UNIVERSITY OF CINCINNATI

May 10 1951

I hereby recommend that the thesis prepared under my supervision by Philip K. Isaacs

entitled The Breaking of Emulsions on Freezing

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Hobe S. Greene

E. F. Harman

FORM 668—G. S. & T. C.—500—5-48

THE BREAKING OF EMULSIONS ON FREEZING

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfilment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
1951

by

Philip Klein Isaacs
B.A. Bard College 1948
M.A. Columbia University 1950

Acknowledgment

The author wishes to express his appreciation to Dr. Hoke S. Greene for his most helpful guidance, and to Dr. Earl F. Farnau for many valuable suggestions.

Table of Contents

Table of Contents
(Continued)

Introduction

The problem of the breaking of emulsions by freezing is an important one in the food, rubber, and petroleum industries. For this reason most work done in this field has been from a practical point of view; various empirical methods have been devised to prevent separation of a bulk free oil layer when an emulsion is subjected to low temperatures. However, little attention has been given to the physico-chemical factors affecting coalescence of droplets while the water around them freezes. Consequently we have undertaken to study several simple oil-in-water emulsion systems with regard to their behavior on freezing under various conditions, and to interpret the results in terms of the physical constants of the substances involved. In addition, an attempt will be made to apply the theory of stability of lyophobic colloids to the data, and to arrive at quantitative expressions relating the extent of deemulsification with various independent variables.

It will be noted that seemingly contradictory results are reported in the literature. This is due to the wide diversity of the systems studied, and to their great complexity. In nearly all cases, the emulsifying agent used was itself colloidal in nature, with several species of surface active substances present; even a pure soap solution contains at least one type of micelle, free

carboxylate ions, undissociated fatty acid, and hydroxyl ions. Interpretation of the behavior of such a system is very difficult, especially if solubilization of the dispersed phase has taken place. In the case of cream, latex, and bitumen a complete analysis of the roles of the various constituents on freezing of the dispersion would be extremely complicated. In our work we have chosen a virtually insoluble and non-polar dispersed phase of low freezing point, and emulsifying agents whose critical micelle concentrations are high enough to enable them to be used well below this region. Therefore, the conclusions reached from our data may not be valid for natural and industrial emulsions, where gelation, tough film formation, and lowered freezing point are likely to be factors determining stability to freezing.

Historical

1. Freezing of simple systems

Among the first references to the breaking of emulsions by freezing was that of Newman[1]. He froze a 95 volume percent benzene emulsion in dilute sodium oleate solution, and noted complete, and apparently irreversible, separation of the benzene upon thawing. He attributed the difficulty in redispersing the benzene to the slow rate at which the soap redissolved after being precipitated by

freezing.

Vickery[2] postulated that an emulsion system completely free of electrolyte should not coagulate on freezing. His results, however, disproved this postulate. A 60% carbon tetrachloride-heptane emulsion (density = 1) stabilized by kaolin broke completely on freezing. Addition of sodium chloride had no effect.

Young[3] made microscopic studies on the freezing of petroleum oil emulsions in cresol-soap solutions. The sequence of events was as follows: first the field was invaded by long needles of ice which crowded the oil globules together causing some of them to coalesce. The ice formed in horizontal lamellae. Thawing produced partial spontaneous reemulsification of the oil immediately, but the globules had a slightly larger average size than the original emulsion. Some oil droplets coalesced to form a separate bulk phase. Young also made observations on the freezing of emulsions in test tubes. Thawing of these samples produced five clearly defined strata: clear oil at the top, heavy cream, unchanged emulsion, dilute emulsion, and finally clear solution. No attempt was made to explain these observations on a physico-chemical basis.

Swingle and Snapp[4] studied the effect of freezing on various oils emulsified in soap solutions. They found that undisturbed freezing and thawing produced no breaking

in any of the samples, while agitation during both freezing and thawing resulted in separation of an oil layer. Supercooling to -8°C occurred when the emulsions were not stirred violently or seeded with ice.

Microscopic observations by Rochow and Mason[5] lead them to important conclusions as to the processes involved in the breaking of emulsions by freezing. They used a 33 volume percent carbon tetrachloride-benzene emulsion stabilized by .5% sodium oleate. Slow freezing of this on a specially designed cold stage showed the globules being flattened against each other by the growing ice dendrites, but no coalescence was observed. No breaking occurred if thawed immediately. Holding at -8°C for 9 minutes resulted in thinning of the membranes about each globule, but thawing still failed to break the suspension. Freezing to -12°C for 10 minutes gave rapid thinning of the membranes and the droplets coalesced on thawing.

They found that increasing the soap concentration produced smaller globules, but clumping of these particles was enhanced by their small size and thus made the emulsion more susceptible to breaking on freezing. Soap curds precipitated during freezing if the initial sodium oleate concentration was greater than 3%. Themembranes were no more durable if the concentration was increased above .5%. They all showed a certain period of durability in the

frozen state, but always thinned after a given length of time. The resistance of the membranes to freezing was proportional to the soap concentration as long as such concentrations were below .5%.

Viscosity of the dispersed phase has no influence on the durability of the membranes, but the actual process of coalescence takes place more slowly when olive oil is used in place of the low viscosity CCl_4-benzene mixture.

Holding at low temperatures without freezing has no effect. An 80% CCl_4 emulsion in .5% sodium oleate showed no breaking after holding at 0°C for 24 hours.

Rochow and Mason conclude from their work that the most important factor in the breaking of emulsions by freezing is the dehydration of the globule membrane - the concentrated solution produced by freezing out of the solute extracts the bound water of the colloid, presumably by osmotic action. Other factors to be considered are: the freezing point of the bound water, time frozen, volume ratios of dispersed and continuous phases, and concentration of emulsifying agent.

Holzapfel[6] made extensive studies on the freezing of hydrophilic colloids and included some work on emulsions stabilized by these substances. She found that an emulsion of benzene in 1% sodium oleate was not affected by freezing with respect to particle size distribution. A similar

emulsion in 1% egg albumin was broken completely by the same treatment. If dilute saponin solution was used as the dispersing medium, particle size actually decreased as a result of freezing. She does not give the experimental procedures for emulsification or freezing. The specific conductance of emulsions was always slightly lower than the pure emulsifying agent solution. This was probably due to adsorption of an appreciable fraction of electrolyte at the interface, and to the presence of non-conducting globules. Freezing at -18°C for two hours produced a 1-2% decrease in the conductivity if particle size remained constant. This regained its original value a short time after thawing. Freezing at -79°C for the same length of time gave a 10% decrease in the conductivity in the case of sodium oleate. These results are interpreted in terms of aggregating and disaggregating effects, but a more complete knowledge of the micdle structure of the various colloids used is needed for a complete explanation.

2. Studies on natural and industrial emulsions.

Most of the work in this field has been done on the freezing of cream and other milk products. The problem is of particular practical importance since dairy products must be stored at low temperatures to prevent spoilage. In addition, the manufacture of ice cream is dependent on

the stability of the cream suspension during freezing. It must be borne in mind, however, that the melting point of butter fat is 37°C and therefore cream is not strictly an emulsion below this temperature. Globules may adhere to one another, but cannot coalesce. This flocculation need not be analogous to coalescence in liquid-liquid systems since the interfacial membranes may be tough enough to prevent coalescence when the particles are melted.

Doan and Baldwin[7,8] published a series of papers on the freezing of cream. They measured the extent of flocculation by pouring the thawed sample over a 30 mesh screen and determined the amount of fat filtered off by a modified Babcock test. They found that the percentage of butterfat flocculated increased in proportion to the initial volume percentage. Almost complete breaking occurred with 40% cream, while only 30% of the total fat was filtered off in the case of 25% cream. Most of the destabilization occurred during the freezing of the last 20% of the water. If thawed when only 80% frozen, about half of the final value was obtained. The length of time held in the frozen state had no influence on the flocculation. Destruction of the suspension by freezing could be reduced almost to 0 by the addition of 10% sucrose.

The authors attempted to explain this behavior on the basis of "internal pressure". They placed a rubber

bulb attached to a mercury manometer in the center of the emulsion to be frozen, and recorded the pressure on the bulb as the ice formed around it. They found that the pressure developed was proportional to the extent of flocculation for various volume percentages milk fat and on the addition of sugar. They concluded from this that high internal pressure ruptures the protective films on the droplets and thus causes them to adhere to one another. This explanation appears to be based on questionable assumptions. First of all, the pressure on the bulb would be a measure of the adhesion of the frozen bulk to the container and the strength of the surface. Both would be dependent upon the shape and nature of the vessel. Secondly, the order of magnitude of the pressures they observed was much lower than the actual pressure freezing water can exert.

Doan and Baldwin discounted the effect of freezing on milk proteins as a factor in flocculation. They found no irreversible coagulation of the proteins on holding frozen for long periods. However, all non-fat milk solids would precipitate on freezing and no longer be able to stabilize the suspension regardless of any chemical changes taking place.

Webb and Hall[9] also did extensive work on the freezing of cream. They found that long storage does in-

crease the extent of flocculation, contrary to Doan and Baldwin's observations. They attribute this to denaturation of the stabilizing protein, presumably casein. The addition of 25% sucrose completely prevented separation of the fatty phase. Webb and Hall note that in addition to lowering the freezing point and raising the viscosity of the aqueous phase, sucrose produced small ice crystals which are always conducive to the stability of frozen suspensions. Gelatin also gives small ice crystals and likewise prevents flocculation.

These workers found that homogenization of the cream increased the destabilization by freezing. The smaller particles produced by homogenization tend to clump more readily than the large globules of untreated cream, and these clumps are apparently responsible for the results obtained. This conclusion was also reached by Rochow and Mason.

Dahle[10], in a review on frozen cream, outlines a theory to explain the results of Webb and Hall. He proposes that the principle factor in determining the extent of flocculation is the hydration of the globules. A high degree of hydration reduces the amount of water available for freezing and deflects the formation of ice crystals, giving small crystal size. This is the case when sugar, gelatin, or sodium alginate is added to cream. Normally

the highly hydrophilic lecithin-protein complex, which is adsorbed on the fat surface, is broken up by freezing thus decreasing the amount of hydration.

Little[11] also reviewed work done on freezing of cream. He points out that the two factors imparting stability to a cream suspension are bound water and adsorbed negative charges. Freezing withdraws the bound water and negative charges, as well as breaks up the lecithin-protein complex. He presents diagrams to show the charge distribution before and after freezing, but fails to give a physico-chemical basis for his conclusions. Little concludes from experimental evidence that increase of viscosity alone from the addition of hydrophilic colloids is not sufficient to insure stability to freezing.

The problem of stability to freezing is important in the field of synthetic rubber technology. Emulsion polymerization at low temperatures gives a better product than when the reaction is carried out at high temperatures. Walker[12] studied the freezing of neoprene latex films in connection with an industrial process. His suspension consisted of the polymer, unpolymerized unsaturated hydrocarbon, a catalyst such as SO_2, and a stabilizing agent. The method used was to freeze a film on a cold drum, and thaw it on a warm bakelite surface. The turbidity of the liquid collected was taken as inversely proportional to

the amount of coagulation. In this way it was found that the temperature of freezing, the rate of thawing and the nature of the emulsifying agent are the most important factors in coagulation. The concentration of emulsifying agent and age of the suspension did not influence the results.

Walker found that very rapid freezing of these films to -10^{o} or $-45^{o}C$ did not affect the dispersion if thawed rapidly as well. Slow thawing, however produced a coagulum. He concludes from this that small ice crystals offer no protection against destabilization during slow thawing. The greatest stability to freezing was exhibited by a latex made with a cetyl alcohol-ethylene oxide condensation product. With sodium oleate or rosinate, coagulation was more extensive, while paraffin chain sulfates and sulfonates offered least protection against breaking by freezing.

Freezing in bulk was also studied. In this work the principle factor was the amount of water frozen. No coagulation occurred in the absence of ice formation, even when supercooling to $-8^{o}C$ took place. This is in accord with the observations of Swingle and Snapp. The amount of water frozen was determined by finding the quantity of heat absorbed when the sample was thawed in a calorimeter. In all cases the latex was agitated while freezing. A

sample stabilized by cetyl trimethyl ammonium bromide was 32% coagulated when 65% of the water had crystallized, and 100% coagulated when 95% of the water was frozen. Similar results were obtained with Daxad 11 (polymerized organic salts of aryl alkyl sulfonic acids), and sodium rosinate. The uncoagulated portions were found in the center of the test tubes, which were the last regions to freeze. Walker concludes from his work that coagulation occurs if the stabilizing agent is incapable of preventing it under the conditions of high concentration produced by freezing. He suggests that future work be concerned with the mode of ice formation, nature of stabilizing agent, and the freedom of movement of the particles during freezing.

Road tar emulsions in soap solutions are used extensively in highway construction. Due to the low temperatures these systems are exposed to, the effect of freezing is important. Gabriel[13] reports that freezing of these concentrated bituminous emulsions gives complete coagulation. The aqueous layer obtained on thawing is almost pure water, indicating that the soap has been extracted by the tar.

A large number of substances have been used to prevent breaking of emulsions by freezing. Patents[14] have been issued on the use of rosin soap, hydrophilic

colloids of various types, and volatile organic liquids such as acetone and alcohols. Compounds of the latter type probably owe their effectiveness to lowering of the freezing point; while ice formation may begin, some liquid will always remain if the temperature is above the eutectic point for the mixture. Glycerin or allyl alcohol are effective at concentrations of about 10%. As mentioned before, edible products contain sodium alginate or gelatin to form a highly viscous gel in the last stages of freezing, thus preventing the globules from coming in contact with each other.

3. Effects of freezing on other hydrophobic colloids.

Gutbier[15] and coworkers did extensive work on the freezing of selenium sols. They found that the longer these sols were dialized, the greater coagulation occurred on freezing. Virtually electrolyte free suspensions were completely and irreversibly coagulated. The addition of .003N HCl, or KCl up to .05N stabilized these sols to freezing. Higher electrolyte concentrations flocculated the unfrozen suspensions. These results are probably the result of zeta potential lowering as the electrolyte concentration approaches zero.

Foote and Saxton[16] froze several sols in a dilatometer to determine the amount of "bound" water. They

assumed that any water unfrozen at -20°C was bound water of hydration of the particle surfaces. Slow freezing of an aluminum hydroxide sol decreased the bound water, but rapid freezing had little effect. A ferric hydroxide hydrosol held water even more tenaciously, while a silica sol gave practically no change in bound water content on repeated freezings.

Flocculation of silica sols by freezing was studied by Hazel[17]. He found that they coagulated readily, but were protected by ion exchange resins. They were also stable in a narrow pH zone. Aged sols flocculated more readily than freshly prepared samples; this was attributed to the larger particle size produced by aging which reduces the total amount of charge per unit mass.

Many workers have reported complete precipitation of gold sols and suspensions of finely divided carbon upon freezing. An interesting observation is reported by Beaver[18]. He found that all crystalloid electrolyte is removed from gold particles when they are precipitated by freezing. Similar results have been obtained on the freezing of cream.

4. Conclusions

No quantitative work has been done on the freezing of simple emulsion systems, nor has any serious attempt

been made to explain the qualitative results obtained on a physico-chemical basis. The most important conclusions that can be drawn from research thus far are as follows:

1. Breaking of emulsions at low temperatures occurs only when water crystallizes, and is dependent on the amount of water frozen.

