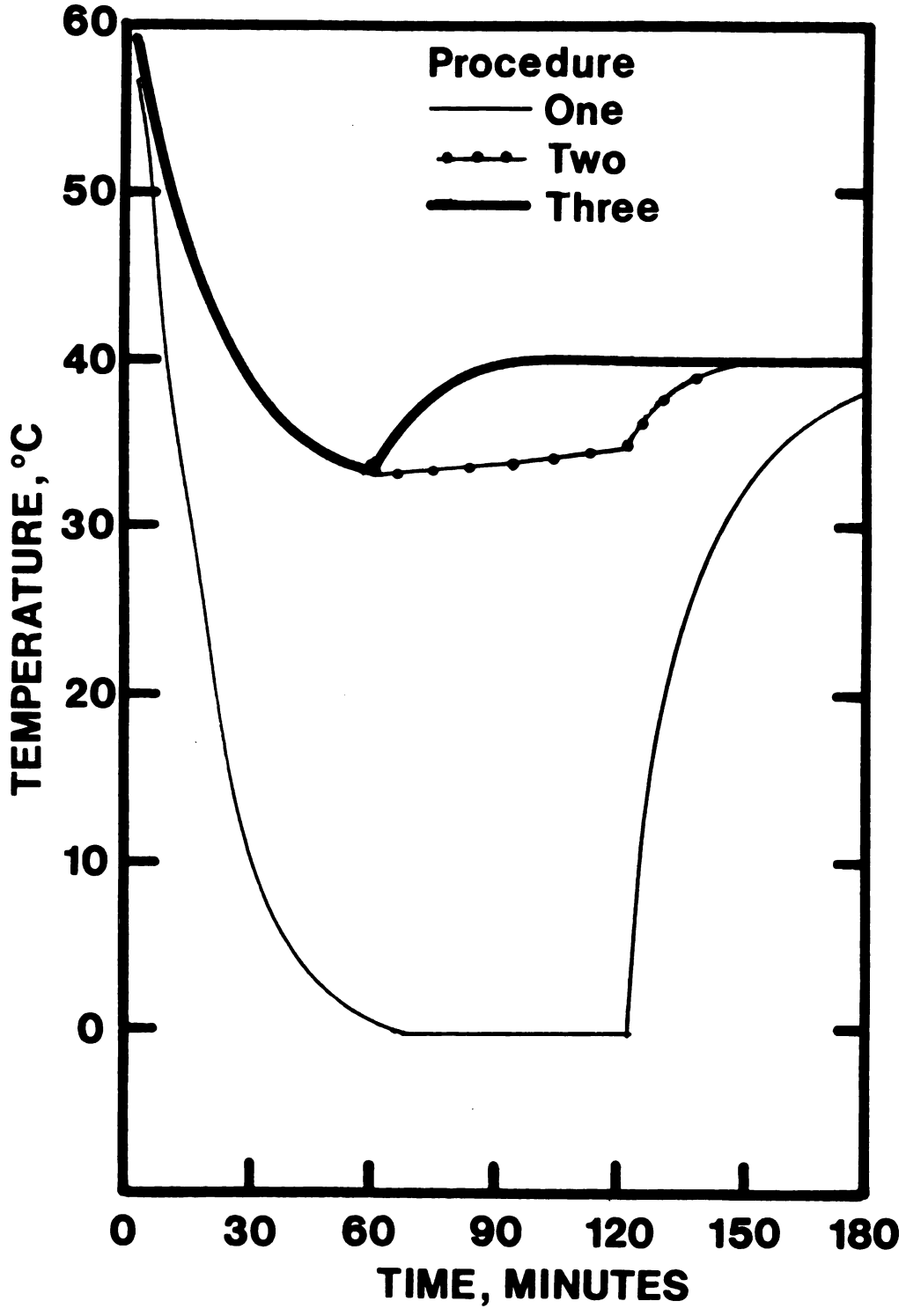


Figure 3.1 Temperature Profiles for Three Crystallization Procedures.

at this time. The sample was then put into the 40 °C temperature bath for the remainder of the crystallization time.

3.3 Crystal-Oil Separation Procedure

After the crystallization was complete the correct amounts of water, electrolyte and surfactant were mixed and brought to 40 °C. Distilled water was used as the base of the detergent solution. The electrolyte used was sodium citrate (Mallinckrodt) and the surface active agent used was sodium dodecyl sulfate (Fisher Scientific).

After preparation the detergent solution was then added to the partially crystallized tallow. The detergent solution was mixed in with a stirring rod. Mixing was carried out until a uniform dispersion was obtained. Previous tests indicated that more intense mixing does not increase olein yield (Glassner, 1983). The dispersion was allowed to sit for one hour before it was centrifuged, with a centrifugal force of 3,600 times that of gravity. A DuPont Sorval RC2-B centrifuge was used for the centrifugation steps.

The dispersion separated into an olein layer on top, a solid crystal layer in the middle and a detergent solution layer at the bottom of the centrifuge tube. The olein was poured out of the centrifuge tubes after the centrifugation. The yield of olein was

calculated by weighing the olein collected and comparing to the amount of tallow originally present.

The crystal layer was recovered by heating the crystal and detergent solution until the crystals melted. The melted mixture was centrifuged to separate the stearin, now in liquid form, and the recyclable detergent solution. The process is schematically diagrammed in Figure 3.2.

Fractionation data were generated using crystallization procedure three except where otherwise noted. A detergent solution to tallow weight ratio of 0.80 was used for all separations except those in which other ratios were specified. The sodium citrate concentration in the detergent solution was 5.0 percent for all separations, unless otherwise specified. The surfactant concentration or weight used was specified for each data point.

3.4 Surface Tension Measurement

A Cenco Tensiometer Model No. 70530 was used to obtain the surface tension measurements. The detergent solution was mixed to the desired concentration. The measurements were taken at 40 °C solution temperature. 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 (Krynitsky and Garrett, 1963). The surface

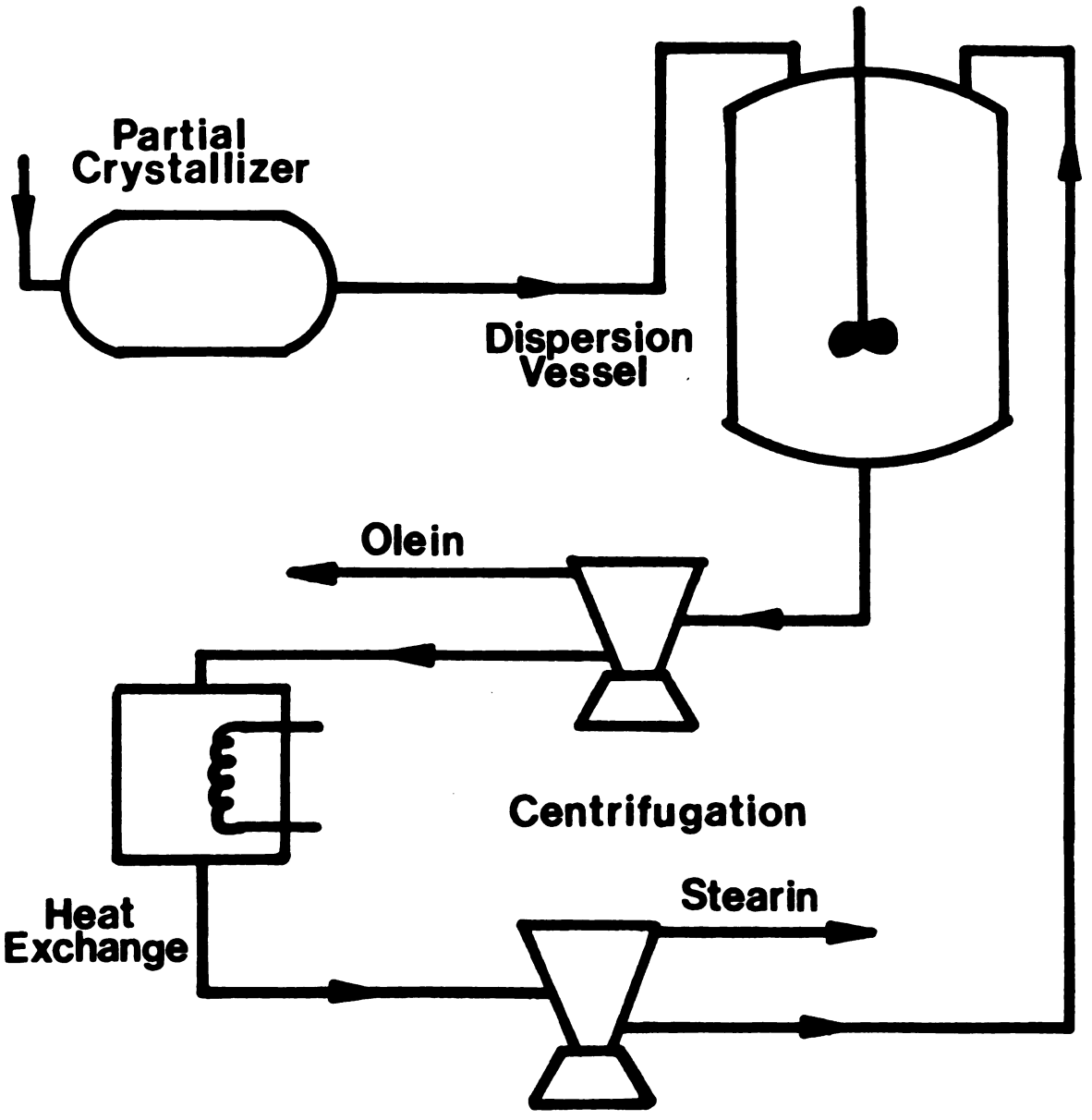


Figure 3.2 Fractionation Process Schematic Diagram.

tension values were corrected as recommended (Zuidema and Waters, 1941; Adamson, 1982).

The surface tension measurements made required the tensiometer previously mentioned, a four inch diameter watch glass, a teflon coated platinum ring and a platinum ring. The platinum rings in this case were six cm circumference rings. The watch glass was the solution holding vessel, which was chosen for its ability to be overflowed to insure a clean air-liquid interface. The watch glass was cleaned for each solution by rinsing throughly with tap water and then with distilled water.

The solutions were prepared with the desired amounts of distilled water, sodium dodecyl sulfate and sodium citrate. Since the capacity of the watch glass was slightly under 100ml, using 100 ml of distilled water provided a good basis. After the solution was heated to the correct temperature of 40 °C, the solution was poured into the watch glass and the watch glass was slightly overfilled to give a clean liquid-air interface. The appropriate ring was then contacted with the liquid surface. A zero reading on the tensiometer scale was achieved by adjusting the height of the tray holding the watch glass and the tension control for the tensiometer.

The tension control was then slowly increased while the height of the holding platform was lowered so that the zero reading on the tensiometer scale was maintained. This procedure was continued

until the ring was detached from the liquid surface. When the ring detached, the surface tension was read from the graduated dial scale. The appropriate correction factor was applied and the final surface tension reading for the particular solution was obtained (Zuidema and Waters, 1941).

The tensiometer calibration was an essential part of the experimental technique. The recommended procedure was designed to give a direct reading in dynes from the graduated dial. First the lever arm, on which the platinum ring was hung, was clamped in place and the ring was cleaned. The cleaning was accomplished by heating the ring momentarily to a dull red in the oxidizing portion of the flame. The ring was then hung on the hook at the end of the lever arm.

A small piece of paper was put on the ring for use as a platform. The tension control was then adjusted so the lever arm index and its mirror image coincided with the reference line on the mirror. The dial clamp was loosened and the graduated dial rotated until the vernier indicated approximately zero. The tension control was adjusted until the reading was exactly zero.

A mass of 500 to 800 mg weight was placed on the paper platform. The weight was known accurately. The tension control was readjusted so that the index was lined up with the reference line. The dial reading was recorded to the nearest 0.10. Using equation (3.1), the apparent surface tension value was determined.

$$s = Wg^{*}/2L \qquad (3.1)$$

If the recorded dial reading was greater than the calculated value then the lever arm was adjusted by shortening; if the dial reading was less than the calculated value, the lever arm was adjusted by lengthening.

The calibration procedure was repeated by readjustment of the zero position with the paper on the ring after each adjustment of the lever arm length until the dial reading agreed with the calculated value. When the calibration was completed each unit on the dial represented a surface tension measurement unit of one dyne/centimeter.

After completion of the calibration procedure the paper was removed from the ring and the zero position was reset. The tension control knob was turned until the index was aligned with the reference line and its mirror image on the mirror. Then the tension adjustment was loosened until the vernier read zero. The tensiometer was now ready for use.

3.5 Rheology Data Measurement

A Haake RV-12 viscometer, interfaced to a Hewlett-Packard 85 computer and 3497 data acquisition system, was chosen to measure rheological properties of the detergent solution-partially crystallized tallow dispersion. A MV paddle sensor was attached to

the viscometer drive head. Samples were placed in a viscometer cup (See Figure 3.3), having a radius equal to 0.021 m, for testing. Also shown in Figure 3.3 was the paddle sensor used. Its diameter was 0.04143m and its height was 0.02692m. The blade was pitched 15 degrees from a plane through the shaft. The viscometer was equipped with a Haake F3-C water circulator to maintain samples at a constant temperature while collecting data.

The preparation of the dispersion to be tested was the first step. The sample cup needed a total volume of 45 ml liquid to fill it to a level just above the top of the paddle mixer. The partially crystallized tallow was already crystallized by the desired crystallization procedure. Depending on the weight ratio of detergent solution to tallow chosen, the appropriate amounts of partially crystallized tallow and aqueous solution were loaded into the sample cup. The sample cup was then loaded into the Haake viscometer unit. The tallow and detergent solution were mixed in the cup before the cup was loaded. The dispersion was further mixed in the cup during the 60 minute period used to gather the torque versus time data.