2. Suspensions of high dispersed phase content are more susceptible to the breaking effects of freezing than those of low dispersed phase percentage.

3. The nature of the emulsifying agent influences the behavior of an emulsion on freezing.

4. Whether the dispersed phase is a liquid or solid affects its reaction to freezing.

5. Slow thawing is conducive to the destruction of the emulsion.

6. Solutes added to the water may have a protective action against deemulsification.

7. Small ice crystals have less of an effect on the stability of a frozen emulsion than do larger ones.

The influence of some factors varies with the nature of the system studied and the exact conditions employed. For this reason contradictory results have been obtained by different investigators. These points are:

1. Concentration of emulsifying agent.

2. Length of time frozen.

3. Temperature of freezing.

Many explanations have been advanced. The following factors have been suggested as the principle ones in determining the extent of deemulsification on freezing:

1. Freezing point of bound water.

2. The extent of dehydration of the adsorption membranes by osmotic action.

3. Internal pressure.

4. Withdrawal of charge from the membrane.

Theoretical

The coalescence of emulsion droplets during freezing may be considered as the result of the interaction between three forces:

1. The force exerted by the growing ice crystals which presses the globules against each other. This will not produce any effect until the globules have reached close packing. When they have, the force exerted on each globule is equal to the total force applied in a continuous region, due to Pascal's law. It is important to note here that at close packing each globule is surrounded by twelve neighbors, and is thus pressing against each one with equal force. Assuming the ice can exert a given pressure before it envelops a droplet, the maximum force

it can exert will be proportional to one half the area of a single droplet, or for n droplets:

$$F_I = kr^2n \qquad (1)$$

F_I is the ice force, k is a constant and r is the radius of the droplets, assumed to be of uniform size. This ice force will have another effect, that of deforming the droplets to ellipsoid shapes; it is proportional to the interfacial tension and the radius for large droplets[19], becoming more complicated for smaller ones.

2. The force of repulsion between the double layers of the droplets. This is given by Derjaguin[20] as

$$F_R = \frac{Dr\kappa\psi_0^2}{4}\left[1 - \operatorname{tgh}\frac{\kappa H}{2}\right] \qquad (2)$$

where D is the dielectric constant of the continuous phase, r, the radius of the droplet, H the distance of closest approach, and ψ_0 is the potential at the surface usually taken as equal to the zeta potential. κ is the reciprocal thickness of the double layer and is calculated from the following equation[21]:

$$\frac{1}{f(kr)}\cdot\frac{u\eta[1+kr]}{r} = 2\sqrt{\frac{DRTc}{2000\pi}}\sinh\frac{F\zeta^e}{2RT} \qquad (3)$$

In this formula u is the electrophoretic velocity, η the viscosity of the continuous phase, F. the faraday in cgs units, c. the concentration of electrolyte, and ζ^e the zeta potential in statvolts. R is the gas constant in

cgs units and T, the absolute temperature. The term f(κr) is known as Henry's function[22] and is equal to 1 if κr is greater than 300. Its minimum value is .67. In our work, κr is never less than 200 and is usually greater than 300, so that this term may be neglected without much error. Both members of equation (3) are equal to the charge density .

Equations (2) and (3) are valid for perfectly spherical droplets only. Deformation produced by ice pressure will increase the radius of curvature and thus tend to increase the repulsive force.

3. The force of attraction between the droplets due to London-Van der Waals interaction. The energy of attraction for two identical spherical colloid particles is given by Verwey and Overbeek[23] as

$$E_A = -\frac{A}{6}\left(\left[\frac{2}{s^2 - 4}\right] - \frac{2}{s^2} - \ln\left[\frac{s^2 - 4}{s^2}\right]\right) \qquad (4)$$

where s is the distance between their centers divided by the radius. A is constant dependent on the nature of the phases, and is usually about 10^{-12}. In our work H/2r is about 10^{-3}, so that the distance of closest approach is almost negligible with respect to the radius. Consequently s assumes a constant value of 2, which is independent of the radius. Therefore the energy of attraction, and hence the force, is not dependent on the size of the globules, if they are perfect spheres.

Coalescence is probable when the force of attraction, or F_A, is greater than the force of repulsion, F_R. This condition holds when the globules are brought close enough so that the attractive forces are appreciable. To do this, work must be done against F_R by the ice force F_I. If there are no other forces than those already discussed, the rate of coalescence should depend on the quantity:

$$F_I - F_{R_{max}} \tag{5}$$

$F_{R_{max}}$ is the maximum value for the force of repulsion which is attained as H approaches 0. In order to get an expression for the rate of coalescence, we must find S as a function of time and hence as a function of concentration of emulsifying agent. This will lead to a second or third order differential equation which, when integrated, would give the total amount of coalescence. Concentration as a function of time depends in turn on the rate of desorption due to decrease in surface area through coalescence, and the rate of freezing out of the solute. To get the overall rate of coalescence, taking into account those droplets already enveloped by the ice, we must subtract a term signifying that the amount of dispersed phase subject to coalescence is being decreased due to envelopment by ice. This term will depend on the rate of freezing. Such an equation would apply to spherical droplets only, so no attempt was made to apply it to our data, where

deformation of the globules is important.

In this discussion we have assumed that coalescence ensues immediately upon close contact between two globules. This will be the case if the interfacial tension is high, but not if it is near 0. The latter case will be discussed later.

Another factor may be of importance in determining the extent of deemulsification. This is the energy liberated in the process of coalescence. The decrease in work content when the mutual surface of the emulsion droplets is decreased is given by:

$$\Delta A = \gamma \Delta a \qquad (6)$$

γ is the interfacial tension and a the surface area. This quantity will also determine the tendency to coalesce. The decrease in work content will be manifested in a rise in temperature of the surroundings and agitation of the aqueous phase. The latter factor will give rise to forces acting in addition to the ice force tending to bring the globules closer to each other. If they are already subject to almost enough force to bring about coalescence, this will increase the rate of coalescence, causing still greater agitation, thus finally resulting in an autocatalytic process.

Experimental

1. Materials

A. Emulsifying agents

The principle emulsifying agent used in this experimental work was sodium decyl sulfonate. It was chosen since its physical properties eliminate many complications that would arise with other surface active agents. Its high critical micelle[24] concentration of .04N (1.0%) minimizes the possibility of solubilization of the dispersed phase when used at .1%. In addition, it is a strong electrolyte which may be considered 100% ionized in dilute aqueous solution. These two facts assure the presence of only one surface active species; in soaps there would be both ions and undissociated fatty acids. The solubility of sodium decyl sulfonate (SDS) was found to be .53% at 0°C, which allows a wide concentration range to be used. The substance crystallizes from supersaturated or seeded solutions as the 3.5 hydrate[25]. Solutions of sulfonates and the dry solids are perfectly stable over long periods of time, showing no tendency to hydrolyze as do the corresponding sulfates in slightly acid media. Temperatures up to 120°C have no effect on SDS[25].

A sample of SDS was obtained in a pure state from the Proctor and Gamble Co. An additional amount was

synthesized by a procedure given by Tartar[26]: 30 g. of n-decyl bromide was refluxed for one week with a solution containing a 10% excess over the theoretical amount of sodium sulfite. After evaporation, the residue was extracted with petroleum ether to remove organic byproducts, and the sulfonate then recrystallized twice from absolute alcohol. Two recrystallizations from water assured freedom from electrolyte impurities. The hydrate thus obtained was dried at 110°C for 4 hours. The resulting anhydride was weighed out to make up solutions.

Sodium dodecyl sulfonate (SDDS) was used for comparative tests. It has a critical micelle concentration[24] of .01N (.27%) and a solubility of about .06% at 0°C. This was obtained from the Proctor and Gamble Co.

Hexadecyl benzyl dimethyl ammonium chloride (HBDAC) was chosen as a cationic surface active agent. Its critical micelle concentration[27] is .0009N (.04%) but it shows appreciable surface activity down to 10^{-5}N, and was therefore used below the cmc. It also behaves as a strong electrolyte. It tends to form very viscous solutions as the concentration increases above about 10%, and is therefore very difficult to crystallize. It is fairly stable to ageing, but dilute solutions tend to show a decrease in pH on long standing due to the formation of HCl. The compound was obtained in a pure state from the Sterling-

Winthrop Research Foundation.

Dodecyl amine hydrochloride (DAH) was prepared from dodecyl amine for several experiments. The free amine was obtained through the courtesy of Dr. Robert Lollar of the Research Laboratory of the Tanners Council of America.

B. Dispersed phase

N-decane was used as the dispersed phase for most of the work. Its boiling point[28] of 174°C/760 mm., and freezing point of -29°C prevents loss by evaporation and allows a wide range of freezing temperatures to be employed without solidification of the hydrocarbon. Its non-polar nature eliminates the possibility of orientation on the concave side of the emulsion droplet. Decane has a density of .730 g./cc. at 20°C which insures a rapid rise of deemulsified oil after thawing. Decane and water are reported as not measureably soluble in one another. This avoids complications arising from impure phases.

Two samples of decane were used. One was obtained from Eastman Organic Chemicals and was badly contaminated with unsaturated hydrocarbons and their oxidation products. It was washed with concentrated sulfuric acid until only a faint brown color appeared, and then treated with acid permanganate until the purple color was no longer discharged.

This was followed by washing with water several times. It was then distilled in vacuo twice at 20 mm. pressure (B.P. 89°C). The decane still contained some oxidation products as noted by their odor. However, it was used as such.

Another sample, free from unsaturation and oxidation products, was obtained later from the Phillips Petroleum Co. This was fractionated at atmospheric pressure, and that portion boiling at 173 - 174°C collected. This sample was used for all later work on zeta potential, interfacial tension, and emulsifier concentration. It will be noted that the two decane samples gave different results with respect to the behavior on freezing with varying emulsifier concentration. Measurements with .5% SDS were made with the Eastman sample. All others were with the Phillips product.

Reagent grade toluene was used for the experiments with this substance.

Distilled water from the tap was used for all work. It had a conductance of 3.5×10^{-6} mhos/cm. at 25°C. This corresponds to an electrolyte concentration of about 10^{-5}N calculated as KCl. The conductance was tested at intervals throughout the course of the experiments and found to be constant.

2. Procedures

A. Preparation of emulsions

All the emulsions were prepared by the use of a standard hand homogenizer. The emulsifying agent solution was made up to the desired concentration by dilution of a stock .5% or .05% solution in a volumetric flask. The desired volumes of decane and emulsifying agent solution were then pipetted into a 50 ml. beaker and passed through the homogenizer until no decane separated as a distinct layer. This required four cycles. Uniformity was insured by passing the emulsion through the homogenizer two more times. Emulsions were made up to total volumes of 6, 12, or 30 ml. The homogenizer was taken apart and cleaned thoroughly at frequent intervals.

Particle size could be varied by adjusting the nozzle of the homogenizer.

Before each freezing experiment a measured amount of emulsion was pipetted into a 25 ml. Erlenmeyer flask fitted with a short air condenser. It was boiled gently for thirty seconds to remove dissolved gases, and then corked tightly and cooled.

In experiments where emulsifying agent concentration or type was being varied, a drop of this emulsion was withdrawn for a particle size distribution count immediately prior to freezing.

The precision of decane and agent concentrations was ‡ .6% for a total of 6 ml., ‡ .3% for 12 ml. and ‡ .1% for 30 ml., all in percentages of percent composition of ingredient.

B. Freezing and thawing

In the initial experiments a dilatometer was used to follow the course of freezing and thawing for all measurements. This is shown in Fig. II. A regulated cooling bath was constructed similar to that designed by Rochow and Mason[30]. It was capable of maintaining the dilatometer within ‡ .2°C for any temperature between -30 and 0°C. The setup is shown in Fig. I. The Dewar flask D was filled with a dry ice - acetone mixture. A current of air was sent through tube T, forcing cold acetone up through tube E and into the separatory funnel. This provided a pressure for continuous circulation through the coils and thence through tube C, to which a copper coil was attached. This coil was immersed in another Dewar flask containing the dilatometer.

A small amount of mercury was added to sidearm S of the dilatometer first. Then eight milliliters of the emulsion as prepared above was added through tube T. Sufficient mercury was then added to tube T to bring the emulsion exactly to the stopcock bore. The apparatus was

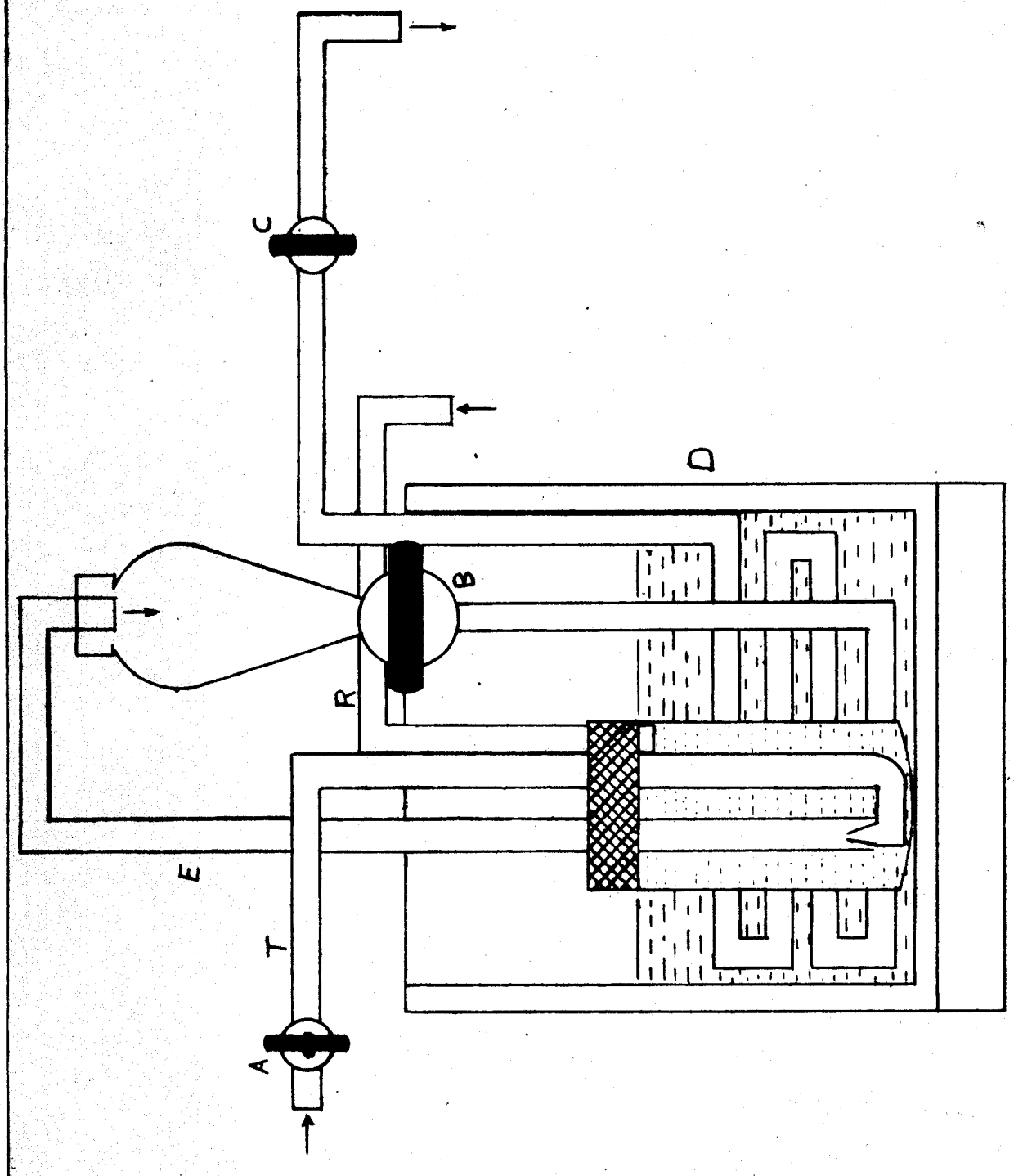


Fig. 1

then immersed in an ice bath and allowed to equilibrate for 10 minutes. A small crystal of ice was inserted through the stopcock, and the latter closed. Finally, the apparatus was immersed in the freezing bath; the course of freezing was followed by noting the rise of the mercury in the side arm. The temperature was regulated by varying the flow of cold acetone from the circulator. This was accomplished by manipulating stopcocks B and C and the rate of air flow through stopcock A. Readings of the mercury height were taken every minute until no further rise was noted. After holding for two more minutes in a completely frozen state, the dilatometer was removed and placed in an ice bath so that the frozen mass should be at $0^{o}C$ throughout when thawing began. After five minutes thawing was begun in a water bath held at the desired temperature. The fall of the mercury was followed until it reached a minimum and began to rise slowly, indicating that thawing was complete. The slow rise was due to the warming of the mercury and emulsion resulting in a slight expansion. The stopcock was then opened and the deemulsified decane forced upward into the calibrated tube, where the volume was read. At intervals of five minutes the decane - emulsion interface was agitated to insure complete coalescence of all large drops. Readings were taken every five minutes until a constant volume of decane was obtained.