The Haake temperature bath was set to 40 °C to bring the viscometer to the necessary 40 °C temperature about 15 minutes before the viscometer cup was loaded. The viscometer was zeroed before and after loading the viscometer cup. The rotational rate was set at 120 rpm and the collection of data was begun. After 60 minutes the

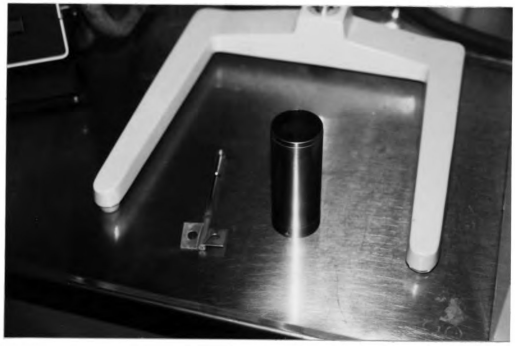


Figure 3.3 Mixer Viscometer Paddle and Cup.

data collection was ended and the data was processed. A raw data output and a graph of torque versus time was printed.

Torque as a function of the rotation rate was then measured for the dispersion. A rotation rate was set and the torque was recorded at that rotational rate. The rotation rate was reset and the torque was again recorded. After this was done for fifteen rotation rates ranging from one rpm to 180 rpm the data were printed. Both the raw data and a graph of torque versus rotation rate were printed.

A program for the HP-85 for power-law fluids was used to analyze the data collected. The program calculated the consistency coefficient, K, and the flow behavior index, n. The torque versus rotational rates were assumed to be those of a power law fluid near the rotational rate in question. A plot of log (torque) versus log (rotational rate) was therefore a straight line. The program calculated the slope of this line from which the flow behavior index n was obtained. The consistency coefficient, K, was then obtained by using a ratio of the common shear stress-shear rate equation for two fluids. Since the torque was directly proportional to the shear stress for both the dispersion being tested and for the known fluid, the proportionality constant canceled out of the ratio when the torque was substituted for the shear stress. The only unknown was the consistency coefficient, K, of the dispersion tested, which was then calculated.

Both the K and n values were printed out by the program. These parameters were necessary for calculation of an apparent viscosity. The values were printed allowing calculation of an apparent viscosity according to equation (3.2).

$$\eta_a = K(k'\omega)^{n-1}. \qquad (3.2)$$

Equation (3.2) was evaluated at 60 rpm giving an apparent shear rate ($k'\omega$) equal to 28.02 s^{-1}.

3.6 Crystal Size Measurement

Photomicroscopy was used to determine the size of crystals produced by various crystallization procedures. The photomicroscopy was conducted on an American Optical Phase Star microscope fitted with a Kodak 35 mm camera. The film used was Kodak Type 2415, a high resolution black and white film. D-19 developer was used to develop the film. A developing time of four minutes was used.

The photomicroscopy was done in a 37 °C constant temperature cubicle. The high temperature was necessary to keep the oil in the oil-crystal mixture from crystallizing onto the crystals. The partially crystallized tallow from all three procedures was photographed.

3.7 Olein Emulsification Measurements

Tests were conducted to determine the amount of surfactant required in the detergent solution to emulsify olein. Olein previously obtained from completed fractionations was mixed with detergent solutions containing various concentrations of surfactant. The mixture was then centrifuged under the same conditions used during normal separations. The olein was observed after centrifugation for the presence of emulsified olein. Tests were conducted for a wide range of surfactant concentrations with the object of determining the highest detergent solution surfactant concentration possible before emulsified olein was left after centrifugation.

RESULTS AND DISCUSSION

4.1 Proposed Mechanism for the Separation of Liquid and Solid Phases

Detergency theory was used to explain the crystal size and surfactant concentration effects on the production of emulsified olein described by Glassner (1983). Agitation provided after the addition of the detergent solution to the partially crystallized oil assists in contacting the oil, crystal and aqueous phases. When a three-phase contact point was created, the high concentration of surfactant in the aqueous solution rolled-up the oil from the crystal surface almost immediately.

Figure 4.1 shows the process for the small single crystals generated by the partial crystallization procedure. Microscopic observation of the components of the process provided the basis for the mechanism diagrammed in Figure 4.1. Stages A and D were observed directly. Stages B and C were proposed based on detergency theory. The intermediate steps occur rapidly enough that they were not observed by microscopic techniques.

The spherulitic crystals, as shown in Figure 4.2, were wetted in a similar way with the same end result except for the size of the olein droplets formed. The detergent wetting of the polycrystalline spherulites into the aqueous phase was attributed

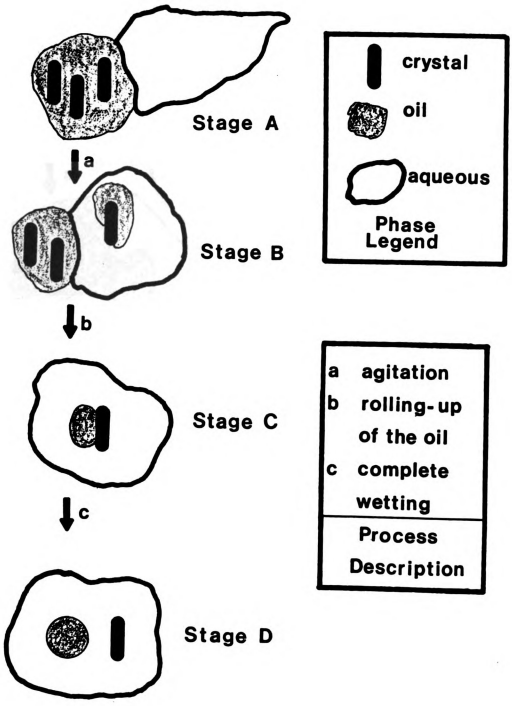


Figure 4.1 Rolling-Up Detergency Mechanism for Individual Tallow Crystals.

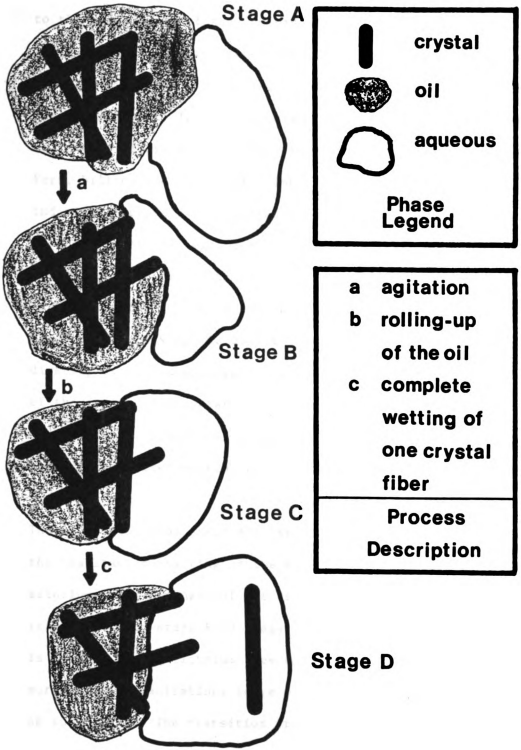


Figure 4.2 Rolling-Up Detergency Mechanism for Crystal Agglomerates.

to the breaking up of the individual crystals from the spherulites. The surfactant solution penetrated the boundaries between the individual crystal fibers, and they were then separated from the large aggregate. This was observed for triglyceride matter as well as textile fibers (Scott, 1963; Fort, Billica and Grindstaff, 1966; Fort, Billica and Grindstaff, 1968). As the oil rolled-off the individual crystals it remained in contact with oil surrounding the rest of the crystal agglomerate. When the last individual crystal was wetted, the oil became an emulsified oil droplet that was much larger than the droplet from a small single crystal. Stage A was observed directly by microscope. Stages B and C were not observed directly by microscopic methods. After stage D was formed the rest of the crystal agglomerate was wetted quickly. Microscopic observation revealed both single crystals and spherulitic agglomerates after wetting was complete.

The transition from stage A to stage B depended on agitation and the resultant contacting of the crystals and the detergent solution. The strength of the detergent solution controlled the transition from stage B to stage C. High surfactant concentration is present the equilibrium lies to a stage D situation. Low surfactant concentrations leave oil contacting the crystal surface, as in stage B. The transition from stage C to stage D in addition to requiring adequate detergent strength requires aqueous volume to accomodate the crystals.

Increasing the surfactant concentration with no change in oil droplet size is known to stabilize emulsions, especially with sodium dodecyl sulfate as the surfactant. If the oil droplet size was increased, with the surfactant concentration remaining the same, less force was required to coalesce the larger droplet with other oil droplets.

Poot et al. (1975) found that when using a 5% sodium dioctylsulfosuccinate solution, the oil droplets must be greater than 12 microns in diameter for them to coalesce during centrifugation. The final surfactant concentration was one to three percent by weight of the aqueous solution, or 2.0 to 7.5% by weight of the fat. Certainly, the allowable low range of oil droplet size depends on the surfactant type and concentration.

The principles of detergency applied to the fractionation process provided a mechanism to help explain fractionation results. Further experimentation to determine operating conditions for maximizing the olein yield were conducted based on this basic principle. The effects of the crystal size, surfactant concentration, aqueous solution to tallow weight ratio and dispersion rheology were investigated.

4.2 Crystallization Results

Crystallization procedures two and three were similiar to procedures that can be used with scraped surface heat exchangers to

produce partially crystallized fats. A typical commercial process might use a precooler followed by a constant temperature crystallization unit. The difference between commercial crystallization and the procedure two and three crystallizations was that the procedure two and three crystallizations had very little agitation during the crystallization. In these bench scale experiments, agitation was not required for heat transfer. The amount of shear due to a scraped wall exchanger is small because low rotation rates are used. The low shear rates should have little effect on the crystal nucleation and growth. Therefore, the crystals produced in the non-agitated vessels were assumed to be representative of crystals that might be produced in a scraped surface exchanger.

The crystals produced in the crystallization step are important to the success of a fractionation (Glassner, 1983). Photomicroscopy of the crystals from each crystallization was done to characterize the size of crystals produced by each procedure. Figures 4.3 and 4.4 show representative crystals from the second and third crystallization procedures. Satisfactory photographs were not obtained for crystallization procedure one. The length of the individual crystals and the size of the crystal agglomerates were determined by Figures 4.3 and 4.4 and other similar photomicrographs. The diameter of the crystals was determined by looking at higher magnification photomicrographs of the crystals.

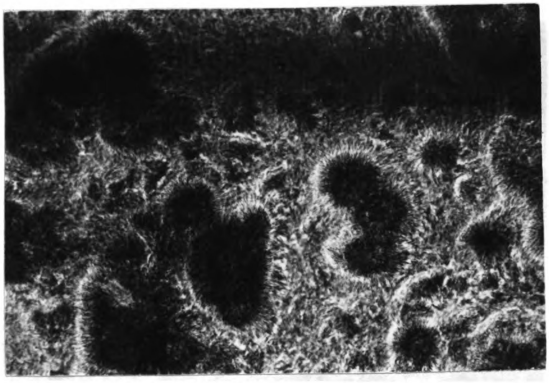


Figure 4.3 Photomicrograph of Procedure Two Crystals, 100X Magnification.

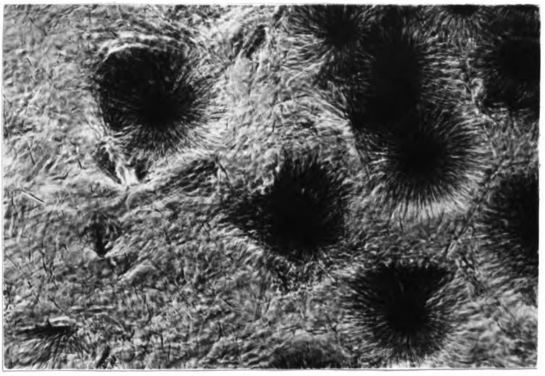


Figure 4.4 Photomicrograph of Procedure Three Crystals, 100X Magnification.

Scanning electron microscopy of the crystals was done to obtain better resolution pictures of the crystals. The normal procedure is to freeze a oil-crystal mixture and look at the cross section. Since the crystals produced were long, thin needle-like crystals the above procedure was not appropriate. In order to obtain the length and diameter dimensions of the crystals it was desired to look at the crystals alone.

Crystals were obtained after the separation step and cleansed with ethyl alcohol to remove all traces of water (Jewell and Meara, 1970). Replicas, as desribed by Jewell and Meara (1970), could not be produced. The crystals were mounted on an SEM stub, sputter coated and photomicrographs were taken. Figures 4.5 (1,000X) and 4.6 (700X) show the results of SEM microscopy. The heat generated by the electron beam in the SEM's vacuum was sufficient to melt the crystals. The sputter coating of the crystals caused extensive melting also. The results were no help in determining the size of crystals produced and the SEM technique was abandoned.

Crystallization procedure one crystals were extremely small. The light microscope resolution was poor even at 2,000 times magnification. These crystals were initially unstable alpha type crystals. The alpha crystals were rearranging into the next most stable form, betaprime, at the 40 °C final crystallization temperature used (Hoerr, 1960).

Figure 4.5 SEM Microscopy of Fat Crystals, 1,000X Magnification.

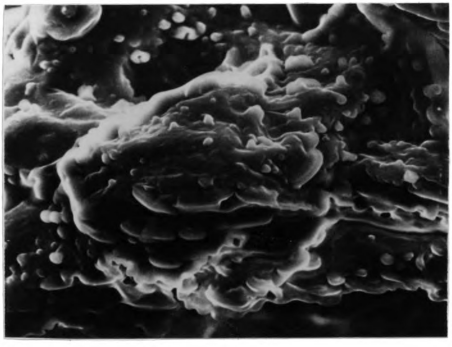


Figure 4.6 SEM Microscopy of Fat Crystals, 700X Magnification.

The crystallization procedure two and three crystals were much easier to observe. They were more well defined than the procedure one crystals and existed in the stable tallow crystal form, betaprime. The procedure two crystals existed both as single crystals and spherulitic agglomerates of individual crystals. The procedure three crystals were primarily spherulitic agglomerates. The average size of the procedure two crystal agglomerates 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.

Betaprime crystals are usually orthorhombic and, therefore, are regular extended length polyhedrons (Chapman, 1962). The features of the minor axes of the crystal were not discerned under the microscope. The assumption of a cylindrical crystal simplified surface area and volume calculations. The crystals actually grow in layers (Jewell and Meara, 1970) and the length of the crystals is due to the apparent ease of adding to a layer (See Figure 2.1) as opposed to beginning a new layer. This results in the crystals having a length/diameter of 75 or more.

The single crystals were estimated to make up about 20 percent of the crystal mass in the procedure two crystallization. The average size of the procedure three spherulites was 60 to 80 microns in diameter. The individual crystals making up the spherulitic crystals were 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 4.1 summarizes the dimensions of the crystals from procedures two and three. The calculations for Table 4.1 are shown in Appendix B.

4.3 Separation Results

Figure 4.7 shows the results of separations conducted on tallow samples crystallized by each of the three crystallization procedures. The crystallization procedure had a large effect on the separation results. Procedure one had a maximum olein yield of 51 percent. This maximum occurred in a broad SDS concentration range of 0.4 to 1.1 percent. 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.

The olein yields obtained after using crystallization procedure one were too low for the procedure to be useful. The low yield was attributed to the high degree of supercooling used to crystallize the procedure one crystals. The low temperature trapped oil components which would not have crystallized at 40 °C, except for being subjected to the fast cooling and low intermediate temperature of the process.

The olein yield reached a maximum of 79 percent for crystallization procedure two. This maximum occurred at an SDS concentration of

Table 4.1

Crystal Sizes Produced by Procedures Two and Three

	Two	Three
Crystal Shape	Cylindrical	Cylindrical
Crystal Diameter	0.3 microns	0.6 microns
Crystal Length	30 microns	50 microns
Average diameter of spherulites.	50 microns	80 microns
Crystal volume	2.1 microns^3	14 microns^3
Crystal surface area	28 microns^2	95 microns^2
Surface area/volume	13 micron^{-1}	6.8 micron^{-1}

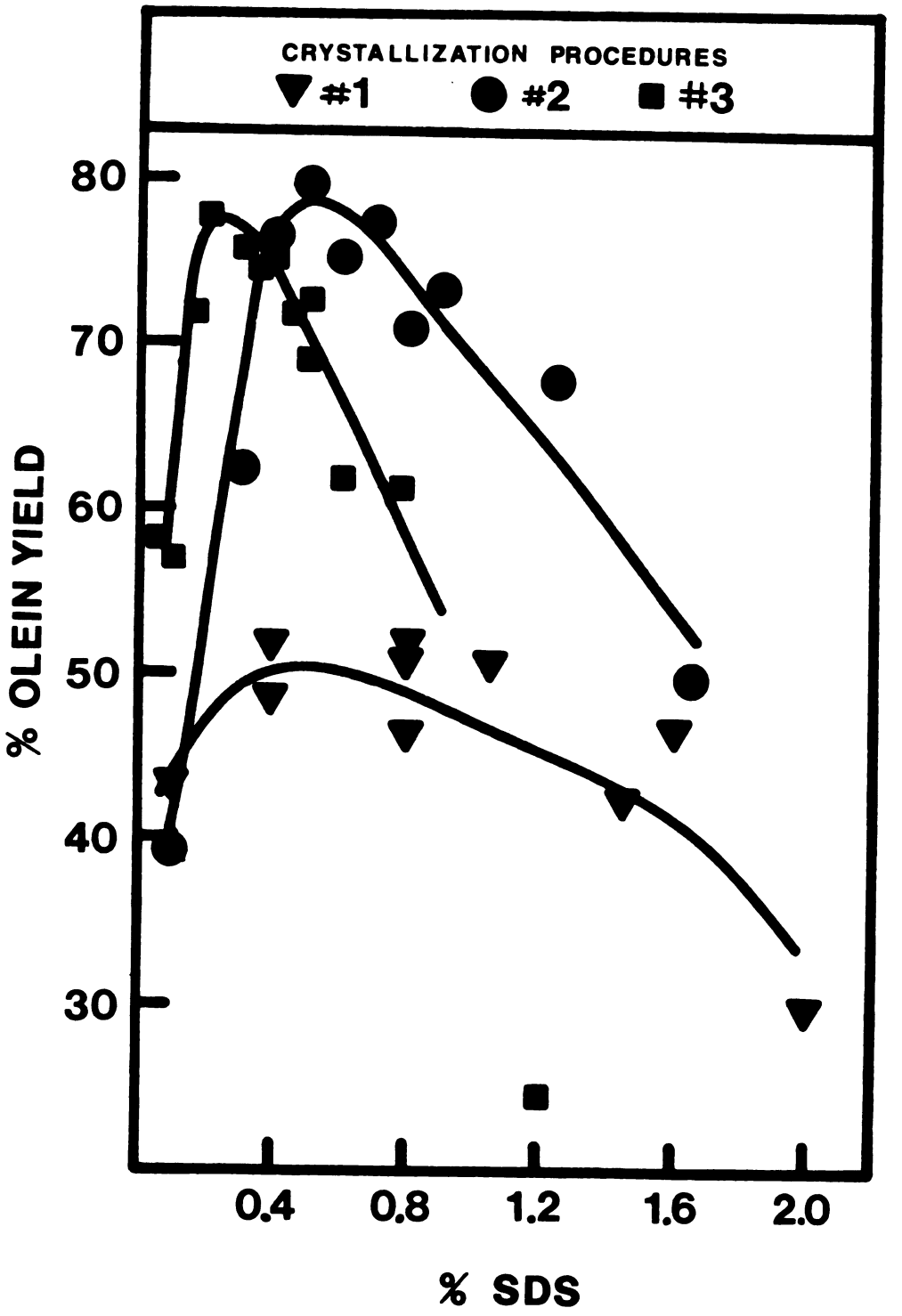


Figure 4.7 Separation Results from Three Different Crystallization Procedures.

0.50 percent. At concentrations above 0.50 percent olein yield was reduced by the formation of emulsion. At SDS concentrations below 0.30 percent, the olein yield was lowered due to ineffective wetting of the crystals into the aqueous phase.

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

The maximum yield from crystallization procedures two and three was essentially the same. The procedure one crystals were not desirable for a good chemical separation. The difference in the maximum olein yield for procedures two and three was insignificant. The crystal mass was almost identical for the two cases based on the maximum yield of olein. The stearin fraction left in both cases was free of olein because it had no yellow color, which indicated the presence of olein. At an olein yield of 5 percent below the maximum olein yield, the yellow color was easily seen in the stearin fraction from both procedures.

The separation data were taken as evidence of crystal size directly affecting the amount of surfactant required for the separation. The crystal sizes and SDS required are further analyzed in section 4.5.

4.4 Electrolyte Concentration Effects

The choice of sodium citrate was chosen as the electrolyte for the detergent solutions because of favorable status as a food additive and as an antioxidant for fats (Dugan, 1976). The performance of sodium citrate was no better or worse than other suitable electrolytes such as sodium sulfate.

The role of the electrolyte, sodium citrate, concentration in the separation step was investigated by using various electrolyte concentrations for the separation step while holding other variables constant. The weight ratio of the detergent solution to partially crystallized tallow was 0.93. The weight of sodium dodecyl sulfate was 0.45g per separation. The results are shown in Figure 4.8. The olein yield increased as a function of the electrolyte concentration until an electrolyte concentration of 5.0 percent was reached. The olein yield neither increased nor decreased above an electrolyte concentration of 5.0 percent, but at concentrations above 8.0 percent increased amounts of emulsified olein were noted. The role of the electrolyte is further discussed in section 4.6.

4.5 Analysis of Separation Results

The calculated total surface areas for the crystals of procedures two and three show that procedure two produced crystals with 1.9

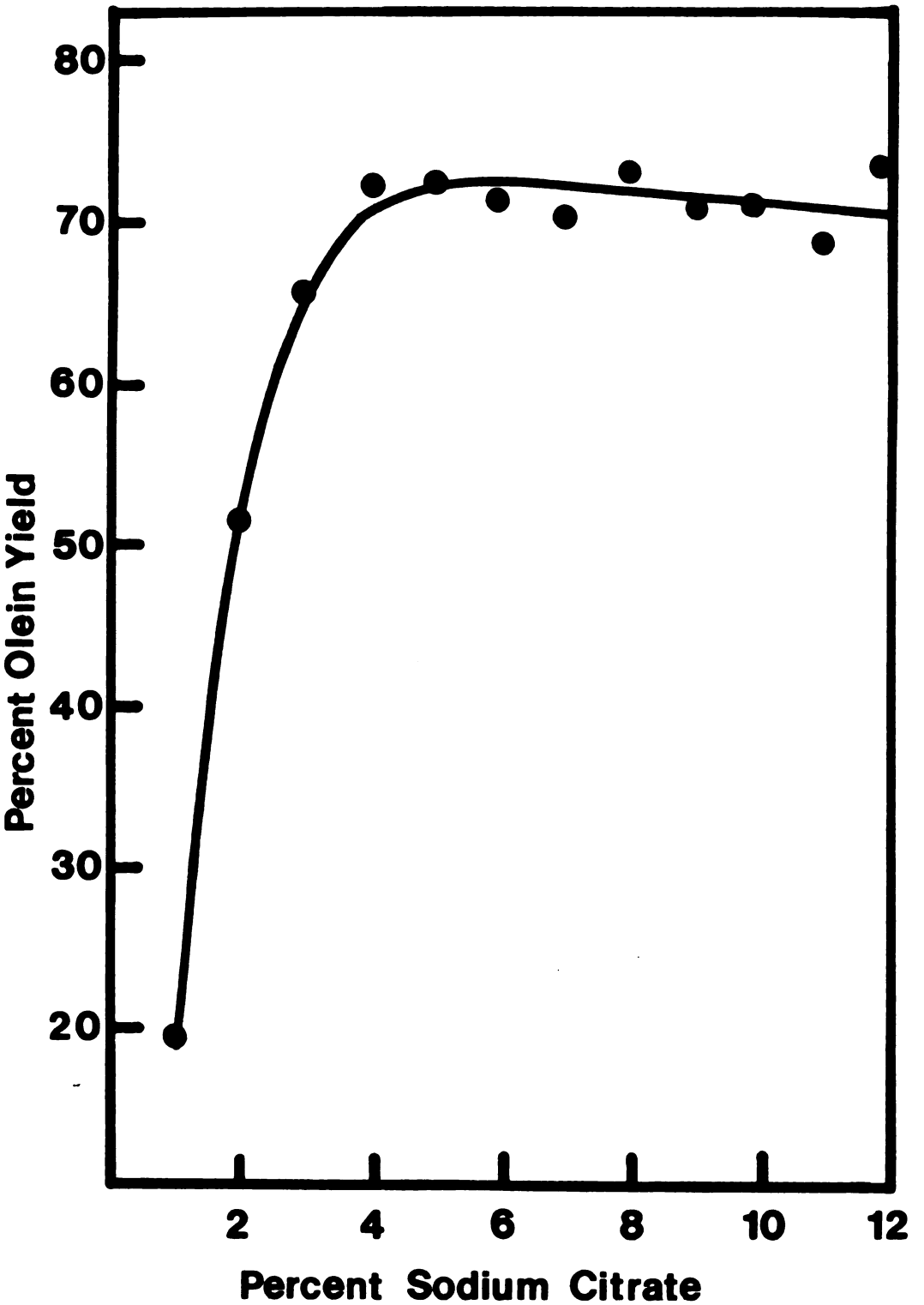


Figure 4.8 Olein Yield as a Function of the Electrolyte Concentration in the Detergent Solution at 40 °C. Tallow Weight was 170 g per sample; SDS Weight was 0.45 g per sample; and the Weight Ratio of Detergent Solution to Tallow was 0.93.

times as much surface area per unit volume as procedure three. The numbers used for this calculation are shown in Table 4.1. The optimum SDS levels for procedures two and three differed by a factor of 2.5, based on the concentration, or weight, of surfactant required. The ratio of optimum surfactant concentrations was dependent on the specific concentrations used. Therefore, this ratio could be different if a more continuous range of surfactant concentrations was used. Since the calculated surface area for procedures two and three differed by about the same factor as the difference in the required weight of SDS, crystal surface area may be the parameter determining the amount of surfactant required for a successful fractionation.

To help determine the effect of crystal surface area on the separation step, experiments were performed to determine where the SDS was distributed after the dispersion of tallow and detergent solution had formed. The method of Moore and Kolbesen (1956) for the colorimetric determination of surfactant in the aqueous phase 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 (Rek and Appel, 1979).

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. percent SDS, with an electrolyte concentration of 5.0 percent, would completely emulsify all the

olein present. The aqueous and olein mixture was centrifuged to see whether this processing broke the emulsion and it was found that it did not.

Wetting the solid is preferred by the SDS to remaining in solution or emulsifying the oil. The above results supported this conclusion. This means that very little surfactant was left in the aqueous solution during a successful fractionation. The SDS was almost all at the crystal surface. In cases where too much surfactant was used, the surfactant completely coated the crystal surface and the excess surfactant went into solution and caused emulsified olein product.

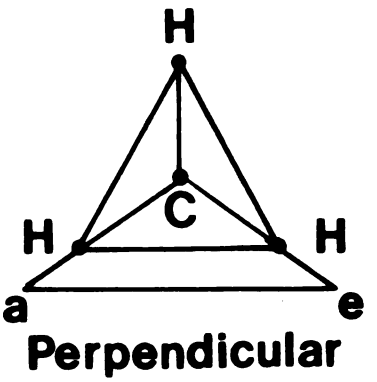
4.6 Surface Coverage by SDS

The electrolyte, sodium citrate, 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 an charged sulfate end. Calculations show (See Table 4.2) that the surfactant molecules had the necessary available area to have coated the crystal surface. Figure 4.9 shows the SDS models used to calculate the crystal surface area occupied by a molecule in the two extremes of possible orientations. Standard molecular bond lengths were used in the calculations (Streitwieser and Heathcock, 1976).