The standard freezing temperature was chosen as $-10^{o}C$, and the standard thawing temperature was $10^{o}C$. Freezing and thawing times under these conditions were both ten minutes.

The mercury height could be measured to the nearest .05 cm. The difference between the initial and final heights was then precise to ± .07 cm. which corresponds to ±.14 ml. of water frozen in an 8 ml. sample. The precision of the amount of water frozen at any given time was therefore ±.14 ml. or ±3.5% for a half frozen sample. The error due to the contraction of the mercury on cooling and the contraction of the glass amount to -.02 and +.01 cm. respectively in terms of the height of the mercury column for a range of $10^{o}C$. These are negligible with respect to the error in observing the height.

In the experiments on the effect of emulsifier concentration and type, this procedure was modified. Glass tubes of the same diameter as the dilatometer were employed in order to run three samples simultaneously. Since the volumes used and the freezing conditions were the same, as in the dilatometer measurements, it was assumed that freezing and thawing occurred at the same rates. For these experiments it was found advantageous to regulate the bath temperature by adding small pieces of dry ice periodically, instead of using the coils from the

freezing unit. The tubes were corked to prevent contamination by acetone which might splatter on addition of the dry ice. Thawing was carried out in the manner previously described. The amount of decane deemulsified was determined by direct measurement of the oil layer in cm. This value was converted to ml. by calibration of the tube with a known volume of decane.

In both the dilatometer and test tube experiments, the amount of decane in the bulk layer could be read to the nearest .02 ml. With the standard volume percentage decane used this gave a precision of percentage deemulsification of ±3%.

The rate of freezing and the rate of thawing were varied by changing the temperatures at which these operations were carried out. It was found that the rate of freezing was directly proportional to the temperature of the bath. Almost instantaneous freezing was obtained by spreading the emulsion in a thin film over a copper plate held at $-29^{o}C$.

Thawing while stirring was accomplished by first freezing the sample with a copper wire in the center. This wire was then placed in the chuck of a mechanical stirrer, and upon thawing the entire mass was made to rotate at a constant rate.

C. Particle size counts

The particle size distribution count of an emulsion before freezing was made by first mixing a drop of concentrated agar solution with a drop of the emulsion to prevent brownian movement, and then a cover slip was placed over the mixture. The diameters of at least 100 droplets in four different regions of the slide were recorded. An oil immersion objective and a micrometer eyepiece were used, giving a total magnification of 970 times. The diameters could be measured to the nearest micron. Each scale division in the eyepiece corresponded to 4.5 microns, as determined by the use of a stage micrometer. The total number of droplets per unit volume was measured with a hemacytometer. Each sample was diluted 200 times in the special pipette provided.

A series of experiments were carried out to determine the change of particle size as freezing progressed. A five ml. sample of the emulsion was set in the freezing bath for a given length of time, after which it was quickly transferred to an ice bath. The unfrozen portion was withdrawn with a pipette, and thawing carried out as usual. After mixing thoroughly, a drop was taken out and a count made in the hemacytometer. In this way the number of drops in a known volume was found.

D. Microscopic observations

Several cold stages were devised for microscopic observations during freezing and thawing. The most satisfactory of these is shown in Fig. III. Copper coil A was connected to the circulator shown in Fig. I. Cover slip C was cemented to the end of a copper tube, which was of slightly larger diameter than the microscope objective. G consisted of two glass jars with asbestos insulation between them. No insulation was used on the bottom to allow illumination for the microscopic observations. The thermometer T could be read to ±.05°C. Stirrer S was used at low speed.

A drop of boiled emulsion was placed on cover slip C and the tube immersed in the bath so that only .5 cm. projected above the surface. A smaller cover slip was placed over the drop. The temperature of the bath was lowered quickly by adjusting the rate of flow of the cold acetone from the freezing unit. When 0°C was reached, the temperature was held constant for a short time. A small crystal of ice from the circulator tubes was then placed in contact with the edge of the emulsion to prevent supercooling. After this, the temperature was lowered at the desired rate by manipulation of stopcocks B and C of the freezing unit. Observations were made as to the mode of ice formation, behavior of the

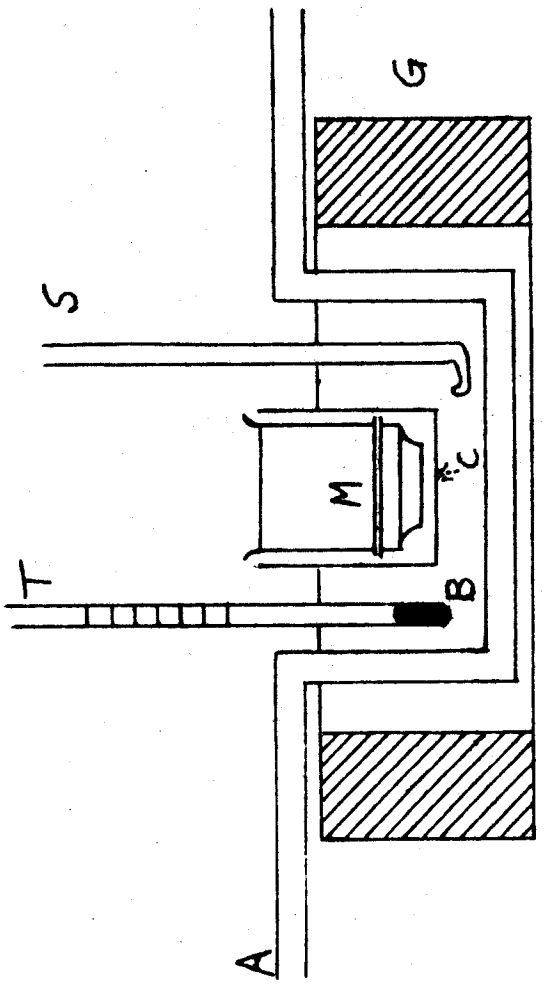


Fig. 3

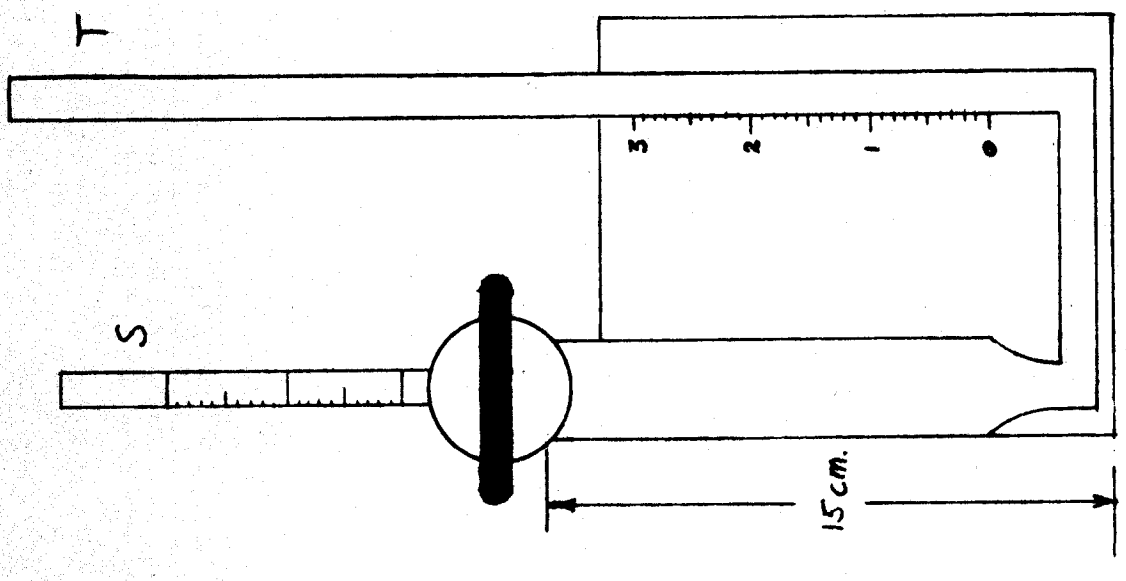


Fig. 2

individual globules, and the extent of coalescence during freezing. Slow thawing was obtained by allowing the bath to warm by itself after turning off the flow of cold acetone. Rapid thawing was produced by running warm acetone through the coil.

The temperature could be maintained to within ±.2°C of a given value. Comparison of the thermometer reading and the point at which pure water began to melt showed that the temperature of the emulsion was within .2°C of the thermometer reading when the bath was stirred at the rate used for all the experiments. Although a stream of cold dried air was blown over the cover slip, condensation of water obscured the view below -15°C.

Instantaneous freezing could be obtained by allowing the film of emulsion to supercool to -10°C, whereupon it solidified into vitreous ice.

Another type of cold stage was used where the final temperature obtained was not important. This consisted of a hemacytometer with cold dried air directed diagonally over the surface of the cover slip. The air was cooled by passage through a coil immersed in a dry ice - acetone bath. Drying was accomplished by passing the air through a meter long glass tube packed with calcium chloride. With this setup a known volume of emulsion could be observed, and the ice crystals could be made to advance at

any desired rate over the field by regulating the air flow. Since the depth of .1 mm. was greater than that for an ordinary microscope slide and cover slip, conditions were obtained more closely approximating those of bulk freezing.

Magnifications of 100 and 470 times were used in most of this work. The oil immersion objective was impractical, since the balsam oil conducted too much heat to the cover slip, thus melting the emulsion.

A polarizing microscope was used in observations on crystallization of the emulsifying agent during freezing.

E. Emulsion analysis

Several experiments were carried out to determine the distribution of emulsifying agent between the bulk aqueous liquid and the decane solution interface. A 10 ml. sample of emulsion of known particle size distribution was centrifuged at 2000 r.p.m. for fifteen minutes. A 5 ml. aliquot of the slightly turbid subnatant solution was then drawn off with a pipette carefully inserted through the creamed emulsion. This was evaporated to dryness on a weighed watch glass. After heating in an oven at 20°C to constant weight, the amount of residue was determined to the nearest hundredth of a milligram. The original weight of the watch glass was then checked by wiping off the residue with a dry cloth. The quantity thus obtained

was compared with the theoretical value found by applying Gibb's law of surface adsorption.

There are several sources of error in this procedure. First of all, the subnatant solution was slightly turbid, indicating that some decane was still dispersed there. Secondly, extensive breaking of the emulsion occurred at the top, giving an oil layer corresponding to half the amount present. It is assumed that the SDS released by this decrease in surface was adsorbed by the thick cream layer below. However, some may have diffused downward to that portion which was decanted. Taking into account only that error from the weighing and volumetric procedures we have that the percent SDS can be determined to ±.002% by this method.

The amount of decane in a given sample of emulsion was measured in order to determine the distribution in the frozen mass. Concentric cylinders of frozen emulsion were extracted with a set of sharp cork borers. These cylinders were melted into calibrated tubes of .3 cm. inside diameter, and the total amount present determined. Then concentrated sulfuric acid was added slowly until the emulsion was completely broken. This usually required an amount of H_2SO_4 equal to that of the emulsion. The volume of decane was then measured and the original volume percentage dispersed phase calculated. This involved four measurements of

height, each precise to .02 cm. The final precision of the percentage decane was therefore ±1% for a 2 ml. sample.

The distribution of emulsifying agent in the frozen mass was determined by the same cork borer technique, with the analysis carried out as in the first procedure in this section.

F. Interfacial tension measurements

A DuNouy interfacial tensiometer was used for all determinations. A series of solutions of increasing concentration were first prepared. Ten ml. of the emulsifying agent solution of lowest concentration was placed in a 50 ml. beaker, which was set in a small ice bath on the adjustable stage of the tensiometer. Ten ml. of decane was then carefully added, with precautions taken to prevent the formation of small droplets. After allowing 10 minutes for temperature equilibrium to be attained, a series of four readings was taken at intervals of five minutes. Only the "pull" values were used. Care was taken to prevent small droplets from adhering to the ring. After each set of readings, the decane was decanted onto the surface of the solution of the next concentration.

Interfacial tensions of HBDAC solutions above .005% were difficult to determine, since each time the

ring broke through the surface, spontaneous emulsification occurred. It was very difficult to cause coalescence of the small droplets thus formed, so that only one measurement with each solution could be made without the interference caused by the droplets.

The particular tensiometer used could not be calibrated to read directly in dynes/cm. due to a replacement part intended for a different model. Consequently the readings were corrected by a factor obtained from known surface tensions. The water - air and benzene - water interfaces at 25°C were used to calibrate the instrument.

A precision of ±.1 dynes was obtainable with the vernier scale on the tensiometer dial. Successive readings usually agreed within ±.2 dynes.