Table 4.2

Calculation of Crystal Surface Area per Surfactant Molecule

	Procedure Two	Procedure Three
Crystal surface area, m^2	28×10^{-12}	95×10^{-12}
Crystal weight/crystal, g	1.89×10^{-12}	1.26×10^{-11}
Number of crystals per 200 ml aliquot	1.8×10^{13}	2.7×10^{12}
Total surface area, m^2	500	260
Optimum gmoles SDS per 200ml aliquot	1.73×10^{-3}	6.93×10^{-4}
gmole SDS per m^2 area	3.5×10^{-6}	2.7×10^{-6}
Crystal surface area per molecule SDS, $\mathring{A}^2$	47	61
Perpendicular area of SDS molecule	$3.5\ \mathring{A}^2$	
Parallel area of SDS molecule	$40\ \mathring{A}^2$	



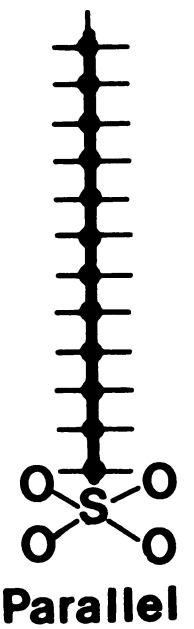


Figure 4.9 Simple Models for Calculating Surface Area Occupied by an SDS Molecule in Two Different Orientations.

The SDS molecules could be either perpendicular or partially parallel 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. Low surfactant concentration meant that there were not enough surfactant molecules to coat the crystals. Low electrolyte concentration meant that the surfactant molecules could not be aligned properly.

4.7 CMC for Detergent Solutions Used for Detergent Fractionation

Detergency theory requires the surfactant concentration to be above the critical micelle concentration (Harris, 1958). Surface tension was measured to determine the critical micelle concentration for SDS solutions with and without electrolyte added. Figure 4.10 shows the surface tension measurements, for the two cases, versus surfactant concentration. One case was with the 5.0 percent sodium citrate in solution and one case was with no electrolyte in solution. The critical micelle concentration for the solution with only surfactant occurred at approximately 0.1 percent at the test temperature of 40 °C. The critical micelle concentration for the surfactant and electrolyte solution was at 0.01%. This shows that the concentration of surfactant required for detergency action was very low. This means that most of the surfactant was at the crystal surface and the solution still had detergency properties.

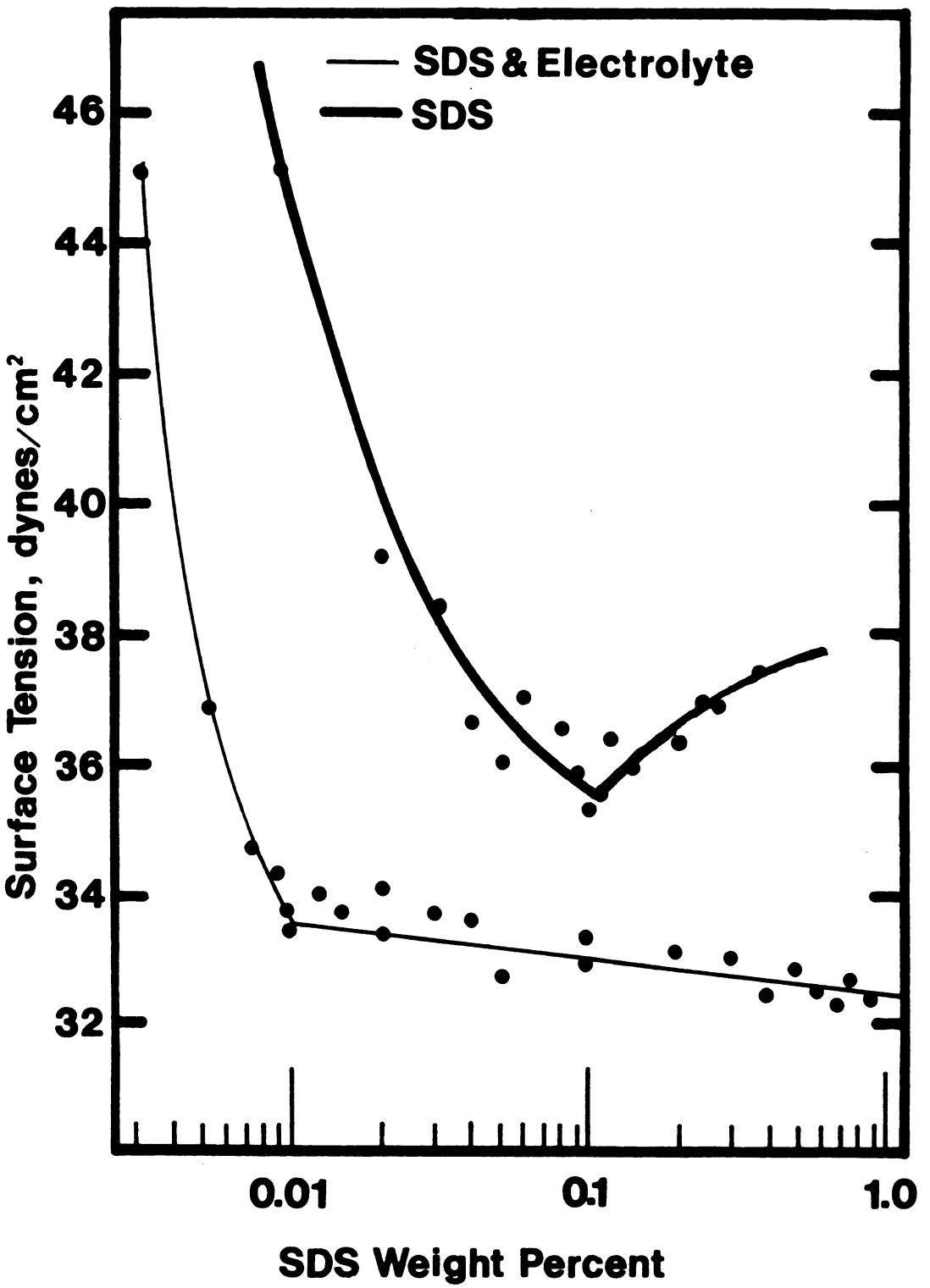


Figure 4.10 Surface Tension of Two Detergent Solutions as a Function of SDS Concentration at 40 °C.

This supported the dependence of the separation solution strength on the surface area of the crystals.

At sufficiently high initial SDS concentrations the crystal surface became saturated or completely covered with the surfactant. The amount of SDS required was dependent on the surface area of the crystals, which depended on the crystallization conditions. The added electrolyte helped orient the surfactant and provided an ionic solution to wet the crystals into the aqueous phase. Inefficient wetting occurred when the electrolyte or SDS concentration was too low. If the concentration of SDS was too high emulsified product resulted.

4.8 Olein yield as a function of the detergent solution to tallow weight ratio

Figure 4.11 shows the results of experiments conducted using various detergent solution to tallow weight ratios 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 aqueous volumes used should have given a maximum olein yield at almost the same weight of surfactant. The expected result was observed closely. The maximum olein yield was at 0.6 g SDS for the 0.62, 0.78 and 0.93 detergent solution to tallow ratios. The

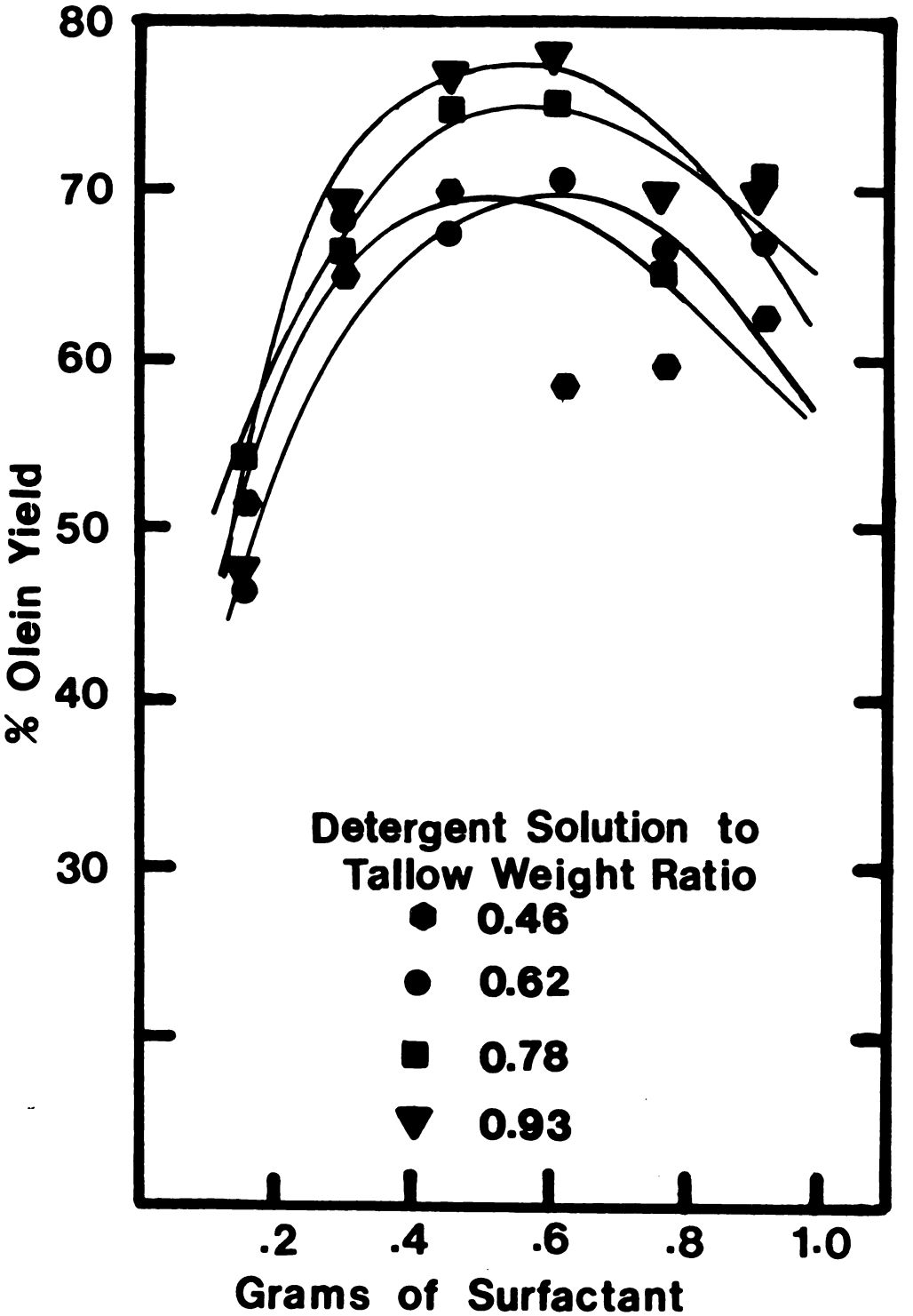


Figure 4.11 Correlation of the Olein Yield with the Weight of SDS Used. Each Curve Represents a Different Weight Ratio of Detergent Solution to Tallow Weight. 5.0 % Sodium Citrate was in the Detergent Solution.

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 0.45g was very close to the olein yield for those ratios at 0.60g surfactant. These results supported the conclusion that the surface area of the crystals determined the required amount of surfactant.

Another interesting feature of the results shown in Figure 4.11 was that the amount of aqueous solution used had a great effect on the olein yield achieved. The olein yield was still rising at the maximum detergent solution to tallow ratio used. The maximum olein yields were 78.0%, 75.3%, 70.6% and 70.1% at detergent solution to tallow ratios of 0.93, 0.78, 0.63 and 0.46, respectively. The reason for the observed effect might be related to the volume available for the transfering crystals to occupy or to overall dispersion viscosity effects.

Various detergent solution to tallow weight ratios were used to show the effect of this ratio on the olein yield over a wide range of values. The results of these tests are compiled in Figure 4.12. It shows that the olein yield rose until a detergent solution to tallow weight ratio of 1.39 was exceeded. The yield of olein was 79.4 percent for the detergent solution to tallow weight ratio of 1.39. Four trials make up each of the data points used in Figure 4.12. The standard deviation of the points is shown in Table 4.3.