G. Zeta potential measurements

Electrophoretic mobility was determined by the moving boundary method using a U tube apparatus designed by Price and Lewis[30]. It is shown in Fig. IV. Electrodes D and E were platinum wires sealed in glass across which a constant potential of 9 volts was applied by battery B. The electrodes A and C in the side arms prevented electrolysis in the main U tube. The anode A was zinc and the cathode C was lead coated with lead dioxide. In this way no gas was evolved in the side arms. The potential at

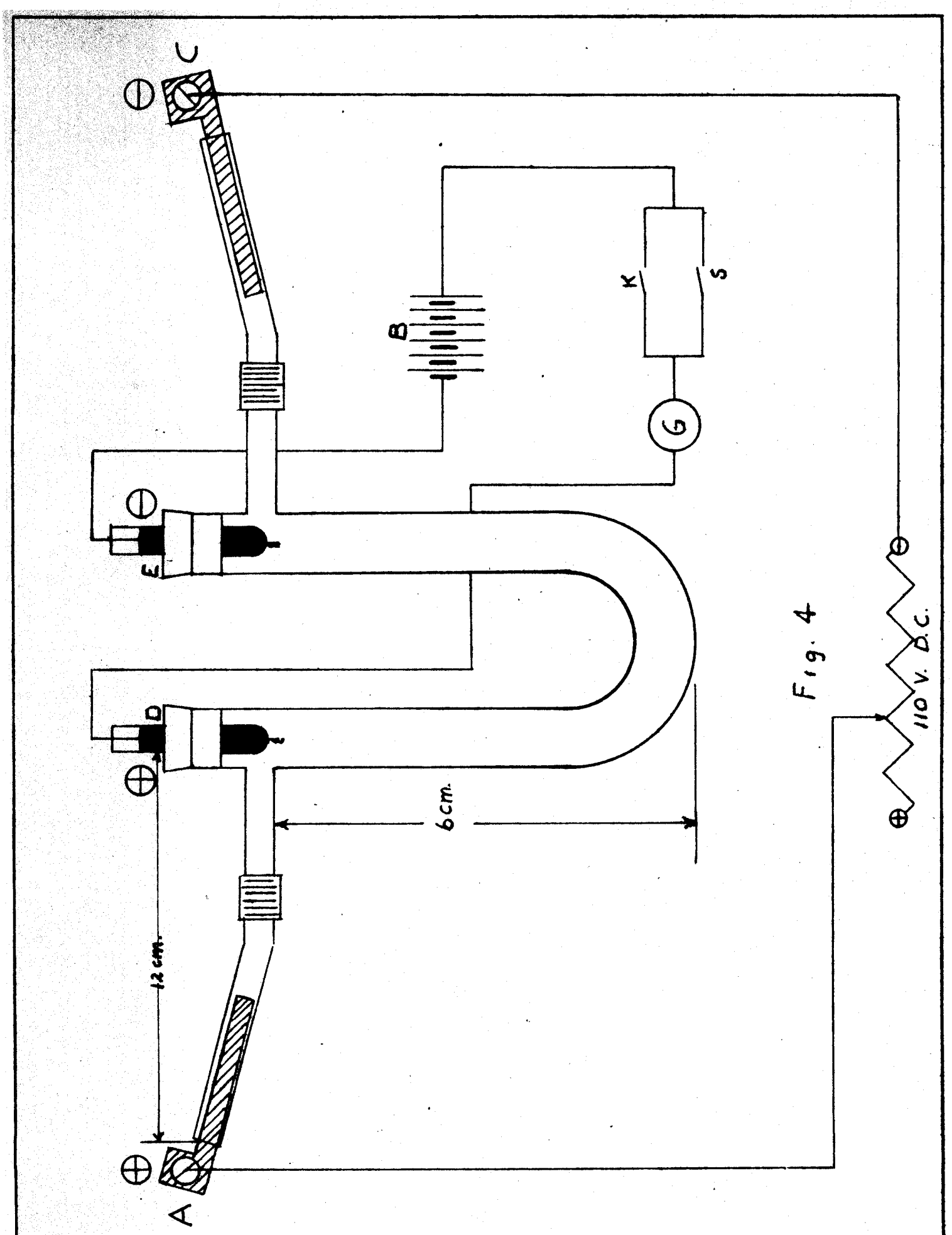


Fig. 4

the platinum electrodes due to the voltage applied across AC was adjusted by the rheostat until the galvanometer G showed no deflection when tapping key K was closed. In this way the potential under which the charged globules migrated was exactly that supplied by the battery, while no current flowed out of the U tube. The length of the side arms was sufficient so that no products of the reactions at electrodes A and C could migrate into the U tube during the time of a single determination. The distance between the electrodes was determined by direct measurement - this does not give an accurate value but it does not affect the precision.

A 30 ml. solution was made up of the desired emulsifier concentration, and a 5 ml. portion withdrawn to make a 5% emulsion with decane. Both the emulsion and clear aqueous phase were then boiled to remove dissolved gases, stoppered tightly, and cooled in an ice bath. The U tube was then placed in a 250 ml. beaker filled with crushed ice and water. This beaker was set in a 400 ml. beaker to provide an insulating air jacket. The emulsifying agent solution was then added to a point about 1 cm. below the side arms, and a further portion used to fill the side arms. The emulsion was then warmed slightly to make it lighter than the solution, after which it was pipetted onto the surface in both arms of the U tube.

Careful stirring brought the boundary in each arm about half way down the column. After five minutes a very sharp boundary had been formed between the dilute emulsion and the pure solution. The final concentration of emulsion was thus about 1% decane; this was still opaque. The high dilution minimized the possibility of a difference in concentration of emulsifying agent on either side of the boundary due to adsorption of an appreciable fraction by the globules.

After allowing 10 more minutes for temperature equilibrium to be attained, the current was turned on and the rheostat adjusted to no galvanometer deflection. Finally, switch S was closed. The position of the boundary in both columns was followed by means of a cathetometer. With the anionic emulsifying agents the boundary in the left hand column rose, while that in the right fell. Readings were taken every fifteen minutes for a period of an hour. Every ten minutes the circuit was checked for balance by opening the switch and pressing key K - usually the rheostat had to be adjusted several times to maintain zero deflection.

The equation for calculation of zeta potential is given by Dickinson[22] as

$$\zeta = \frac{4\pi\eta u}{XD} \cdot \frac{1}{f(Kr)} \qquad (7)$$

where u is the electrophoretic mobility under a potential gradient of X statvolts per centimeter. D is the dielectric constant, and η the viscosity of the aqueous phase. The term $f(\kappa r)$ is Henry's function as explained in the theoretical section. For reasons outlined there, this term will be neglected. In order to calculate the zeta potential in volts, we must convert both X and ζ from statvolts to volts by dividing by 300. This gives the following equation:

$$\zeta_{volts} = \frac{4\pi\eta u (300)^2}{XD} \qquad (8)$$

The value of u was taken as the average of rising and falling boundaries. A sample calculation is given below:

Concentration of SDS: .15%

Temperature: 0°C

Time interval: 44 minutes

Potential applied: 8.34 volts

Distance between electrodes: 14.3 cm.

Potential gradient: .584 volts/cm.

Falling boundary: .52 cm.

Rising boundary: .79 cm.

Average: .66 cm. in 2640 seconds

Velocity: 2.50×10^{-4} cm. per second

Viscosity of water: 1.79×10^{-2} poises at 0°C

Dielectric constant of water: 88 at 0°C

Zeta potential: .10 volts.

The viscosity of the SDS solutions used was measured

with an Ostwald viscometer at 0°C. It was found to be identical with that of water.

The precision of the cathetometer readings was ±.01 cm. For a run lasting an hour, the boundary usually moved about 1 cm. and a total of four scale readings was used. The error in reading the time is negligible with respect to the scale reading uncertainty. This gives a precision of the electrophoretic mobility of $\pm 6 \times 10^{-6}$ cm./sec. The precision of the zeta potential is thus ±.004 volts from equation (8).

3. Results and discussion

A. Properties of the emulsions before freezing

An emulsion of 16.7 volume percent decane was chosen as a standard. This low concentration was chosen in preference to higher values after experimentation showed that a greater range of the amount of deemulsification could be obtained, as well as greater reproducibility on successive trials. In the initial experiments using the Eastman decane, a SDS concentration of .5% was taken as the standard. This concentration gave 100% deemulsification with the purer decane, so that .075% was taken as the standard here.

A typical particle size distribution is shown in

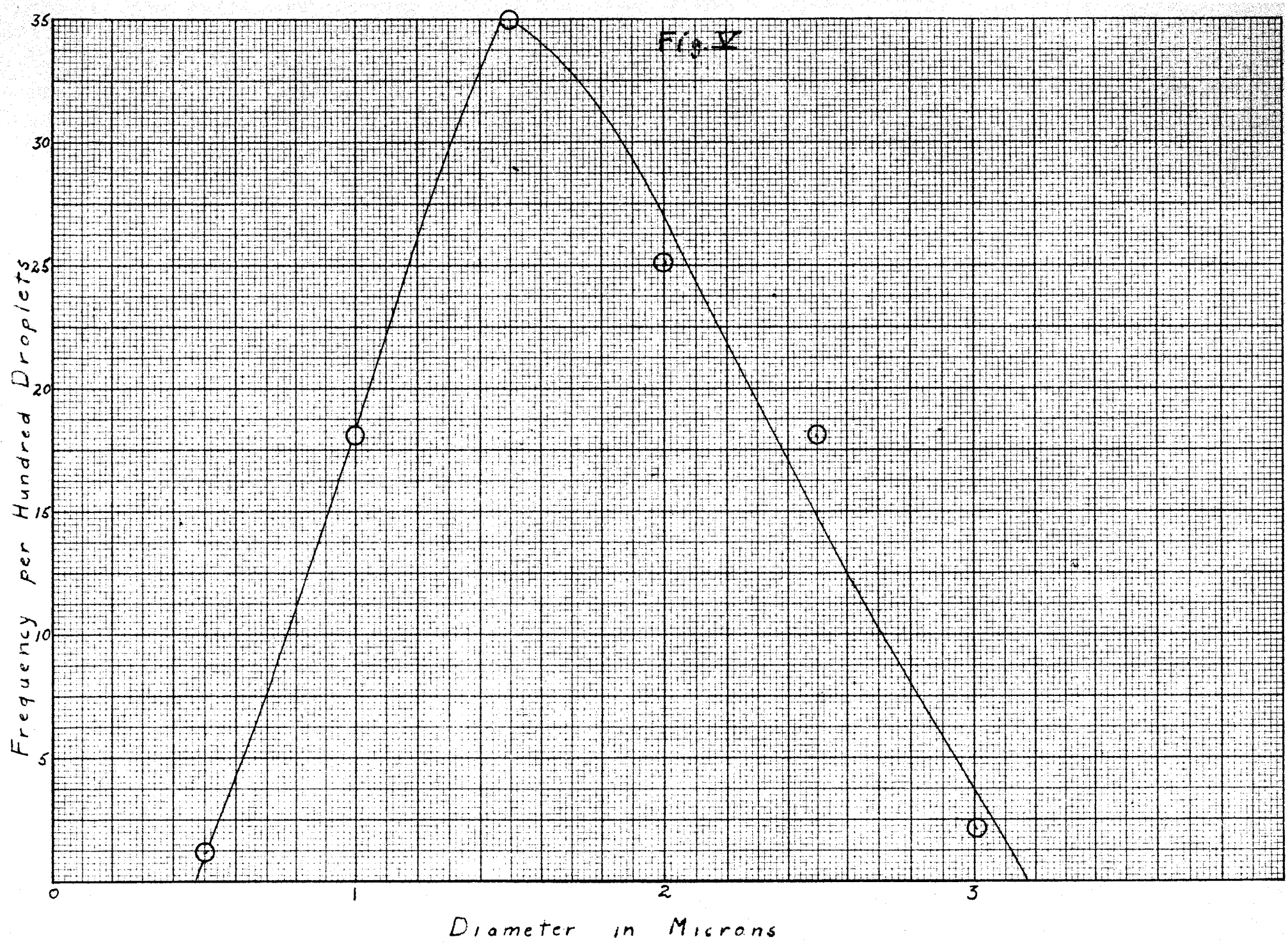


Fig. V. This distribution was reproducible within the limits of experimental error for all the emulsions prepared by the method described except where otherwise noted. However, where the initial SDS concentration was below .015%, or that of HBDAC below .001%, the particle size increased on standing for a short time. For all other cases, this was the distribution at the start of freezing.

There are a number of different criteria of the degree of dispersion of an emulsion. The specific surface, average volume, number of droplets per ml., and average diameter have all been suggested as the best measure of the degree of dispersion. These quantities are tabulated below for the standard emulsion:

Specific Surface ------ 2×10^4 cm.^{2}/ml. decane

Average Diameter.------ 2×10^{-4} cm.

Average Volume -------- 4×10^{-12} cm.^{3}

Number of Droplets ---- 2.2×10^{10} globules /ml. emulsion

1.3×10^{11} globules /ml. decane

The number of droplets was measured in the hemacytometer. This value corresponds closely with the number obtained if all the globules were uniformly 2.5 microns in diameter: 1.5×10^{11} per ml. decane.

Emulsions with greater than .005% surface active agent concentration showed no signs of breaking at room temperature for a period of a day. Below .05% SDS an oil

layer was discernible after 24 hours. Emulsions of SDDS were generally more stable to aging than those of SDS of the same concentration. With HBDAC no oil layer formed after 5 days at .002%. All emulsions were used the same day that they were prepared, so that all samples were completely emulsified when frozen.

The boiling treatment before each freezing experiment was found to have no effect on the particle size.

Microscopic observations on the unfrozen emulsions showed all the particles in brownian motion. No clumping of droplets was seen in any of the emulsions used, except in the presence of .02N sodium chloride.

The electrokinetic potentials and electrophoretic mobilities of decane globules in SDS solutions at 0°C are given in the following table:

Table 1

Temperature: 0°C Concentration SDS in %	Mobility in cm./sec./volt/cm.x10^4	Negative Zeta Potential in volts
0.005	1.75	0.040 ± 0.004
0.0075	2.04	0.047 ± 0.004
0.01	2.10	0.048 ± 0.004
0.015	3.77	0.086 ± 0.004
0.02	4.09	0.093 ± 0.005
0.04	4.38	0.100 ± 0.006
0.05	4.41	0.100 ± 0.005

Table 1 (Continued)

0.06	4.24	0.097 ± 0.005
0.075	4.11	0.094 ± 0.004
0.10	4.29	0.100 ± 0.004
0.15	4.38	0.100 ± 0.004
0.175	4.53	0.103 ± 0.006
0.19	3.59	0.082 ± 0.004
0.20	3.68	0.084 ± 0.004
0.22	3.59	0.082 ± 0.004
0.25	3.68	0.084 ± 0.004
0.40	3.68	0.084 ± 0.004
0.50	4.11	0.085 ± 0.008
Temperature: 22°C		
0.80	7.70	0.10 ± 0.008
1.00	6.70	0.093 ± 0.008

Each value is the average of at least two separate determinations.

The values are plotted in Fig. VI. It will be noted that there are two minima. The first, at about .075%, differs from the maximum at .05% by less than two times the precision, and therefore could be accounted for by the experimental error. However, three successive determinations of the zeta potential at .075% agreed to within .001 volts, so that this minimum probably exists. The sharp drop at .19% may be correlated with similar phenomena

observed by Powney and Wood[31] for sodium dodecyl sulphate and sodium laurate emulsions of paraffin oil. In both these cases a drop of about .03 volts occurred at one-fifth of the critical micelle concentration. Likewise here the drop is about .025 volts at one fifth the critical micelle concentration of 1%. The actual values obtained by Powney and Wood differ from ours; their maximum in both cases was .18 volts at 25°C. The difference in temperature may account for the discrepancy of .08 volts, although both the dispersed phase and emulsifying agents are sufficiently different from ours to produce this effect.

Measurements above .5% were impractical at 0°C due to precipitation of the SDS. The increase in zeta from .5% to .8% may be due to the temperature difference of 22°C.

The zeta potential values obtained for SDDS are given in Table 2.