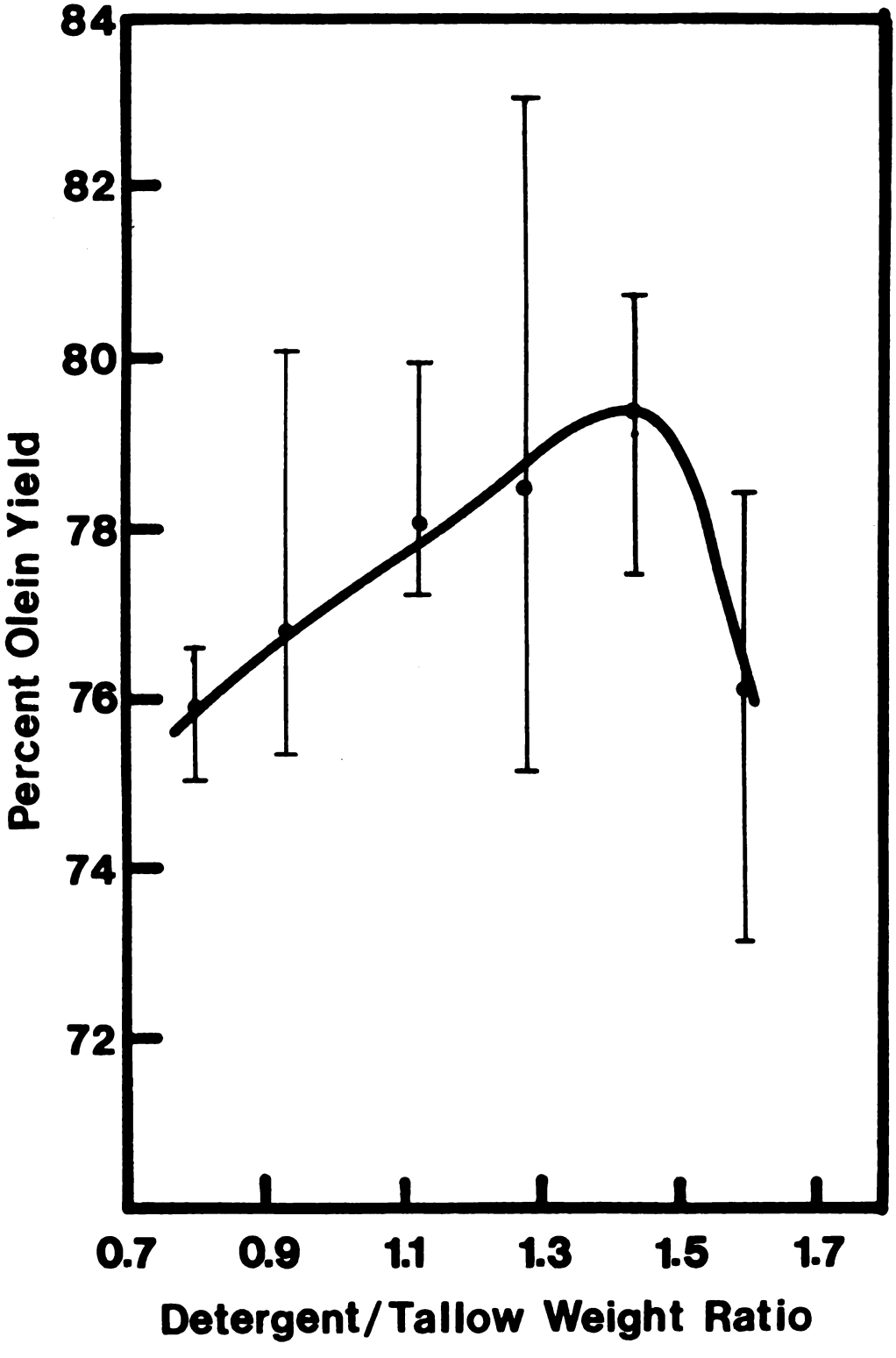


Figure 4.12 Olein Yield as a Function of the Weight Ratio of Detergent Solution to Partially Crystallized Tallow. 0.45 g SDS per sample and 5.0 % Sodium Citrate was in the Detergent Solutions.

Table 4.3

Standard Deviations for Figure 4.12

Weight Ratio	Data Value	Standard Deviation
0.80	75.85	0.70
0.95	77.13	1.96
1.14	78.08	0.79
1.29	78.48	2.92
1.45	79.38	1.23
1.58	76.13	1.99

The drop in olein yield shown in Figure 4.12 when the detergent solution to tallow ratio was increased to 1.54 should not be interpreted to mean that increased detergent solution amounts cause reduced olein yield. It is believed that the olein yield levels off in this detergent solution to tallow ratio range. The lower than expected olein yield was due to the collection methods employed after the separation had been accomplished by centrifugation. The olein was poured off from the stearin layer which formed over the aqueous layer. As the aqueous layer became larger the stearin layer in each centrifuge tube became thinner. Eventually the layer became thin enough that pouring the olein off the top of the stearin layer broke the stearin layer. This made collecting all the olein difficult, which resulted in low olein yields.

The olein yield reached a maximum because the stearin became totally white at a detergent solution to tallow weight ratio of about 1.40. If olein remained trapped in the crystals a yellowish color was observed. This was observed at detergent solution to tallow ratios below 1.00.

The relationship between the detergent solution to tallow weight ratio and the olein yield was due to viscosity or volume available for crystals effects. The increased aqueous phase could lower the dispersion viscosity resulting in increased yields. The increased aqueous phase could have provided a larger volume into which the crystals were wetted. The rheological properties of the various

weight ratios of detergent solution to tallow were studied in light of the above information.

4.9 Torque Measurements

The collection of rheology data was controlled by a data collection program for the HP-85 microcomputer. Torque versus time data were collected as shown in Figure 4.13. It shows torque versus time data collected for a dispersion mixture with a weight ratio of detergent solution to tallow of 0.50. These data were collected to insure a uniform dispersion was formed and to check the time dependent behavior of the suspension.

Although the dispersion was initially mixed, the initial mixing was not complete and the decrease in the torque with time was caused by the separation process itself and continued mixing. The viscosity decreased for 20 to 30 minutes and then came to a constant value. This was the observed pattern for all dispersions observed. The appearance of the dispersion was less grainy after the rheology testing. This indicated that oil-crystal groups or agglomerates were broken apart during the mixing.

The total mixing time was 60 minutes which was equal to the time normally allowed for the dispersion to be formed. The level torque portion of the curve indicated that the rheological properties of the dispersion could be evaluated independent of time. Therefore, the rheological properties of the dispersion after the sixty minute

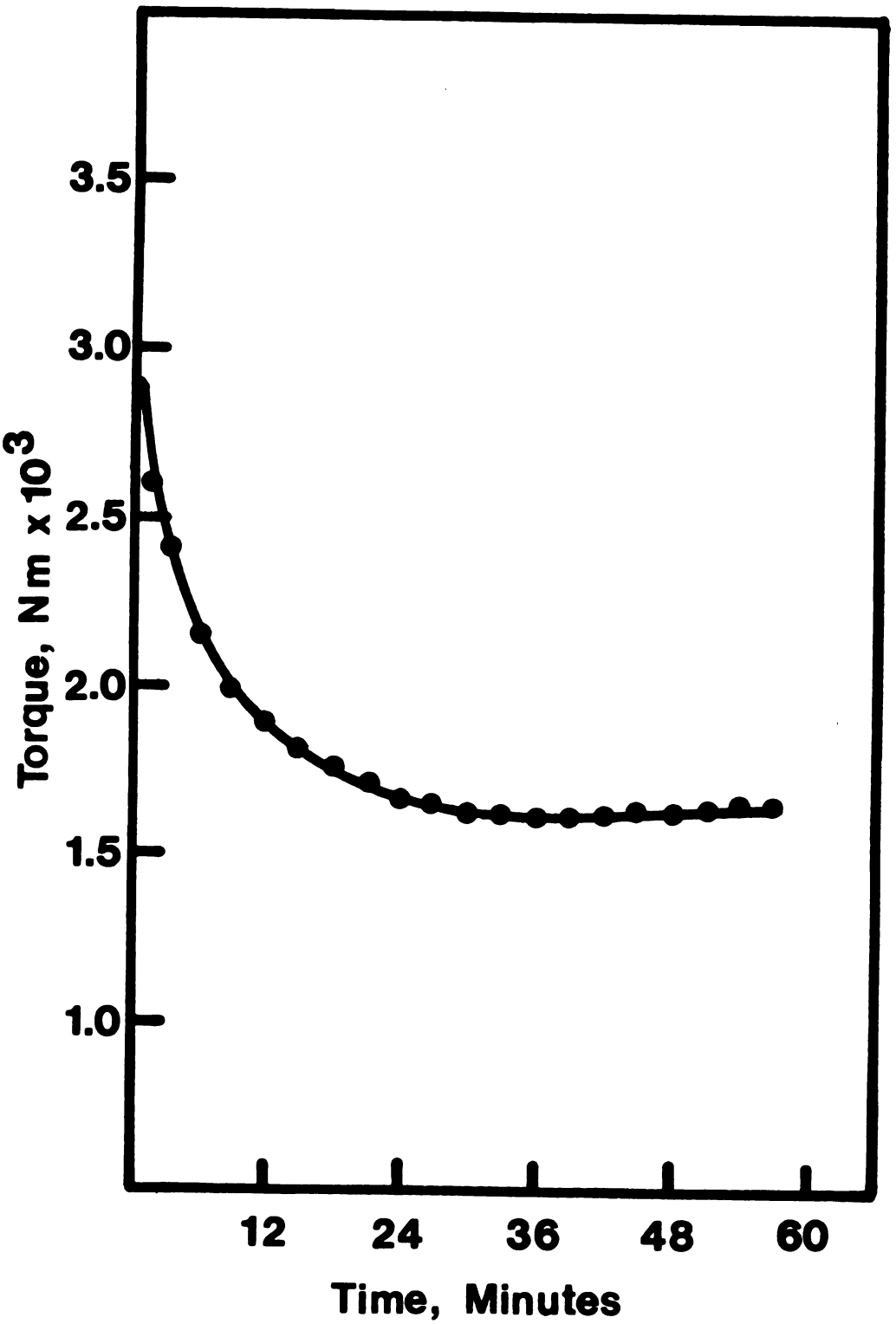


Figure 4.13 Torque Measured as a Function of Time for a Dispersion at a Rotation Rate of 120 rpm.

torque test were representative of the dispersion as it entered the centrifuging operation of a normal fractionation.

The rheological properties of the dispersion were recorded by measuring the torque as a function of the rotation rate. Figure 4.14 shows the torque values collected as a function of the rotational rate. The dispersion used was the same fluid that generated the data for Figure 4.13. The data was then used to determine an apparent viscosity at the chosen rotational rate of 60 rpm. Since the dispersion was non-Newtonian any viscosity was dependent on the shear rate applied to the fluid.

The data were used to construct a plot of the ln(torque) versus the ln(rotation rate). A computer program actually did the analysis. The slope of the plot was determined and was the flow behavior index n. The consistency coefficient was calculated using previously determined standard fluid values, the torque at 60 rpm of the dispersion and the n value of the dispersion to yield K according to equation (4.1).

$$K_x = (M_x(\omega k')^{n_y} K_y)/(M_y(\omega k')^{n_x}) \qquad (4.1)$$

With both K and n determined an apparent viscosity for the dispersion being tested was calculated from equation (4.2).

$$\tau = K(\gamma_a)^n \qquad (4.2)$$

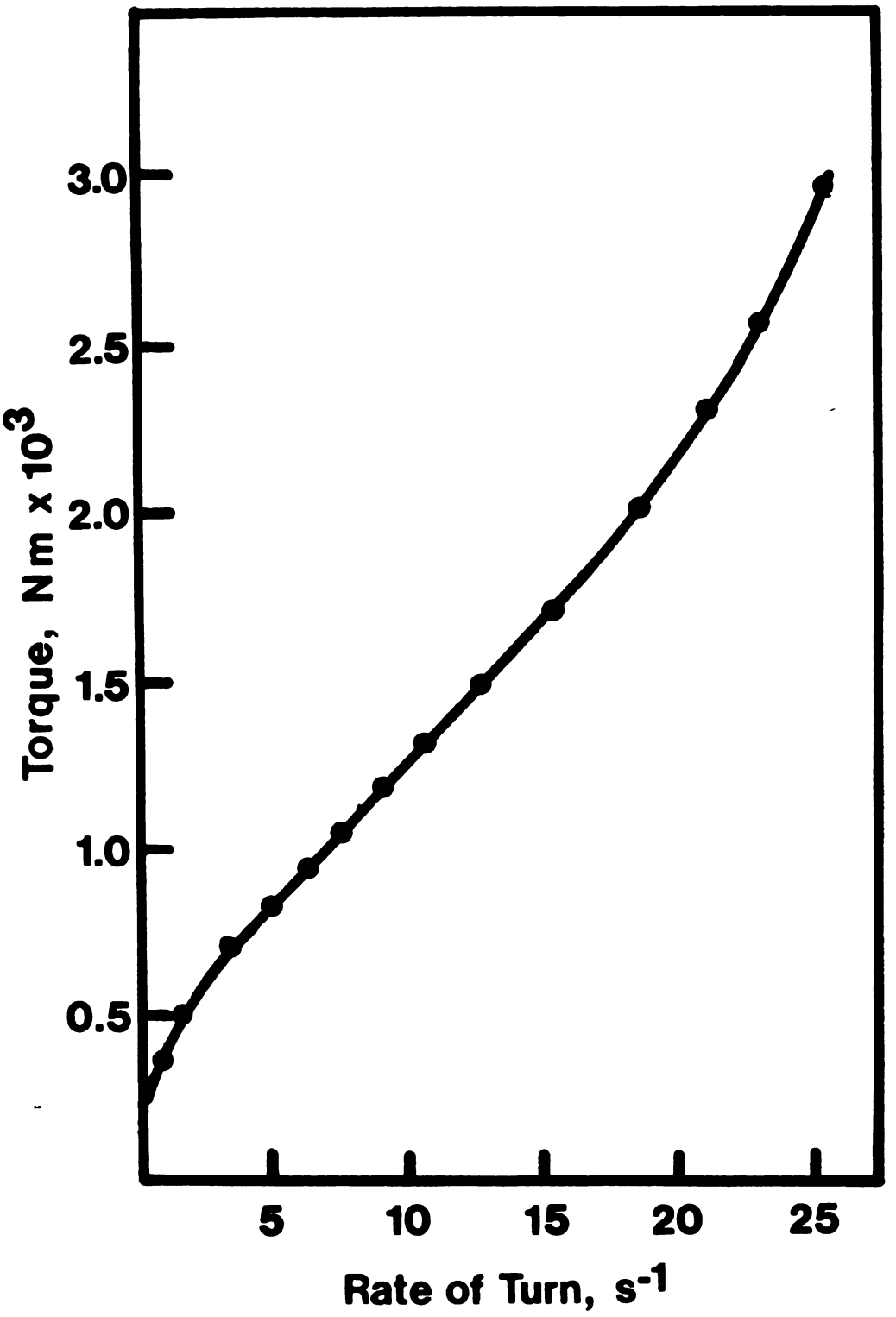


Figure 4.14 Torque Measured as a Function of the Rotation Rate for a Dispersion.

These calculations required that the dispersion was a power law fluid in the range of rotational rates used and the relationship between shear rate and rotational rate shown by Rieger and Novak (1973) was valid. Both of these conditions were satisfied. The values shown in Figure 4.14 yielded a straight line when plotted on log-log graph paper. Steffe and Ford (1985) showed that the Rieger and Novak (1973) relationship holds for the paddle mixer used for these experiments.

Measurements were made for various weight ratios of detergent solution to tallow at two different times with the same partially crystallized tallow to determine the reproducibility of the torque versus rotational speed measurements. It was important to use tallow partially crystallized from the same batch with the same time-temperature history because exactly duplicating a partial crystallization was difficult. This is confirmed by data developed later in this paper (See Figure 4.17).

Figure 4.15 shows two sets of data for detergent solution to tallow weight ratios of 0.50, 0.80, 1.14 and 1.50. The relative error, based on the torque reading, between the two different data sets for a given ratio ranges from one percent to about 28 percent at 60 rpm. However, the readings vary 125 percent from the low to high ratios tested. It was noted that the dispersions had a large amount of irregular solid particles present. Therefore, the reproducibility of the measurements was thought to be good.

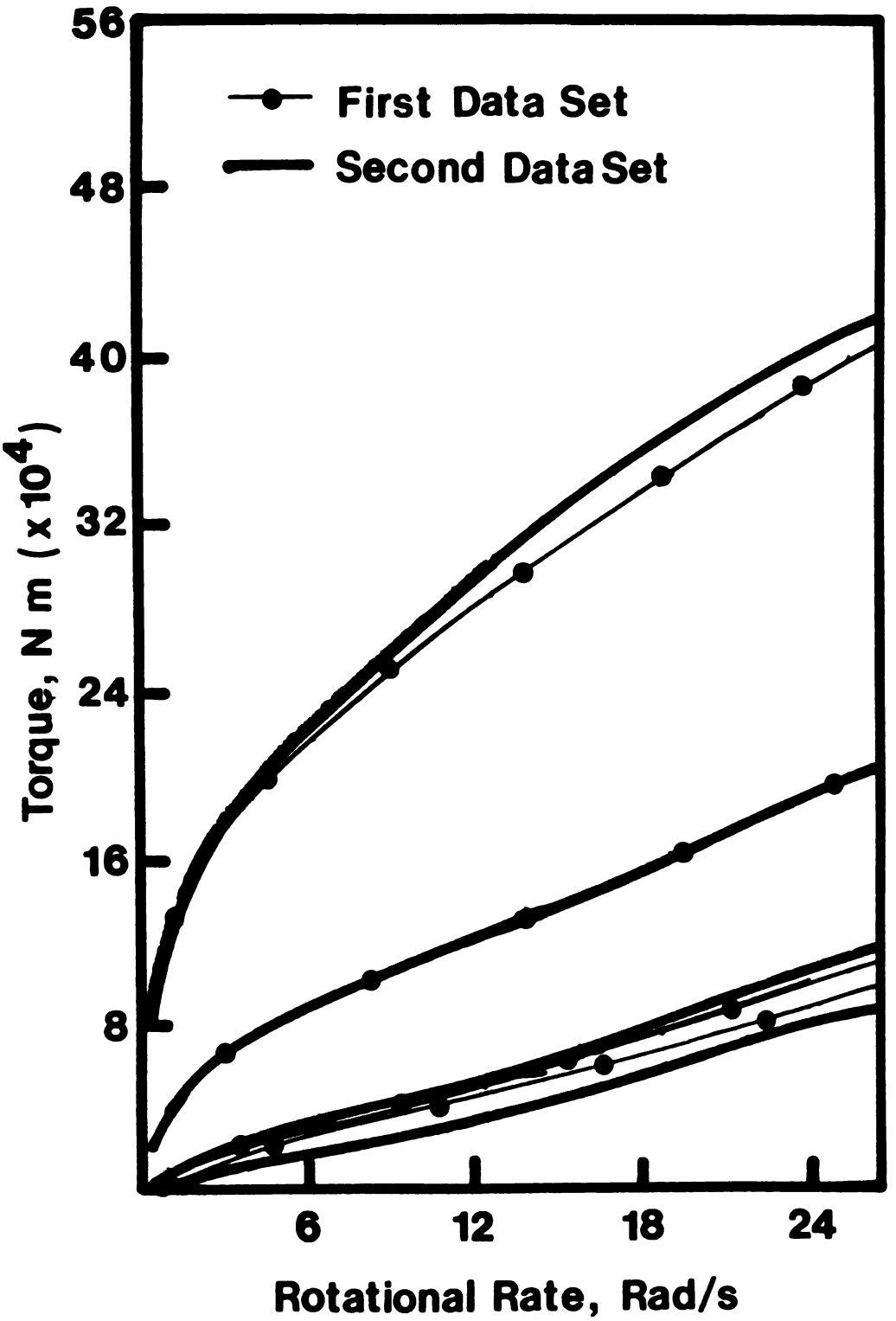


Figure 4.15 Precision Measurements of the Torque as a Function of the Rotation Rate of the Paddle Mixer. Two sets of Data are Plotted to show the Reproducibility of the Measurements. The Curves Represent Detergent Solution to Tallow Weight Ratios of 1.50, 1.14, 0.80 and 0.50 from Low to High Torque Values.

4.10 Apparent viscosity of the dispersions

The apparent viscosity for various detergent solution to tallow weight ratio dispersions at a rotational rate of 60 rpm is shown in Figure 4.16. The natural logarithm of the apparent viscosity was plotted as a function of the olein yield. The olein yield increased as the apparent viscosity was lowered. A dispersion viscosity of about 0.08 Pa s or lower was needed for the maximum olein yield of 79 percent.

There was clearly a relationship between the viscosity of the dispersion before centrifugation and the olein yield obtained after centrifugation. The variation in olein yield was produced by using various weight ratios of detergent solution to tallow. This meant that in addition to controlling the surfactant and electrolyte concentrations, the viscosity of the dispersion formed had to be controlled. This was accomplished by using the appropriate detergent solution to tallow ratio in the dispersion step.

Accepted methods for correlating viscosity as a function of volume percent solids could not be applied to this system (Jeffrey and Acrivos, 1976). One of the methods was the one originally proposed by Einstein (1956) for inert spherical particles of small size compared to the fluid volume in which they were suspended. The crystals of tallow were determined to be not suitable for this type of correlation (eqn. 4.3).

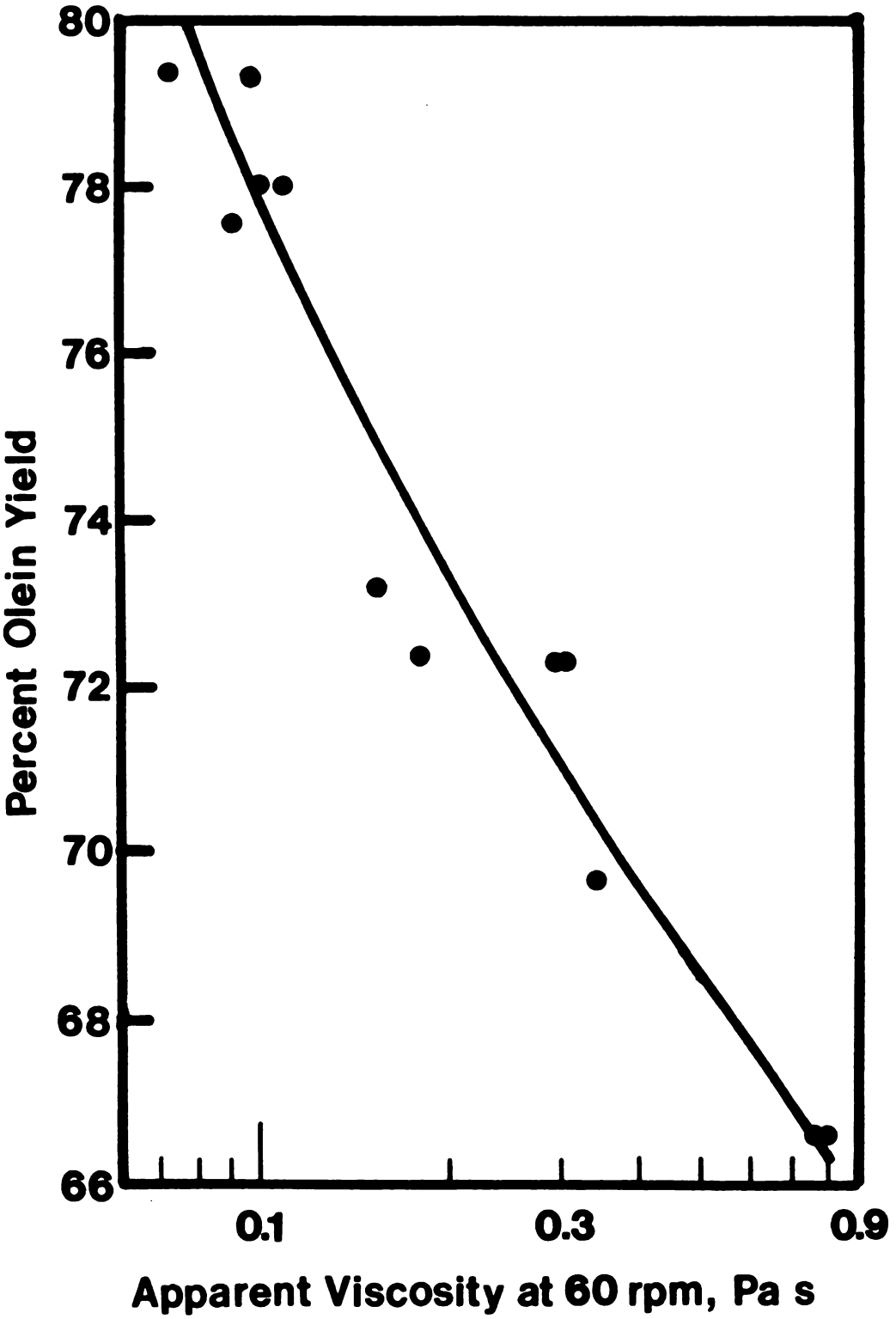


Figure 4.16 Dispersion Apparent Viscosity Plotted Versus the Olein Yield. Various Weight Ratios of Detergent Solution to Partially Crystallized Tallow were used to Produce the Apparent Viscosity Changes.

$$\eta_r = 1+DS, \qquad (4.3)$$

The value of D for inert spheres in solution is 2.5. Correlating the detergent solution-tallow dispersion in this manner yielded D values of about 90. The aqueous phase was the continuous phase in the dispersion. The viscosity was reduced by the viscosity of the detergent solution-olein mixture that resulted from removing the solids from the dispersion. This was chosen because it accurately reflects the medium the crystals encounter.

The correlation did not hold for crystals produced by two different partial crystallizations. Each partial crystallization produced slightly different crystal sizes and numbers of crystals because of the sensitivity of the nucleation and growth of the crystals to the temperatures and processing times used. These slight processing differences caused large variations in the rheological properties of dispersions containing the various partially crystallized tallows.

The tallow crystals were long thin needles with a L/D ratio of about 75. They existed as single crystals and in spherical agglomerates. The spherical agglomerates were far from being inert as the spiny protusions certainly caused them to interact with one another. They may account for a larger effective volume fraction than was ordinarily calculated due to voids in the spherulitic agglomerates occupied by olein. Predicting these interactions and effective solids volume was beyond the scope of current rheological information. Many questions about the behaviour of inert spheres

and cylinders in dispersions have still not been answered (Cheng, 1984; Chaffey and Porter, 1984).

The apparent viscosity has been plotted as a function of the volume percent solids in Figure 4.17. Four different partial crystallizations were used for the dispersion data gathered. Each of the four different symbols represents one of the four different partial crystallizations. Each partial crystallization gave dispersions with their own rheological properties. The trend was for the apparent viscosity to increase as the volume percent solids increased.

The "protective colloids" suggested by Stein and Hartmann (1957) were not tried in this research. They probably were used to adjust the dispersion viscosity to avoid emulsion formation. It would seem that increasing the aqueous viscosity was opposite to the results obtained but the real function of the protective colloids may have been to tie-up left over surfactant so that it could not emulsify the olein.