Table 2

Temperature: 0°C Concentration SDDS in %	Mobility in cm./sec./volt/cm.x10^4	Negative Zeta Potential in volts
0.002	2.19	0.050 ± 0.004
0.01	2.90	0.066 ± 0.004
0.02	3.33	0.076 ± 0.004
0.03	3.60	0.082 ± 0.004
0.04	4.65	0.107 ± 0.008
0.05	3.72	0.085 ± 0.004

Table 2 (Continued)

0.06	2.59	0.060 ± 0.004
0.08	4.11	0.094 ± 0.004

Values above .08% are ruled out by solubility. The values in Table 2 are plotted in Fig. VII. The poor reproducibility of the maximum at .04% is probably due to dilution errors, since the zeta potential falls off rapidly on each side of this maximum. The errors in all the volumetric procedures used can produce a variation of .002% in the concentration.

The shape of the curve is quite similar to that obtained by Powney and Wood for sodium dodecyl sulfate; this is to be expected, since both emulsifying agents contain a twelve carbon chain. The maximum and minimum are both at the same concentration as these authors found.

Since the maxima and minima of these curves will be seen to play an important part in deemulsification, it may be well to arrive at least at a qualitative explanation for them. Thomas[32] gives data obtained by DuNouy on the equilibrium surface tensions of very dilute sodium oleate solutions. At the concentration corresponding to complete coverage of the surface with flat molecules, there is a sharp minimum in the surface tension curve. As the concentration is increased, a second minimum is found where the next largest dimension of the molecules is parallel

with the surface. Finally, the deepest minimum occurs when the molecules become perpendicular to the surface. The cross sectional area of a saturated paraffin chain is given by Thomas as about 1.8×10^{-15} cm^2. Data to be presented shows that the surface excess for SDS is about 3.5×10^{-10} equivalents per cm^2. in a .19% solution. This is about 2×10^{14} molecules per cm^2. which occupy about .38 cm^2. when perpendicular to the interface, and about .60 cm^2. when presenting their next largest dimension. It must be remembered, however, that the area occupied is given for an uncharged molecule; the data was obtained with palmitic acid. Consequently the effective area required for the decyl sulfonate anion will be greater tham this. Therefore, while the actual paraffin chains occupy 60% of the area lying horizontally, the high electrostatic repulsion between them may cause a shift to the vertical upon increasing the concentration. Since this shift to a new arrangement is known to affect surface properties, it is probable that it affects the zeta potential as well. The sharp drop at .19% for SDS and at .06% for SDDS may be due to such a critical orientation. Further evidence for this is the ratio of the two concentrations at the minima for SDS and SDDS. They are as 3:1 while the respective values of $\frac{\partial \gamma}{\partial c}$ are as 1:2.5. Hence by Gibb's law approximately the same surface concentration is reached at .06% SDDS as for

SDS at .18%. The shallow minimum at .075% SDS may be due to the next largest dimension of the molecules oriented parallel to the surface. One would expect the vertical shift to have the greatest effect.

The state of aggregation of the SDS molecules is not a factor in the zeta potential curve in this concentration region. The equivalent conductance was found to be perfectly linear in this region, ranging from 33.4 at .001% to 32.4 at .20%, for the pure solutions at 0°C. If any sort of micelle had formed, the equivalent conductance would show a sharp fall or rise. Consequently the zeta potential drop is probably due to phenomena associated with the decane-solution interface.

The zeta potentials obtained for decane globules in HBDAC are given in Table 3.

Table 3

Temperature: 0°C Concentration HBDAC in %	Mobility in cm./sec./volt/cm.x10^4	Positive Zeta Potential in volts
0.001	1.17	0.040 ± 0.004
0.002	2.36	0.054 ± 0.006
0.005	2.45	0.056 ± 0.008
0.010	2.36	0.054 ± 0.006
0.020	2.92	0.068 ± 0.008

These values showed poorer reproducibility than

than those for the anionic emulsifying agents. This may be due to the high sensitivity to the presence of small quantities of electrolyte impurities from the distilled water and other sources, such as small amounts of rust from the homogenizer. Data to be presented will indicate that this zeta potential can be lowered to 0 with less than .1N NaCl. The general shape of the curve is in accord with that obtained by Powney and Wood for dodecyl pyridinium chloride, and that given by Alexander and Johnson[33] for hexadecyl trimethyl ammonium chloride. In neither of these cases is there any sharp minimum or maximum, and the values obtained were much lower than for the corresponding concentrations of anionic emulsifying agents. This latter fact is due to the adsorption of OH^- ions which normally are capable of giving a potential of -.04 volts to a hydrocarbon dispersed in pure water. These values for HBDAC are seen to be about .04 volts lower than those of SDS. These values are plotted in Fig. VIII.

The interfacial tensions between decane and solutions of the three emulsifying agents are given below, and all are the average of two separate determinations.

Table 4

Temperature: 0°C Concentration: SDS in %	Interfacial tension in dynes/cm.	Concentration: SDDS in %	Interfacial tension in dynes/cm.	Concentration: HBDAC in %	Interfacial tension in dynes/cm.
0.000	45.3 ± 0.5	0.000	45.3 ± 0.5	0.0000	45.3 ± 0.5
0.002	42.8 ± 0.3	0.002	40.1 ± 0.3	0.0001	28.0 ± 0.6
0.005	42.5 ± 0.2	0.005	38.5 ± 0.2	0.0002	22.2 ± 0.6
0.010	41.5 ± 0.2	0.010	34.5 ± 0.2	0.0004	17.5 ± 0.5
0.025	38.6 ± 0.2	0.015	32.2 ± 0.2	0.0005	15.8 ± 0.5
0.033	37.2 ± 0.2	0.020	29.8 ± 0.2	0.001	13.5 ± 0.3
0.040	36.4 ± 0.3	0.030	27.0 ± 0.2	0.002	11.0 ± 0.2
0.050	35.7 ± 0.3	0.040	26.3 ± 0.2	0.003	9.2 ± 0.2
0.060	35.5 ± 0.3	0.055	25.3 ± 0.2	0.005	7.6 ± 0.2
0.075	35.1 ± 0.2	0.070	24.0 ± 0.2	0.007	6.2 ± 0.3
0.095	33.6 ± 0.2	0.10	20.8 ± 0.2	0.008	5.5 ± 0.3
0.100	34.1 ± 0.2			0.012	3.5 ± 0.4
0.120	33.5 ± 0.2			0.015	2.1 ± 0.5
0.150	31.6 ± 0.2			0.02	1.6 ± 0.5
0.250	27.8 ± 0.2				
0.350	23.4 ± 0.2				
0.50	17.1 ± 0.2				
1.00	10.4 ± 0.2				

These are plotted in Figs. VI, VII and VIII. It will be noted that in all three cases, there is a region of almost constant slope at high concentrations, followed by a short interval in which the slope changes rapidly, and then another constant slope region at low concentrations. This is known to be characteristic of surface active substances.

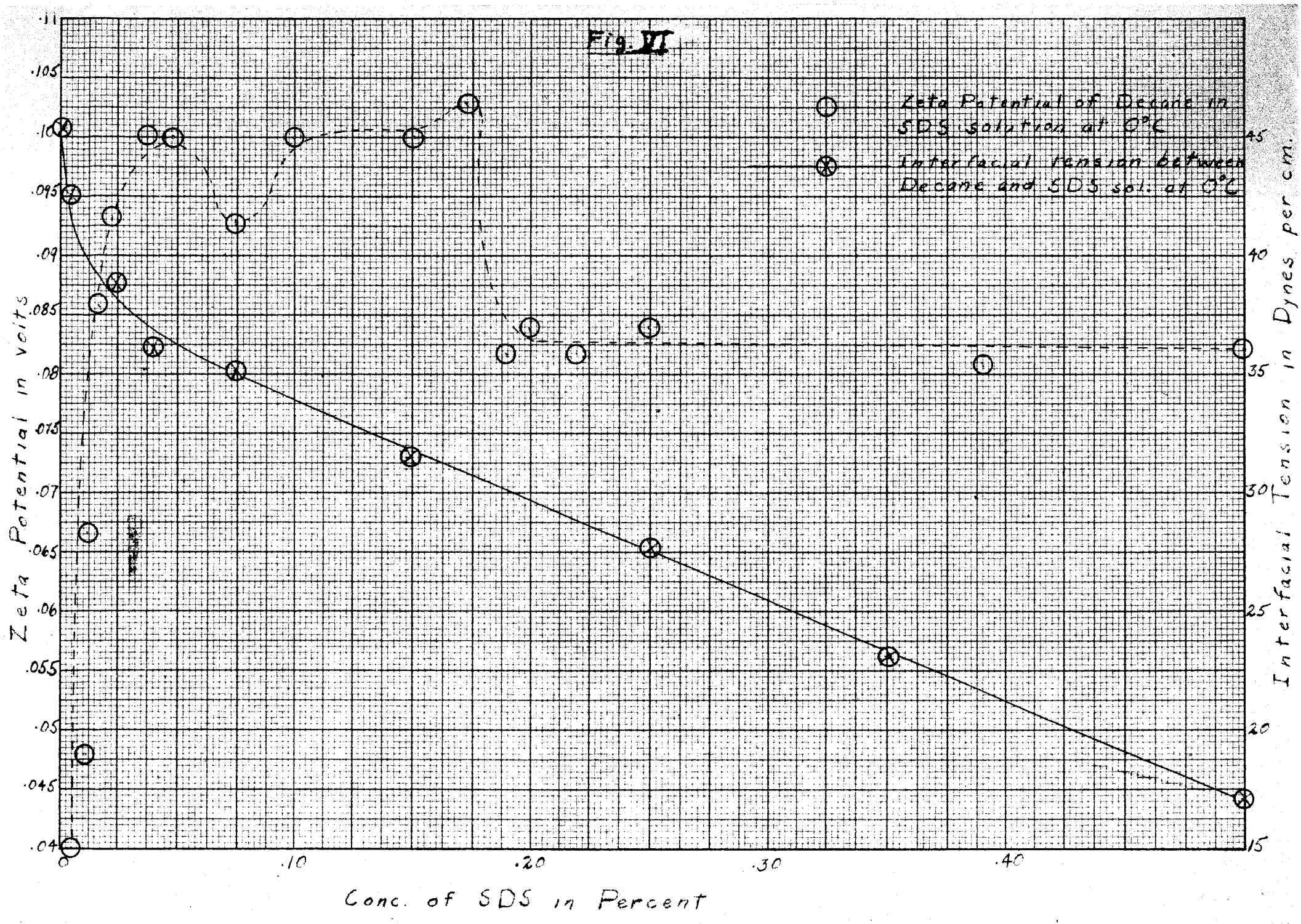
Recently[34] a paper was published giving a value of 53.12 dynes/cm. for the interfacial tension between water and decane at 0°C. The sample used was specially purified. This is almost 8 dynes/cm. greater than our figure. It is probable that the decane used in our experiments contained some branched chain hydrocarbons which boil at the same temperature as normal decane, and which have a lowering effect on the interfacial tension. Nevertheless, since the same sample was used for all measurements where interfacial properties were calculated, this discrepancy should not nullify any of our results.

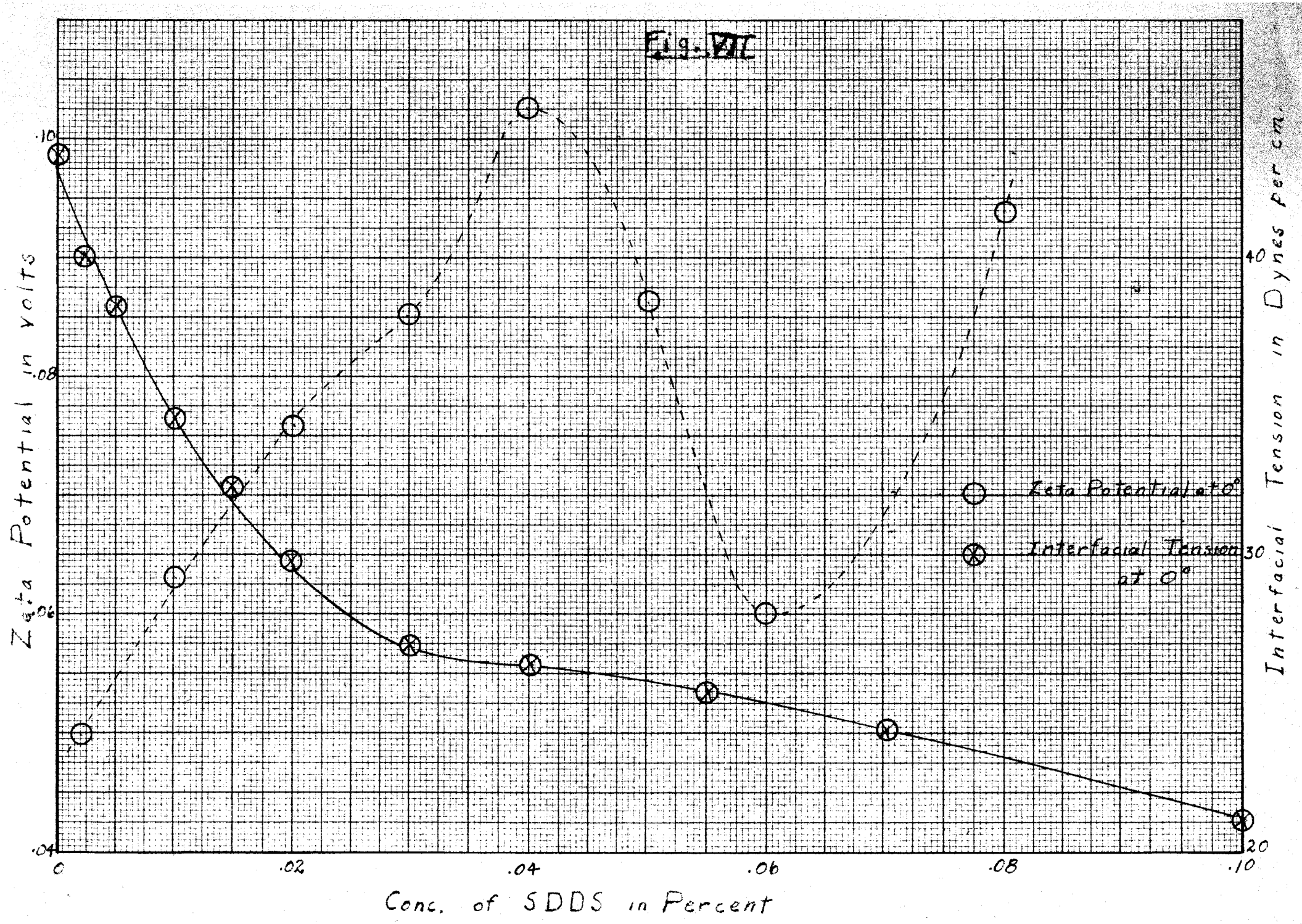
The validity of Gibbs law of surface adsorption for SDS was tested according to procedure E. The equation used was derived in the following manner:

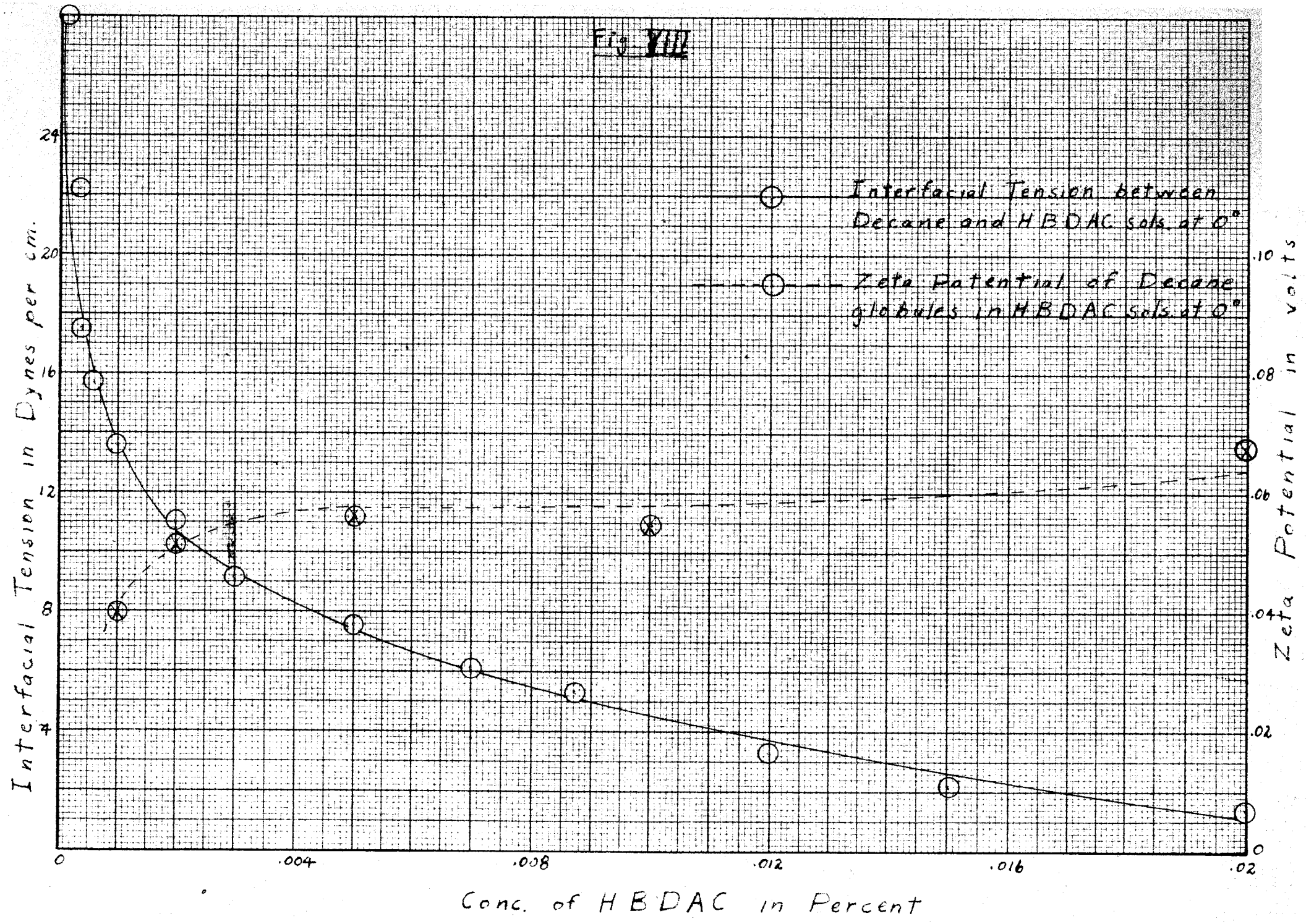
Let c_o = total moles of emulsifying agent per liter of water

c = final bulk concentration per liter of water

e = surface concentration of emulsifying agent in moles per cm^2. of interface







s = total area of interface per liter of water

$x = es$ = total moles of emulsifying agent at the interface.

$$c = c_o - es$$

$$e = \frac{-c}{RT} \cdot \frac{\partial \gamma}{\partial c}$$

$$x = es = -\frac{cs}{RT} \cdot \frac{\partial \gamma}{\partial c}$$

$$c = c_o - \frac{cs}{RT} \frac{\partial \gamma}{\partial c}$$

$$c = \frac{c_o}{1 - \frac{s}{RT} \cdot \frac{\partial \gamma}{\partial c}} \qquad (9)$$

Applying this to an initially .1% SDS - 16.7% decane emulsion of the standard particle size distribution, we have:

$$s = 4.2 \times 10^6 \text{ cm}^2./\text{l. } H_2O$$

$$c_o = 4.19 \times 10^{-3} N$$

$$\frac{\partial \gamma}{\partial c} = -9.64 \times 10^2 \text{ dynes/cm. eq.}$$

$$RT = 2.27 \times 10^{10} \text{ ergs/mole}$$

$$c = 3.48 \times 10^{-3} N = .084\%$$

Table 5 gives values calculated in this way as compared with the experimental figures.

Table 5

Temperature: 25°C

16.7% Decane

Initial SDS Concentration in %	Final Concentration by Experiment	Final Concentration by Equation (9)	Deviation
0.10	0.080 ± 0.002	0.084	-0.004
0.03	0.015 ± 0.002	0.0146	+0.0004
0.02	0.010 ± 0.002	0.0097	+0.0003

The agreement between experiment and theory is good. The .004% deviation with the .1% value is easily accounted for by the sources of error enumerated in the section on procedures.

B. Mechanics of freezing

Microscopic observations afford the best picture of the mechanical processes involved in freezing an emulsion. However, it must be borne in mind that the conditions under which a film of emulsion freezes on a slide are considerably different from those obtained with a large cylindrical tube.

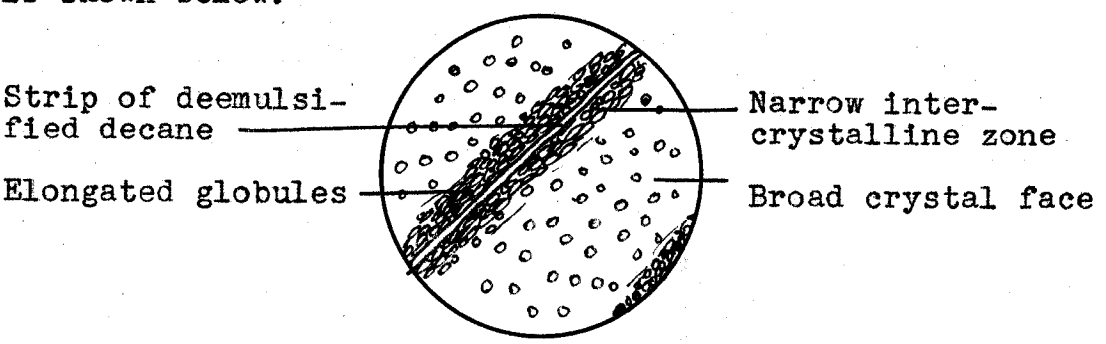
A .5% SDS - 16.7% decane emulsion was frozen slowly using the cold stage shown in Fig.III. Long pointed needles of ice advanced over the field at first. These crystals widened slowly, pressing globules between them;

the globules were in violent agitation during this process. Coalescence did not begin until almost all the water was frozen, and the globules crowded into the narrow intercrystalline zones. Finally in the completely frozen state a continuous strip of deemulsified decane separated the ice crystals. Uncoalesced individual droplets, apparently almost touching each other, were embedded in the ice directly adjacent to this continuous strip of decane. These droplets were for the most part elongated, with the longest axis parallel to the crystal face. During and immediately after slow freezing at $-1^{o}C$, some globules were observed between the broad crystal faces. These were separated from each other by at least 2 microns, and hence showed no tendency to coalesce. When frozen at this temperature, the ice crystals were about 100 microns across, and extended across the entire slide. When the temperature was lowered to $-3^{o}C$, the globules in these wide spaces gradually became less distinct, and finally disappeared altogether, while the droplets in the narrow zones remained visible. Lowering the temperature to $-10^{o}C$ produced no further change. The temperature was then raised slowly giving the first signs of motion in the intercrystalline zones at $-2^{o}C$. Some coalescence was observed here, and a few small droplets began to move. The hitherto invisible globules between the broad crystal faces reappeared at this temperature

and became more and more distinct as 0°C was approached. This was evidenced by their outlines becoming darker. Finally at 0°C complete melting had occurred. The strips of decane gradually assumed spherical shape. Some coalescence was observed for about 5 seconds after thawing, but only about one out of a thousand droplets was visibly enlarged by coalescence in this stage. Globules were of two sizes only; from 60 - 80 microns in diameter, and unchanged or 2 - 3 microns in diameter.

These results could be duplicated using different rates of freezing; the only difference being in the width of the ice crystals. Rapid freezing gave smaller crystals.

A diagram of a typical emulsion frozen on a slide is shown below:



An important conclusion to be drawn from this work is that the smallest dimension of the ice crystal reaches its maximum value first, followed by broadening until the maximum width is obtained, and finally the length increases until some obstacle is reached. These conclusions are supported by the work of Kalb[35], who further states that

tabular crystals usually prevail near 0°C. Ice usually is of a hexagonal structure, which tends to obscure the junctures between the crystals when observed under the microscope. The crystals are said to form a skeletal structure first, and then fill out.

Further information as to the structure of the frozen emulsion was obtained by examination of a .5 mm. thick cross section from an emulsion frozen in bulk at -10°C. Ice crystal size was measured with a micrometer eyepiece with 40 power total magnification. The following dimensions were found:

Thickness: 0.015 mm.
Breadth: 0.15 mm.
Length: 4.00 mm.

Each crystal extended from close to the periphery to the center of the frozen mass. The breadth given is that at a point half way between the center and periphery. It was found that the outer .5 mm. of the frozen cylinder always showed a different structure from that of the inner portions. The crystals directly in contact with the glass had their longest axis parallel to the glass, while the next layer of crystals were perpendicular to the surface.

A clearer picture of the relationship between the crystal size and distribution of the droplets may be obtained from the following calculations:

1) Volume of emulsion: 5 ml. (16.7% decane)

2) Number of crystals in this volume: 7×10^5

3) Number of globules in this volume: 1.3×10^{11}

4) Number of globules per crystal: 1.9×10^5

5) Number of globules per narrow intercrystalline zone: 1.1×10^5

6) Average volume of a globule before freezing: 4×10^{-12} cc.

7) Volume of decane in narrow zone: 4.4×10^{-7} cc.

The figure for (5) was obtained by taking 60% of (4) since it was found, as will be discussed later, that only 60% of the dispersed phase is subject to deemulsification in the narrow intercrystalline zones. The other 40% appears to be protected between the broad crystal faces.

From these figures we may calculate that the globules form a mass of about 7 globules across and extending .4 cm. or 2000 globules long, assuming a rectangular or cylindrical form for each intercrystalline zone. This picture would vary with the rate of freezing and shape of the container.

Other workers[7] have found a decidedly greater concentration of dispersed phase in the inner portion of the frozen bulk than in the outer portions. This effect was enhanced by slow freezing. In order to rule out this factor as a complication, we made measurements to determine

the distribution of dispersed phase and emulsifying agent in the frozen and partly frozen masses. Using the cork borer technique described, the following data was obtained:

Table 6

Frozen at -10°C for 10 minutes
Emulsion as a whole: .5% SDS, 16.7% decane

Volume	% Decane	% SDS
Outer 20%	13 ± 1	0.41
Next 58%	17 ± 1	0.50
Inner 19%	19 ± 1	0.56

These results show that only a small change of concentration occurs with respect to radial distance from the center, both for decane and SDS. The ratios of SDS to decane concentrations are the same for all three sections, which means that there is no separation of the two during freezing in terms of the macroscopic picture.

C. Influence of variables

a. Effect of concentration of emulsifying agent

All these experiments were done with the Phillips decane. The results obtained are in Table 7. All values are the average of at least two determinations made at different times, using freshly prepared emulsions for each test. The second column is the percentage of the total amount of decane present that was deemulsified. The third column represents the percentage of the maximum value that could be obtained with unagitated freezing and thawing; namely, 60%. This relative deemulsification will be used in discussions and calculations for reasons explained below.

Table 7

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

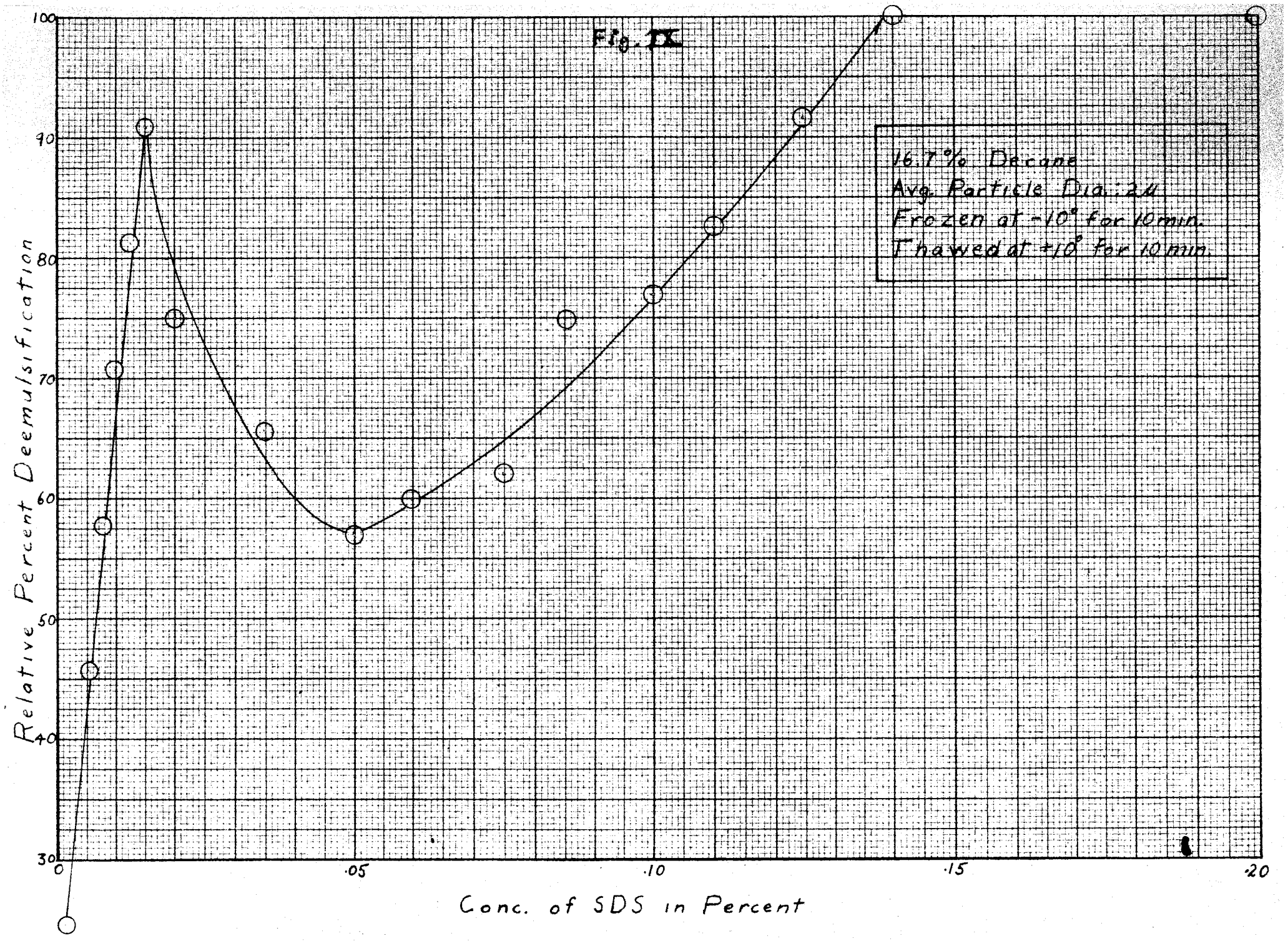
Concentration SDS in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.002	15 ± 3	25 ± 5
0.005	28 ± 3	46 ± 5
0.0075	35 ± 3	58 ± 5
0.01	43 ± 3	72 ± 5
0.0125	49 ± 3	83 ± 5

Table 7 (Continued)

Concentration SDS in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.015	55 ± 3	92 ± 5
0.02	45 ± 4	75 ± 6
0.035	40 ± 3	66 ± 5
0.05	38 ± 3	57 ± 5
0.06	36 ± 4	60 ± 7
0.075	37 ± 4	62 ± 7
0.085	45 ± 3	75 ± 5
0.10	46 ± 3	77 ± 5
0.11	50 ± 3	83 ± 5
0.125	55 ± 3	92 ± 5
0.14	60	100
0.20	60	100
0.50	60	100

All deemulsification values were exactly reproducible for the same sample of emulsion, but varied slightly between different samples of the same concentration.

The concentrations listed are those of the emulsifying agent solution before the addition of decane. By equation (9), the actual concentrations in the bulk aqueous phase before freezing are .834 times the initial value when $\frac{\partial \gamma}{\partial c}$ is 9.6×10^2 and .50 times the initial value when $\frac{\partial \gamma}{\partial c}$ is 4.6×10^3. These relationships will hold only when



the volume percentage decane is 16.7% and the specific surface, 2.0×10^4 cm.^{2}/ml. decane. When freezing starts, both the decane globules and emulsifying agent will become more concentrated until the close packing ratio for spheres of the same size is reached; namely 74 volume percent. We will make two assumptions with regard to this:

1. Both constituents of the emulsion are frozen out completely until close packing is reached; ice does occlude either one.

2. Surface equilibrium is maintained between the concentrating emulsifying agent and the decane-solution interface.

Using these two assumptions we may calculate the actual bulk concentration when the close packing ratio is reached. The surface per liter of aqueous phase in this state is 5.7×10^2 cm.^{2} and the overall concentration is 14.3 times the initial overall value, since the aqueous portion is only 26% of the total liquid volume which has decreased from 1 ml. to .225 ml. Substituting the appropriate figures in (9) we find that the bulk aqueous concentration has increased 4.2 times the initial overall quantity. Thus for an initially .10% SDS emulsion, the concentration at close packing is .42%. Since the slope of the interfacial tension curve is constant above .05%, this same increase in bulk concentration may be assumed for the range of values used.

The remaining emulsifying agent is adsorbed within the approximately .002 microns of the double layer. Since this represents a negligible total volume, it may be considered to be effectively removed from the bulk liquid.

As the ice begins to envelop the droplets themselves, after close packing has been reached, and to cause them to coalesce,we will assume that the SDS molecules primarily adsorbed are not pushed ahead by the ice, but remain at or near the surface when frozen.

In any case we may conclude that there is 14.3 times as much emulsifying agent per unit volume of aqueous phase when coalescence begins, that is, at close packing, than before freezing began, in an initially 16.7% dispersed phase emulsion.

The data in Table 8 are plotted in Fig. IX. The ordinate is the relative deemulsification. The curve reaches a maximum value of 60% of the total decane present deemulsified which is taken as 100% relative deemulsification. This occurs at about .14% SDS, and increasing the concentration above this gives the same value. The explanation of this maximum is to be found in microscopic observations. A certain portion of the droplets were entrapped between the broadest crystal faces and these were far enough apart to prevent their coalescing with one another. It is possible, therefore, that 40% of the droplets, when frozen in bulk, are protected in this manner. Some coalescence of

these does occur, as will be shown in a later section, but they do not reach a sufficiently large size to coalesce ultimately to give a continuous decane phase. We know that the average width of an ice crystal, frozen under the standard conditions, is .015 mm. Since there are about 10^6 crystals in a 5 ml. sample, this gives a total area of 6000 square centimeters between the broad crystal faces. Such an area could accomodate about 1.5×10^{11} droplets of 2 micron diameter without their touching one another. This is about 23% of the total number of droplets present in 5 ml. so that 40% would fit in with some coalescence. We have seen that this is the case. Since 40% does not contribute to the bulk layer after thawing, the factors affecting the amount of deemulsification apply only to the remaining 60%. Thus the relative deemulsification was chosen for quantitative treatment of the variables.

For the purpose of analysis, the curve in Fig. IX will be divided into three concentration ranges:

1. <u>From .05 to .14% SDS</u>

In this region it was found that rate of freezing had no effect on the amount of decane that rose to the surface. This indicates that when a certain SDS concentration has been reached during freezing, there unsues complete and very rapid coalescence of those droplets not yet engulfed by the ice. The zeta potential shows a sharp drop between .18% and .19% SDS, the probable reasons for which

were outlined previously. At .14% in Fig. IX the concentration at close packing corresponds to .59% in the free aqueous phase. Apparently the actual zeta potential at this concentration has just reached a sufficiently low value for rapid coalescence to begin and to proceed to completion. The discrepency between .19% and .59% is explicable on the basis of orientation of the paraffin chains. The sudden fall in zeta potential is determined by the space relationships between the paraffin chains and the surface available for them. It is known that the close approach of two charged emulsion droplets causes a decrease in the charge density on their opposing faces due to electrostatic repulsion. Thus, molecules of emulsifying agent are pushed aside at the point of closest approach. At .59%, we find that 112% of the surface would be covered by the calculated surface excess of vertically orientated SDS molecules of 1.8×10^{-15} cm.^{2} cross sectional area. Either this is not reached, or several layers of molecules are present. When the repulsive forces of a second droplet decrease the density, it is possible that the resultant surface concentration is equal to that of a .18% SDS solution with an isolated droplet. The zeta potential at that point may therefore be .03 volts higher than the surrounding surface. Any further increase in concentration will decrease the zeta potential and result in coalescence. In addition, the presence of a second double layer near a

given area will tend to prevent a shift from horizontal to vertical orientation of the $DS^{\ominus}$ ions, since the effective distance between the droplets would be decreased by this process. If the vertical orientation is connected with a fall in zeta potential, this factor will also tend to increase the potential above .19%. Even if our calculation of the close packing concentration is erroneous, the error is more likely to be on the side of low concentration due to non-attainment of equilibrium. Thus it is improbable that the actual bulk concentration is .19% when the overall concentration has increased 14 times the initial value of .14%.

In any case, we will assume that the fall in zeta potential for two globules in close contact has been shifted to a concentration 3.1 times that for an isolated droplet.

If the concentration at close packing is less than .59%, the droplets will be engulfed by the ice with little or no coalescence before this concentration is reached. During the freezing of the emulsion itself, the bulk concentration will increase due to three possible factors. First, by freezing out of the bulk SDS alone, leaving most of the primarily adsorbed molecules associated with the surface of the globules in the frozen state. Moreover, it is difficult to conceive of a mechanism whereby the adsorbed paraffin chains could be desorbed during freezing. The second mode of concentration increase is through the deformation of the

globules remaining in the liquid water phase due to the force exerted by the ice. For perfect spheres, 26% of the liquid remaining is water, but deformation of the globules considerably reduces the relative volume of water, and thus tends to increase the concentration of solute with respect to the surface area of the globules. Finally, any coalescence will decrease the specific surface of the decane and thus would increase the bulk SDS concentration. Regardless of what factors are involved, the amount of decane subjected to .59% SDS and above will probably coalesce completely and rapidly due to the sudden fall in zeta potential. That fraction of the emulsion protected by high zeta potential will be proportional to the quantity: $(.59 - C_{cp})$ where C_{cp} is the SDS concentration in the bulk aqueous phase at close packing. This fraction should not contribute to the bulk layer on thawing. The equation thus becomes:

$$RD = 100-k(.59-C_{cp}) \qquad (10)$$

where RD is the relative deemulsification.

If no coalescence occurred before .59% was reached, and the concentration increased linearly with the amount of watef frozen, the value of k should give 0 deemulsification when C_{cp} is 0. Examination of Fig. IX shows that this is not the case. Extrapolation of the line at 0 concentration gives a D intercept of 28. Thus the concentration in the unfrozen aqueous portion is 28% greater than expected. This is due to either a decrease of 28% in the specific surface

of the frozen droplets, a desorption of 28% of the SDS by freezing, or by increasing deformation as freezing progresses. The latter is the most likely possibility. This gives a value of k of 122. The final equation is thus:

$$RD_{(.05\% - .14\% \text{ SDS})} = 100 - 122(.59 - C_{cp}) \qquad (10a)$$

$$RD = 28 + 122C_{cp}$$

$$RD = 28 + 512\ C_o \qquad (11)$$

The following table gives the data:

Table 8

Initial Concentration SDS in %	Close Packing Concentration SDS (C_{cp})	$28+122\ C_{cp}$	Relative Deemulsification (RD)	Deviation
0.05	0.21	54	57 ± 5	3
0.06	0.25	59	60 ± 5	1
0.075	0.32	67	62 ± 7	-5
0.085	0.36	72	75 ± 5	3
0.10	0.42	79	78 ± 5	-1
0.11	0.46	84	83 ± 5	-1
0.125	0.52	92	92 ± 5	0
0.14	0.59	100	100	0

Average ± 1.8%

The average deviation is thus less than the precision of the measurements. The wide deviation of the .075% value indicates that some other effects may be playing a part in this case. The experimental values for this concentration ranged from 68% to 55%, with the 55% figure reproducible

exactly for the same sample of emulsion.

It should be noted here that we have assumed a constant .103 volt zeta potential above .17%, where the maximum is in Fig. VI. The only shift is in the fall to .08 volts.

2. From .015% to .05% SDS

In this region the curve in Fig. IX falls sharply as concentration is increased from .015 to .035%. Calculation of the SDS concentrations rises over the same interval. We shall assume that no shift in the zeta potential occurs as seems to be the case with higher concentrations, where a critical orientation probably determines the potential. According to equation (5), the rate of coalescence at any given time should be inversely proportional to the force of repulsion between the droplets, at constant ice force. If the process is autocatalytic, the extent of coalescence should depend on the rate of coalescence at the beginning, or when the globules have just reached their close packing ratio. Consequently, the force of repulsion at close packing should determine the extent of deemulsification.

In order to apply equation (2) we must know the distance of closest approach H. Actually this should vary with the force of repulsion under the influence of a constant ice force, but since F_I cannot be calculated with any degree of precision due to deformation of the globules,

an arbitrary distance will be taken. The attractive forces between the globules do not extend over a much greater range than a molecular length. Consequently we will choose .001 microns or 10^{-7} cm. - this is about 2/3 the length of a SDS paraffin chain or decane molecule.

A sample calculation is given below:

$$F_R = \frac{D_r \zeta^2 K}{4}\left[1 - \tanh \frac{KH}{2}\right]$$

$$\frac{u\eta[1+Kr]}{r} = 2\sqrt{\frac{DRTc}{2000\pi}} \sinh \frac{F\zeta}{2RT}$$

C_o = .02% SDS

C_{cp} = .097% = 3.65×10^{-3} N

ζ = .10 volts = 3.33×10^{-4} statvolts

u = .15 cm./sec./statvolt/cm.

H = 10^{-7} cm.

r = 10^{-4} cm.

f(K r) = 1

F/2RT = 6.39×10^{3}

$\sqrt{\frac{DRT}{2000\pi}}$ = 1.78×10^{4}

K = 3.4×10^{6} cm.$^{-1}$

F_R = 6.9×10^{-4} dynes

Table 9 gives the calculated force of repulsion for spherical droplets for each of the concentrations used. The specific surface for the first two concentrations was found to be 1.7×10^{4} cm.^{2} per cm.^{3} decane, which is less than the value of 2.0×10^{4} obtained for higher concentrations.

This factor results in an increased C_{cp} as calculated by equation (9).

Table 9

The equation for the deemulsification in this region is:

$$RD = k / F_R \qquad (12)$$

$$RD_{(.015\%-.05\%SDS)} = .516 / F_R \qquad (12a)$$

The value for k was taken as the average of the last three figures in column 7. The 5% deviation for the .015% sample is within the limit of experimental error. However, since the curve falls rapidly as concentration is decreased beyond this, it is probable that those factors tending to decrease the deemulsification are also operative with .015%, thus causing a lower value than would be expected from the force of repulsion alone.

Continuing these calculations of concentrations to .14% SDS, we find a continuous increase in the force of repulsion. Thus the increase in deemulsification from .05% to .14% is probably due to the sudden fall in zeta potential, and hence in replusive force, that occurs when .59% SDS is reached. By equation (2), the force of repulsion would suddenly fall to .67 of its former value at .59%. This would increase the rate of coalescence 1.5 times, which would in turn increase the rate still further by auto-catalysis.

Table 9

Initial Concentration SDS in %	Concentration Close Packing C_{cp}	ζ in volts	κ in $cm.^{-1} \times 10^{+6}$	F_R in dynes $\times 10^4$	Relative Deemulsification (RD)	$(F_R)(RD)$	Deviation
0.015	0.072	0.094	2.85	5.31	92 ± 5	0.489	-5
0.02	0.095	0.100	3.40	6.90	75 ± 6	0.517	0
0.035	0.150	0.100	4.03	7.86	66 ± 5	0.519	0
0.05	0.210	0.103	4.85	8.98	57 ± 5	0.512	0
						Average	± 1.2 %

3. From .002 to .015% SDS

In this region there is a linear fall in the curve as concentration is reduced. However, the zeta potential falls sharply in this interval, and the interfacial tension rises rapidly, both of which might be expected to give lowered stability to freezing. The explanation is indicated by microscopic observations. For all concentrations above .015%, the droplets were seen to flow readily to the narrow intercrystalline zones during the last stages of freezing. Below .015% they do not, but adhere to the ice on first contact. This effect increases as the initial concentration is lowered, so that at .002% the droplets spread on the ice crystals during the first stages of freezing, forming irregularly shaped films. In the final frozen state there were no droplets of circular outline embedded in the ice as at higher concentrations, but there were irregular masses homogeneously distributed throughout the ice. This means that the droplets fail to concentrate in the narrow intercrystalline zones and become close packed there. They are thus protected to a certain extent between the broad crystal faces. We would expect, however, that since there is room for only about 24% of the droplets in these broad zones, some increase of particle size would take place. This was observed, but no quantitative measurements were made.