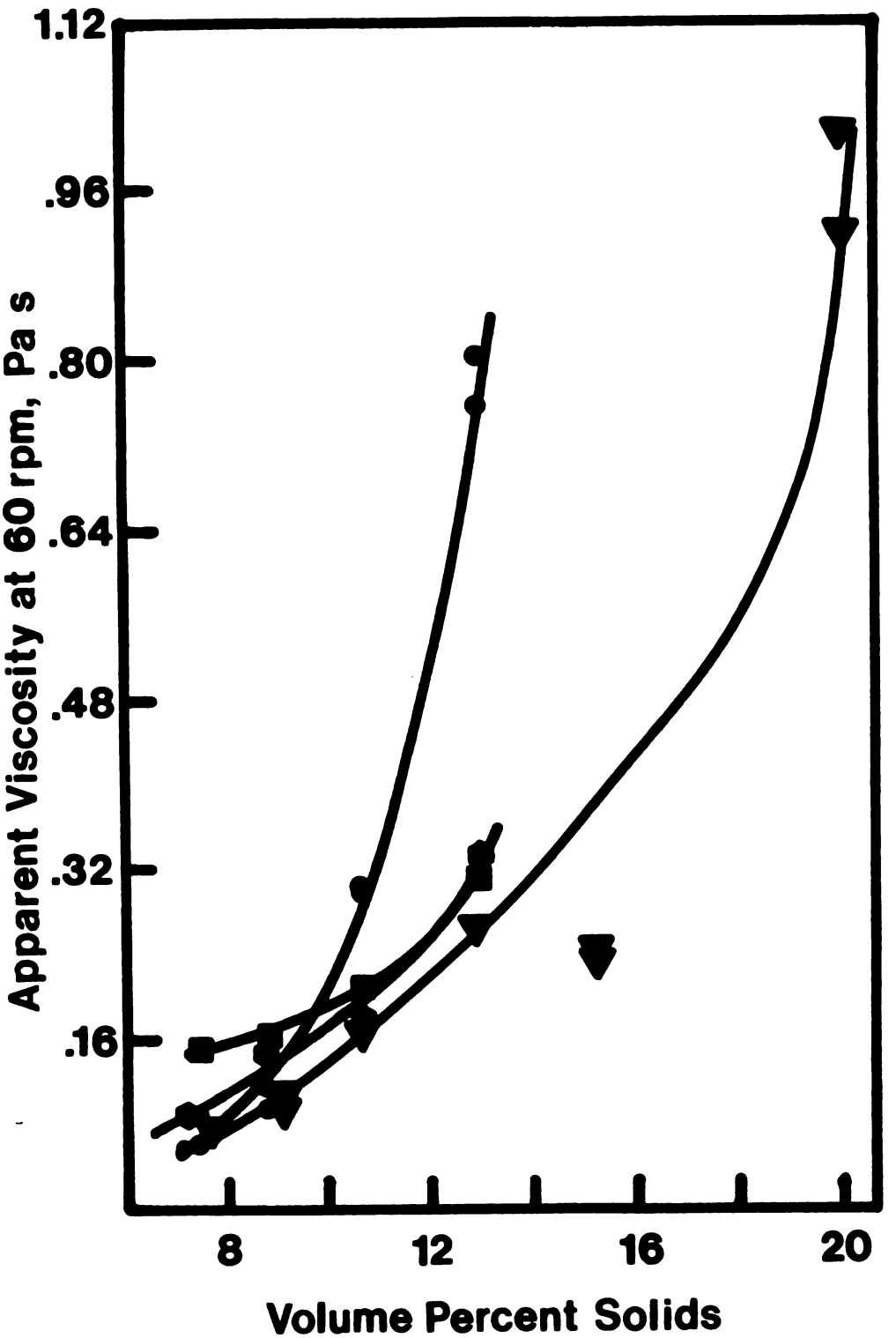


Figure 4.17 The Apparent Viscosity of the Dispersion as a Function of the Percent Solids in the Dispersion. Four Different Sets of Data Shown; Each Corresponds to a Separate Partial Crystallization.

CONCLUSIONS

Detergency phenomena was found to explain the separation mechanism. At sufficiently high initial SDS concentrations, the crystal surface became saturated or completely covered with the surfactant. The amount of SDS required was dependent on the surface area of the crystals, which depended on the crystallization procedure. The added electrolyte helped orient the surfactant and provided an ionic solution to wet the crystals into the aqueous phase. If the concentration of SDS was too high emulsified olein product resulted.

The crystals formed during the crystallization stage affected the separation results. The required surfactant quantity was determined to depend on the surface area of the crystals produced. Increased amounts of surfactant were required for crystals with more surface area. The relationship was directly proportional meaning twice as much surface area required twice as much surfactant. Use of a very rapid temperature drop (crystallization procedure one) to crystallize the tallow resulted in more crystal mass than more slowly cooled crystallization procedures (crystallization procedures two and three). The larger crystal mass affected the separation in two ways. Since more crystal mass was present, the chemical difference between the two fractions was less than for the fractions produced by a more slowly cooled tallow. The surfactant required for separation was increased

because of the large surface area of the small crystals.

The electrolyte concentration affected the olein yield. Low electrolyte concentration reduced the ability of the surfactant to wet the crystals into the aqueous phase. A minimum level of sodium citrate for maximum separation efficiency was 5.0 % by weight of the detergent solution. Using more electrolyte than necessary showed a tendency to increase the formation of emulsified olein.

The ratio of detergent solution to tallow weight affected the olein yield. If this ratio was too low maximum olein yield was not obtained. The olein yield increased as the detergent solution to tallow weight ratio was increased until the maximum olein yield was reached. For the crystals from procedure three the optimum detergent solution to tallow ratio was 1.4. Ratios above 1.4 gave the same olein yield as the 1.4 ratio.

Maximum olein yield was achieved at a low apparent viscosity. An apparent viscosity at 60 rpm of 0.8 Pa s was observed when maximum olein yields were obtained. The apparent viscosity was dependent on the crystals formed during the partial crystallization of tallow and the weight ratio of detergent solution to tallow.

RECOMMENDATIONS

Research of the detergent fractionation has left some ideas for exploration. These ideas relate to the development of the process and its control as well as fundamental concepts that need to be developed. One important factor, especially for process development, is the world-wide slump in commodities prices. The price of competing fats and oils have come down dramatically from the early 1980 highs. This means that unless a superior result is obtained by using a fractionated oil product, the economic incentive to use the fractionated oil does not exist.

For some countries, where fractionation plants for palm oil and beef tallow exist, economic limitations and national shortages make continued fractionation activities rational. For other countries, such as the United States, starting up of fractionation processes is not economically warranted now. Because of the above reason, recommendations concerning process piloting and process control are not priority research topics in the opinion of this researcher. They are included in the recommendations made because at some future time they may be more desirable.

1. The size of the crystals, especially the diameter, needs further investigation. The SEM could be used for the size determination if a suitable crystal replication technique can be developed. One suggestion would be to find a material which is

liquid at a temperature below 40 °C but could be solidified to form a replica of a mass of crystals. A polymer of some type might be the answer. It could be solidified and then the crystals could be dissolved away. The replica could then be viewed by the SEM.

2. The effect of the crystallization procedure on the processing requirements needs further investigation. A pilot scale partial crystallization system is needed to test process variable control as a function of the crystallization procedure. A scraped wall vessel and a jacketed vessel are needed to develop various crystallization results. The dispersion would then be formed in the jacketed vessel and separation results could be estimated by taking a small sample of the dispersion to be centrifuged, if large scale centrifugation facilities were not available. The crystallization requirements and the process control necessary to ensure an efficient separation could be determined in detail from this system.

3. The mixer viscometer might be used to control the dispersion conditions. The olein yield dependence on the apparent viscosity could be further tested with the pilot scale system described above.

APPENDIX A.

Table A.1.

Separation Results from Three Different Crystallizations

Figure 4.7 Data.

Separation conditions: 1. Various surfactant concentrations, 2. 5.0% sodium citrate for electrolyte, 3. Weight ratio detergent solution to tallow = 0.62 and, 4. Crystallization procedure one used.

7-2-84 to 7-18-84 data

SDS Weight (grams)	Olein Yield (percent)
0.10	43.4
0.40	51.9
0.40	48.3
0.80	46.1
0.80	51.9
0.80	50.8
0.80	45.6
1.10	50.4
1.40	42.2
1.60	46.6
2.00	0.0
2.40	30.0

Table A.1. continued

Separation conditions: 1. Various surfactant concentrations, 2. 5.0% sodium citrate, 3. Weight ratio of detergent solution to tallow = 0.62 and, 4. Crystallization procedure two used.

SDS Weight (grams)	Olein Yield (percent)
0.10	39.5
0.30	62.2
0.40	76.2
0.50	79.5
0.60	75.0
0.70	77.2
0.80	70.4
0.90	72.9
1.30	67.6
1.70	49.2

Table A.1. continued

Separation conditions: 1. Various surfactant concentrations, 2. 5.0% sodium citrate, 3. Weight ratio of detergent solution to tallow = 0.62 and, 4. Crystallization procedure three used.

SDS Weight (grams)	Olein Yield (percent)
0.05	58.1
0.10	56.9
0.15	71.7
0.20	77.8
0.20	77.6
0.30	75.6
0.35	74.1
0.40	75.2
0.45	71.4
0.50	72.6
0.50	68.6
0.60	61.5
0.80	61.3
1.20	completely emulsified

Table A.2.

Olein Yield as a Function of the Electrolyte Concentration in the Detergent Solution at 40 °C.

Figure 4.8 Data.

Separation conditions: 1. Surfactant weight 0.45g, 2. Various electrolyte concentration, 3. Weight ratio of detergent solution to tallow = 0.93, 4. Average sample weight = 170g and, 5. Crystallization procedure three.

1-14-85 to 1-16-85 Data.

Electrolyte Concentration	Olein Yield
2.0 %	51.4 %
4.0 %	72.3 %
6.0 %	71.5 %
8.0 %	73.2 %
10.0 %	71.4 %
12.0 %	73.8 %
1.0 %	19.6 %
3.0 %	65.9 %
5.0 %	72.4%
7.0 %	70.2 %
9.0 %	71.0 %
11.0 %	68.9 %

Emulsion observed at 9 to 12% concentrations.

Table A.3.

Preliminary Correlation of the Olein Yield with the Ratio of Detergent Solution to Tallow Weight.

Figure 4.11 Data.

Separation conditions: 1. Various surfactant weights, 2. 5.0% sodium citrate, 3. Weight ratio of detergent solution to tallow, 4. sample weight = 165 g and, 5. Crystallization procedure three.

9-18-84 to 10-5-84 Data

SDS Weight (grams)	Aqueous Volume (ml)	Olein Yield (percent)
.1565	75	51.8
.1565	100	46.4
.1565	125	54.1
.1565	150	46.0
.3079	75	69.6
.3069	75	60.0
.3069	100	66.2
.3079	100	70.0
.3069	100	66.2
.3069	125	66.7
.3079	125	67.1
.3069	125	64.8
.3079	150	71.7
.3069	150	66.2
.4567	75	70.1

Table A.3 continued

SDS Weight (grams)	Aqueous Volume (ml)	Olein Yield (percent)
.4567	100	67.7
.4567	125	74.1
.4567	150	77.0
.6262	75	58.4
.6262	100	70.6
.6102	125	75.3
.6102	150	78.0
.7717	75	59.7
.7717	100	66.3
.7691	125	65.3
.7691	150	69.8
.9174	75	62.5
.9174	100	65.3
.9174	125	72.0
.9174	150	70.5

Table A.4

Calibration Data for Ring Method of Surface Tension Determination for the Cenco Tensiometer.

Calibration of Tensiometer with teflon coated platinum ring.

Weight	Tension (dynes/cm)
4-22-85 data	
400 mg	30.8
500 mg	38.0
600 mg	46.0
700 mg	53.5
800 mg	61.2
900 mg	68.7
5-19-85 data	
400 mg	30.8
500 mg	38.4
600 mg	46.0
700 mg	53.7
800 mg	61.5
900 mg	69.0
1000 mg	76.7

Distilled Water measurements (dynes/cm) at 28 °C.

70.9 71.2

70.9 70.8

70.8 71.3

Actual value at 28 °C = 71.7 dynes/cm

Table A.5.

Surface Tension of a Detergent Solution as a Function of Surfactant Concentration at 40 °C.

Figure 4.10 Data.

Ring method of surface tension determination.

Aqueous solution containing 5.0 % sodium citrate and varying amounts of sodium dodecyl sulfate.

SDS concentration	Surface tension (dynes/cm)
	5-19-85 data
0.1	33.4, 33.3, 33.3, 33.3, 33.4.
0.05	32.6, 32.7, 32.6, 32.7, 32.8.
0.3	32.3, 33.1, 32.9, 33.4, 33.1.
0.4	32.3, 32.5, 32.5, 32.3, 32.5.
0.5	32.5, 33.2, 32.7, 32.8, 33.0.
0.6	32.8, 32.3, 32.4, 32.2, 32.6.
0.7	32.4, 32.3, 32.4, 32.2, 32.3.
0.8	32.2, 32.8, 32.8, 32.9, 32.9.
0.9	32.2, 32.3, 32.4, 32.4, 32.5.
1.2	32.7, 32.6, 32.4, 32.8, 32.7.
0.01	33.4, 33.8, 33.2, 33.3, 33.2.
0.2	32.9, 33.0, 33.1, 33.2, 33.2.
0.001	34.5, 34.2, 33.3, 33.5, 33.6.

Table A.5 continued.

Aqueous solution containing 5.0 % sodium citrate and varying amounts of sodium dodecyl sulfate.

SDS concentration	Surface tension (dynes/cm)
	5-23-85 data
0.002	52.5, 52.2, 50.8, 50.0, 49.5.
0.005	37.7, 36.5, 37.3, 36.7, 35.8.
0.0075	34.3, 35.6, 34.7, 34.5, 34.5.
0.009	34.2, 34.1, 34.3, 34.3, 34.4.
0.01	34.0, 33.8, 33.7, 33.8, 33.7.
0.011	34.0, 33.7, 33.7, 33.7, 33.6.
0.013	34.2, 34.0, 34.0, 33.9, 33.9.
0.016	34.1, 33.8, 33.6, 33.5, 33.6.
0.02	33.5, 33.2, 33.5, 33.4, 33.4.
0.03	33.8, 33.7, 33.7, 33.6, 33.5.
0.02	34.2, 34.0, 34.1, 33.9, 34.1.
0.04	33.7, 33.6, 33.4, 33.5, 33.6.
0.1	33.5, 33.2, 32.8, 32.6, 32.5.

Table A.5 continued.

Surfactant only solutions

SDS concentration	Surface tension (dynes/cm)
	5-21-85 data
0.1	35.7, 35.3, 35.3, 35.5, 35.4.
0.2	35.8, 36.7, 36.4, 36.2, 36.5.
0.3	37.2, 37.2, 37.1, 36.9, 37.0.
0.25	37.0, 37.0, 36.9, 36.5, 37.1.
0.2	36.8, 36.2, 36.0, 36.3, 36.2.
0.15	36.3, 36.0, 35.6, 35.6, 35.8.
0.05	36.2, 36.0, 35.9, 35.9, 36.0.
0.01	47.0, 43.4, 44.2, 44.5, 44.6.
0.02	39.4, 39.3, 39.7, 38.8, 38.8.
0.03	39.4, 38.6, 38.0, 38.6, 37.3.
0.04	36.5, 36.8, 36.8, 36.3, 36.7.
0.06	37.0, 37.0, 36.8, 37.3, 36.8.
0.08	37.2, 36.7, 36.4, 36.3, 36.0.
0.10	35.3, 35.2, 35.3, 35.4, 35.3.
0.11	35.8, 35.6, 35.5, 35.5, 35.5.
0.12	36.0, 35.6, 35.4, 35.5, 35.1.
0.13	36.5, 36.4, 36.3, 36.4, 36.4.
0.14	35.9, 35.8, 35.8, 35.8, 35.6.
0.2	36.7, 36.5, 36.5, 36.5, 36.5.

Table A.6.

Olein Yield as a Function of the Weight Ratio of Detergent Solution to Partially Crystallized Tallow.

Figure 4.12 Data.

Separation conditions: 1. 0.45g sodium dodecyl sulfate, 2. 5.0% sodium citrate, 3. various weight ratios of detergent solution to tallow and, 4. 164 g average tallow sample and, 5. Crystallization procedure three.

2-20-85 Data.

Weight ratio of detergent solution to tallow	Olein Yield
0.85	75.1 %
0.91	80.1 %
1.12	79.4 %
1.28	83.0 %
1.41	80.2 %
1.64	77.3 %
2-6-85 Data.	
0.74	75.2 %
0.96	75.4 %
1.10	77.9 %
1.31	76.8 %
1.44	80.7 %
1.54	75.7 %

Table A.6 continued.

2-13-85 Data.

Weight ratio of detergent solution to tallow	Olein Yield
0.80	76.5 %
0.96	75.4 %
1.17	77.3 %
1.33	75.2 %
1.49	77.5 %
1.57	73.1 %
2-18-85 Data	
0.83	76.6 %
0.95	76.4 %
1.16	77.7 %
1.23	78.9 %
1.44	79.1 %
1.56	78.4 %

Table A.7.

Torque Measured as a Function of Time for a Dispersion.

Figure 4.13 Data.

Detergent solution-tallow dispersion data obtained using mixer viscometer.

Dispersion conditions: 1. Partially crystallized tallow by procedure number three, 2. Weight ratio of detergent solution to partially crystallized tallow = 0.50 and, 3. The rotation rate used was 120 rpm.

4-4-85 Data

Time (minutes)	Torque (N-m x 10^3)
.6512	2.772
1.918	2.579
3.181	2.412
4.444	2.287
5.705	2.178
6.971	2.102
8.234	2.042
9.497	1.986
10.76	1.948
12.03	1.904
13.29	1.867
14.55	1.840
15.82	1.805
17.08	1.796
18.98	1.789
21.50	1.733

Table A.7 continued

4-4-85 Data

Time (minutes)	Torque (N-m x 10^3)
24.66	1.659
27.82	1.653
30.98	1.641
34.13	1.633
37.29	1.619
40.45	1.635
43.61	1.638
46.76	1.646
49.92	1.656
53.08	1.674
56.24	1.042 (60 rpm)

Table A.8.

Torque Measured as a Function of the Rotation Rate.

Figure 4.14 Data.

Dispersion data obtained using paddle mixer viscometer.

Dispersion conditions: 1. Partially crystallized tallow by procedure number three, 2. Weight ratio of detergent solution to partially crystallized tallow = 0.50 and, 3. Various rotation rates were used. 4-4-85 Data

Rotation Rate (Rad/sec)	Torque (N-m x 10^3)
.5371	.2659
.2105	.2905
.3075	.2952
.4045	.3356
.6151	.3546
.8255	.4026
1.036	.4268
2.086	.5794
4.166	.7854
6.278	.9535
8.374	1.116
10.48	1.295
12.59	1.484
15.75	1.763
18.90	2.073
22.06	2.434
25.21	2.944

Table A.9.

Precision Measurements of the Torque as a Function of the Rotational Rate of the Paddle Mixer.

Figure 4.16 Data.

Dispersion conditions: 1. Partially crystallized tallow by procedure number three, 2. Various weight ratios of detergent solution to partially crystallized tallow and, 3. Various rotation rates were used. 3-11-85 Data

Speed of Rotation	Torque(N-m)				
Rad/sec	Weight Ratio of detergent solution to tallow				
	0.50	0.50	0.80	1.14	1.50
0.139	0.000658				
0.150		0.000818	0.000160		0.000030
0.210	0.000839	0.000988	0.000205	0.000065	0.000031
0.403	0.000971	0.001147	0.000261	0.000083	0.000056
0.613	0.001123	0.001264	0.000304	0.000097	0.000051
0.824	0.001150	0.001321	0.000347	0.000125	0.000056
1.033	0.001223	0.001404	0.000397	0.000121	0.000063
2.084	0.001585	0.001703	0.000565	0.000171	0.000090
4.159	0.001955	0.002104	0.000720	0.000260	0.000149
6.280	0.002279	0.002438	0.000872	0.000342	0.000203
8.362	0.002546	0.002729	0.001005	0.000417	0.000256
10.48	0.002777	0.002983	0.001130	0.000494	0.000312
12.58	0.003007	0.003216	0.001243	0.000564	0.000376
14.68	0.003218		0.001377		
15.74		0.003542		0.000686	0.000481
18.88	0.003598	0.003848	0.001610	0.000816	0.000602

Table A.9 continued.

Dispersion conditions: 1. Partially crystallized tallow by procedure number three, 2. Various weight ratios of detergent solution to partially crystallized tallow and, 3. Various rotation rates were used. 3-14-85 Data

Speed of Rotation	Torque(N-m)				
Rad/sec	Weight Ratio of detergent solution to tallow				
	0.50	0.50	0.80	1.14	1.50
0.150		0.000202	0.000055	0.000047	.
0.166	0.000667				0.00157
0.210	0.000826	0.000268	0.000047	0.000060	0.001815
0.404	0.000951	0.000315	0.000064	0.000065	0.001953
0.614	0.001046	0.000354	0.000074	0.000087	0.002104
0.825	0.001137	0.000385	0.000089	0.000090	0.002224
1.04	0.001218	0.000420	0.000098	0.000104	0.002350
2.09	0.001502	0.000549	0.000144	0.000146	0.002766
3.14	0.001708		0.000182		0.003074
4.16	0.001875	0.000722	0.000219	0.000215	0.003324
6.29	0.002172	0.000868	0.000290	0.000284	0.003793
8.37	0.002426	0.000997	0.000354	0.000341	0.004188
10.48	0.002656	0.001124	0.000421	0.000408	0.004563
12.59	0.002866	0.001234	0.000508	0.000476	0.004903
15.76	0.003155	0.001405	0.000605	0.000588	0.005413
18.90	0.003432	0.001586	0.000735	0.000713	0.005896
22.06	0.003706	0.001760	0.000875	0.000851	.
25.22	0.003975	0.001949	0.001024	0.000995	0.006852
28.4		0.002153	0.001179	0.001145	.

Table A.10

Dispersion Apparent Viscosity Plotted Versus the Olein Yield

Figure 4.17 Data.

Partially crystallized tallow was fractionated and dispersion data was collected using various weight ratios of detergent solution to partially crystallized tallow.

Weight Ratio	Rad/ sec	Torque N-m	Rad/ sec	Torque N-m	n	K	Na Pa s
			3-11-85 Data				
0.50	1.033	1.22E-3	6.28	2.28E-3	.345	7.11	0.8013
0.80	1.035	3.97E-4	6.28	8.72E-4	.437	2.00	0.3069
1.14	1.036	1.21E-4	6.28	3.42E-4	.577	0.49	0.1201
1.50	1.037	6.27E-5	6.28	2.03E-4	.649	0.23	0.0711
0.50	1.036	1.40E-3	6.28	2.44E-3	.306	8.66	0.8571
			3-14-85 Data				
0.00	1.033	2.35E-3	6.28	3.79E-3	.265	15.44	1.3328
0.50	1.035	1.22E-3	6.29	2.17E-3	.320	7.37	0.7637
0.80	1.034	4.20E-4	6.29	8.68E-4	.402	2.24	0.3053
1.14	1.035	9.76E-5	6.29	2.90E-4	.603	0.38	0.1017
1.50	1.035	1.04E-4	6.29	2.84E-4	.554	0.44	0.0997
			Sheared tallow data				
0.50	1.035	3.03E-4	6.28	7.29E-4	.486	1.42	0.2562
			4-4-85 Data				
0.50	1.036	4.27E-4	6.28	9.54E-4	.445	2.13	0.335
0.80	1.036	2.30E-4	6.28	5.15E-4	.446	1.15	0.181
1.14	1.037	1.98E-4	6.28	4.27E-4	.426	1.02	0.150
1.50	1.036	1.55E-4	6.29	2.55E-4	.276	1.00	0.090

Table A.10 continued.

Separation data for the various weight ratios.

Weight Ratio	Olein Yield
4-1-85 Separation Data (for 4-4-85 rheology data)	
0.50	69.7%
0.80	72.4%
1.14	73.2%
1.40	77.6%
3-11-85 Separation Data (for 3-11 and 3-14-85 rheology data)	
0.50	66.2%
0.80	72.3%
1.14	78.1%
1.50	79.4%

Table A.11.

The Apparent Viscosity of the Dispersion as a Function of the Percent Solids in the Dispersion.

Figure 4.18 Data.

Dispersion conditions: 1. Various weight ratios of detergent solution to tallow used to generate various solid fraction contents, 2. Various crystallization procedures used.

Percent Solids	Apparent Viscosity
3-11-85 Data, Crystallization procedure three.	
12.9	0.8013
10.6	0.3069
8.8	0.1201
7.5	0.0711
12.9	0.8571
3-14-85 Data, Crystallization procedure three.	
20.0	1.3328
12.9	0.7637
10.6	0.3053
8.8	0.1017
7.5	0.0997
4-4-85 Data, Crystallization procedure three	
12.9	0.335
10.6	0.181
8.8	0.150
7.5	0.0897

Table A.11 continued.

Percent Solids	Apparent Viscosity
4-15-85 Data Crystallization procedure two	
12.9	0.311
10.6	0.211
8.8	0.164
7.5	0.158
12.9	0.288
5-23,24-85 Data, Crystallization procedure three.	
20.0	0.922
20.0	1.014
15.2	0.237
15.2	0.241
12.9	0.272
10.6	0.172
10.6	0.177
8.8	0.124
8.8	0.105
7.5	0.0758
7.5	0.0758

APPENDIX B.

B.1 Table 4.1 Calculations.

1. Calculation of single crystal surface area.

The assumed crystal shape was cylindrical; The crystal diameter was 0.3 microns and the crystal length was 30 microns.

S.A. = $3.14xDxL + 3.14xD^2/4$

= $3.14x0.3x30 + 3.14x0.3x0.3/4$

= $28.26microns2 + 0.07\ microns^2$

= $28.33\ microns^2$ = $28\ microns^2$

2. Single crystal volume calculation

V = $3.14xD^2xL/4$

= $3.14x0.3x0.3x30/4$

= $2.1\ microns^3$

3. Calculation of single crystal surface area per unit single crystal volume.

Surface area per crystal/ Volume per crystal

= $28microns^2/2.1\ microns^3$

= $13\ microns^{-1}$

B.2 Table 2 Calculations.

1. Calculation of the weight per individual crystal

Crystal volume times crystal density equals the crystal weight.

Weight = $2.1 microns^3 x (0.9 g/cm^3) x 1 cm^3 / 10^{12} microns^3$

= $1.89 X\ 10^{-12} g$

2. Calculations for the number of crystals in a standard 200ml or 170g aliquot.

Number of crystals per 200 ml aliquot equals the crystal weight per 200 ml aliquot divided by the crystal weight per crystal.

No. crystals/200 ml = $.20 x 170 g / 1.89 X\ 10^{-12} g$

= $1.8 X\ 10^{13}$

3. Calculation of the total crystal surface area.

The number of crystals times the area per crystal equals the total crystal surface area.

Total S.A. = $1.8 X\ 10^{13} x 28\ microns^2 x 1 m^2 / 10^{12} microns^2$

= $500\ m^2$

4. Calculation of the optimum gmoles SDS per 200 ml aliquot.

Optimum gmoles SDS equals optimum SDS weight divided by the gram molecular weight of a SDS molecule.

gmoles SDS = .500g/288.1g/gmole

= $1.73 X\ 10^{-3}$ gmoles SDS

5. Calculation of the gmole SDS per m^2 surface area.

= gmole SDS per 200 ml aliquot divided by total surface area per 200 ml aliquot

= $1.73X\ 10^{-3}/500\ m^2$

= $3.5X\ 10^{-6}$gmole/m^2

6. Calculation of the available surface area per molecule of SDS. The surface area per gmole SDS divided by Avogadro's number equals the crystal surface area per molecule.

= $1/(3.5X\ 10^{-6}x6.023X\ 10^{23})$

= $4.8X\ 10^{-19}m^2$ = 48 $\mathring{A}^2$

7. Calculation of the area occupied by a SDS molecule.

Case I. Perpendicular to crystal surface

Assume triangular orientation of hydrogen molecules at end of SDS molecule. Use C-H bond lengths to estimate an area.

C-H bond length 1.095 $\mathring{A}$.

Using a triangle surrounding the three hydrogens by .5 times the C-H bond length yields a triangle with area calculated as: = $0.5x2.86Ax2.46A = 3.5\mathring{A}^2$ (See Figure 4.9)

Case II. SDS molecule parallel to the surface

Estimate by using a rectangle 11 carbon-carbon bonds long plus a carbon-hydrogen bond by 2 carbon-hydrogen bonds wide.

$A = 2.19\text{Å} \times (11 \times 1.54\text{Å} + 1.09\text{Å})$

$= 40\text{Å}$

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