This explanation is supported by our observation

that decane will not spread at a pure water-air interface, but will at an ice-air interface. Since it wets ice better than water, it will tend to adhere to the ice until the SDS concentration is high enough to reverse the situation. We would therefore expect that the curve should be related to the spreading coefficient of decane at the ice-solution interface. In general, the spreading coefficient is given by:

$$S = W_a - W_c \qquad (13)$$

where W_a is the work of adhesion, and W_c the work of cohesion. According to Adam,[36] the work of cohesion is given by:

$$W_c = \gamma_w + \gamma_{Ice} - \gamma_{Ice-w}$$

and the work of adhesion is

$$W_a = \gamma_D + \gamma_{Ice} - \gamma_{Ice-D}$$

where γ_w is the surface tension of the aqueous phase, γ_D that of the decane, and γ_{ID}, γ_{Iw} are the respective interfacial tensions. These relationships are combined with

$$\gamma_{ID} - \gamma_{Iw} = \gamma_{wD} \cos\theta$$

where θ is the angle of contact between the decane and ice, to give

$$S = \gamma_w - \gamma_D + \gamma_{wD} \cos\theta$$

For two pure phases $\gamma_w - \gamma_D$ is their interfacial tension. In these dilute solutions we may equate the two so that (13)

becomes:

$$S = \gamma_{wo} + \gamma_{wo}\cos\theta$$

The higher the spreading coefficient, the greater the amount of decane still emulsified aftef freezing. Thus

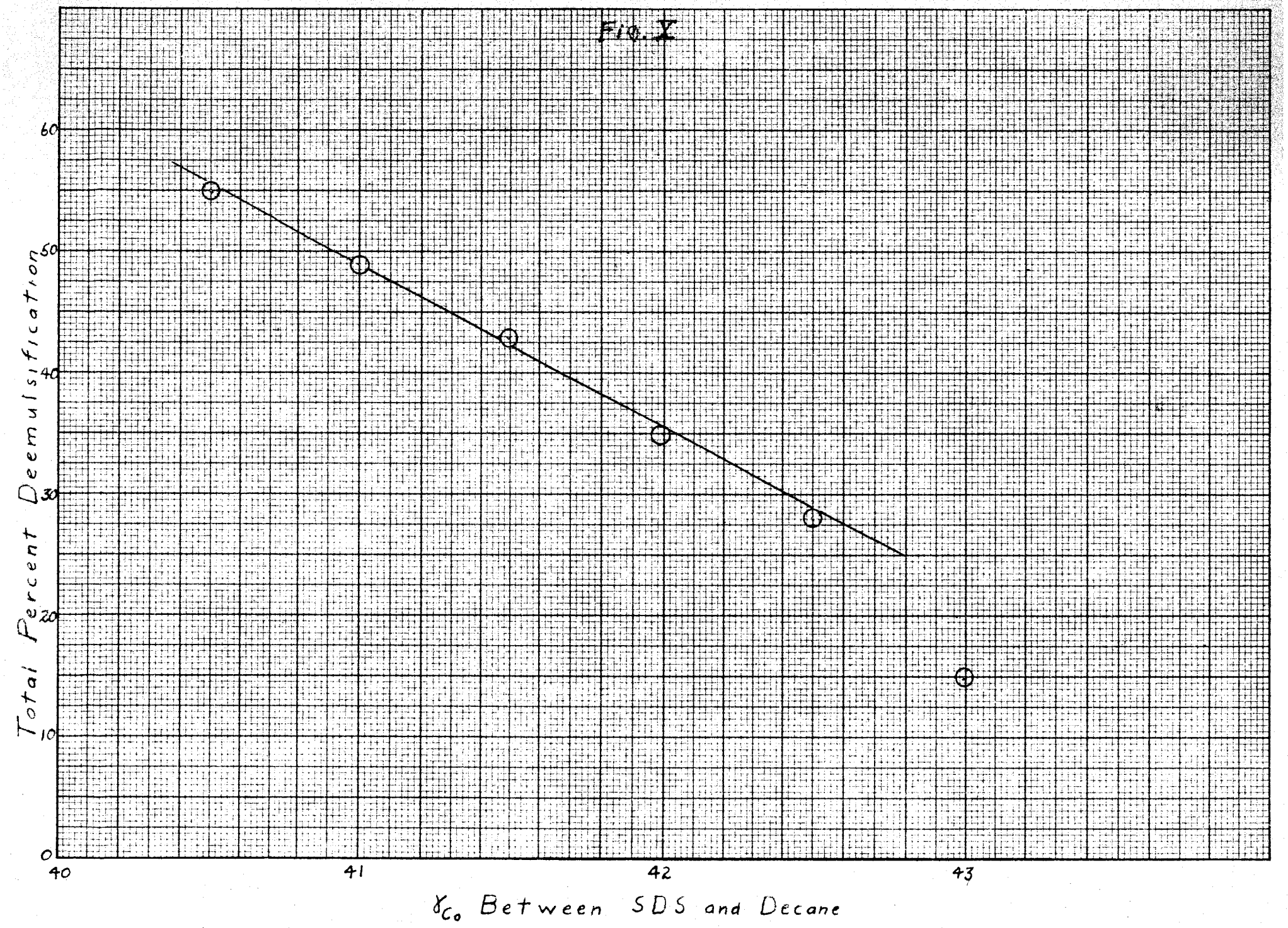
$$100 - TD = kS = k(\gamma_{wo} + \gamma_{wo}\cos\theta)$$

$$TD = -k\left(\gamma_{wo} + \gamma_{wo}\cos\theta - \frac{100}{k}\right) \qquad (14)$$

Table 10 gives values of the interfacial tension for the initial concentrations and the corresponding TD. The total deemulsification is used here, since the amount of continuous organic phase obtained is assumed to be the maximum obtainable in each case, due to the low zeta potential. The concentration is of course changing throughout freezing, so that it will range from .0018% to saturation in the .005% sample. However, in this region the slope of the interfacial tension curve is constant, so that we may choose the initial SDS concentration in the pure solution; the interfacial tensions during freezing will be proportional to this.

Table 10

Initial Concentration SDS in %	Interfacial Tension in dynes/cm.	Total % Deemulsification (TD)	Deviation
0.002	43.0 ± .5	15 ± 5	-4
0.005	42.5 ± .2	28 ± 5	0
0.0075	42.0 ± .2	35 ± 3	0
0.010	41.5 ± .2	43 ± 3	0
0.0125	41.0 ± .2	49 ± 3	0
0.015	40.5 ± .2	55 ± 3	1
		Average	± 1%



A plot of interfacial tension as the abscissa with total deemulsification as the ordinate is shown in Fig. X. Disregarding the last point, where the uncertainty of the interfacial tension is ±.5 dynes, we find the slope to be -13.5, and the TD intercept as 600. We then have the following equation, where TD is the total deemulsification:

$$TD_{(.002\%-.015\%\ SDS)} = -13.5\,\gamma_{wo} + 600$$

Expressing this in terms of equation (14):

$$k(100 - 13.5\,\gamma_{wo}\cos\theta) = 600$$

$$TD = -13.5(\gamma_{wo} + \gamma_{wo}\cos\theta - 7.4)$$

At γ = 37 dynes/cm., cos θ = -1 and θ = 180°. At 0% SDS, γ = 45.3 dynes/cm. and the angle has decreased to 145°. Therefore wetting of the ice by the decane is best at a high interfacial tension.

The question remains as to why the deemulsification remains at the maximum as the close packing concentration is increased above .6%, although the zeta potential rises in this region. It is probable that precipitation of the emulsifying agent is of importance here. Observations were made with a polarizing microscope on cross sections of a .5% SDS emulsion frozen at -10 C to determine this. It was first ascertained that crystals of SDS hydrate give alternately blue and yellow coloration as the nicol prisms

are rotated. No SDS crystals were distinguishable in the frozen mass, since the ice crystals also were deeply colored. Upon slow thawing of the cross section, SDS crystals were seen in the freshly melted aqueous phase. They were about 50 microns long and 10 microns wide, and frequently were associated with masses of droplets. These crystals dissolved slowly after the ice was completely melted. No crystals could be observed during similar observations on a .10% SDS emulsion frozen in bulk. However, the emulsifier must be present in some form of aggregates when the mass is frozen. These may be submicroscopic crystals or even large micelles.

With the .5% sample, onee SDS crystal nuclei have formed, precipitation should keep the concentration from rising much above the solubility of SDS at 0°C except during very rapid freezing. An experiment was carried out to determine the extent of supersaturation possible with SDS. Ten ml. of a 1.7% sample was held at 0°C for ten minutes. No precipitation was observed. After fifteen minutes very large crystals began to grow slowly. Slight agitation at this point resulted in immediate and complete solidification of the solution. In this manner, the agitation produced by crystal growth and coalescence of the droplets could prevent a high degree of supersaturation from being attained. Thus the concentration would remain at a point where low zeta potential prevails.

The Eastman decane gave a 78% relative deemulsification at .5% SDS as compared with 100% for the Phillips sample used in this work. This decreased linearly to 60% at .05% SDS. A difference in the zeta potential caused by the presence of oxidation products in the Eastman sample could cause this discrepancy.

Results with Sodium Dodecyl Sulfonate

This substance was used to check the observations and conclusions obtained with SDS, since it is of the same chemical nature. Table 11 gives the effect of initial emulsifier concentration.

Table 11

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Concentration SDDS in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.001	12 ± 3	20 ± 5
0.002	30 ± 3	50 ± 5
0.003	42 ± 3	70 ± 5
0.005	60 ± 3	100 ± 5
0.0075	55 ± 3	92 ± 5
0.01	45 ± 3	75 ± 5
0.015	15 ± 3	25 ± 5
0.02	20 ± 5	33 ± 8

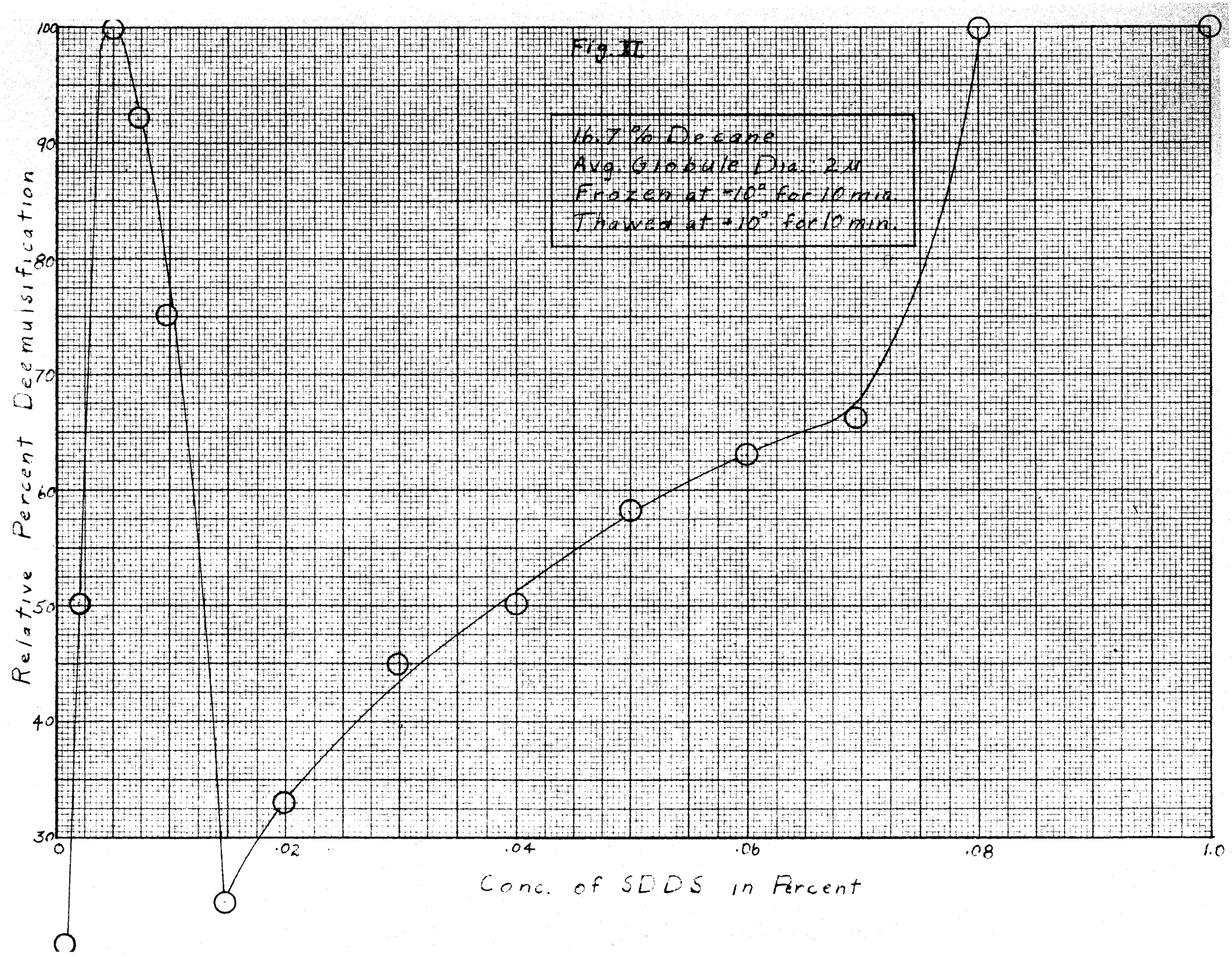
Table 11 (Continued)

Concentration SDDS in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.03	27 ± 6	45 ± 10
0.04	30 ± 3	50 ± 5
0.05	35 ± 3	58 ± 5
0.06	38 ± 3	63 ± 5
0.07	40 ± 3	66 ± 5
0.08	60 ± 3	100 ± 5
0.10	60 ± 3	100 ± 5

The relative deemulsification is plotted against the concentration of SDDS in Fig. XI. The curve will be analyzed in three sections as with SDS.

1. From .015% to .10% SDDS

Since this portion of the curve in Fig. XI is not linear, it does not follow equation (10), which was developed for SDS. As shown in a later section, the deemulsification for this region is dependent on the rate of freezing, while the corresponding values for SDS are not. This suggests that some other factor is operative. The zeta potential curve for SDDS shows a sharp rise after the minimum at .06%. Consequently, the concentration may pass through the low zeta potential range rapidly for the concentrations between .015% and .07%, resulting in less total coalescence. However, the point at which the maximum deemulsification is reached corresponds exactly with the predicted value by



analogy with SDS. If the fall in zeta potential at the close packing concentration is shifted to 3.1 times the concentration for an isolated droplet, the minimum value of .06 volts should be obtained at a close packing concentration of .184%. Applying equation (9) to an initially .08% SDDS emulsion, we find a close packing concentration of .186%. Hence, complete and rapid coalescence is to be expected at this point. At higher concentrations, precipitation of the SDDS will be important, maintaining a constant concentration near .06%, where the zeta potential is lowest.

2. From .005 to .015% SDDS

This concentration range may be explained on the same basis as the range from .015 to .05% SDS. Table 12 gives the force of repulsion at H = .001 μ for each of the concentrations.

Table 12

Substituting the value of k from column 7 of Table 12 in equation (14) we have:

$$RD_{(.005\%-.015\%\ SDDS)} = \frac{.146}{F_R} \qquad (12b)$$

The constant was taken as the average of the last three values in column 7.

Table 12

Concentration SDDS in %	C_{cp} in %	ζ in volts	κ in $cm^{-1} \times 10^{+6}$	F_R in dynes $\times 10^4$	%RD	$(RD)(F_R)$	Deviation
0.005	0.006	0.05	0.33	0.21	100	0.021	0
0.0075	0.022	0.075	1.08	1.62	92 ± 5	0.149	1
0.010	0.026	0.080	1.38	2.00	75 ± 5	0.150	2
0.015	0.039	0.107	2.45	5.50	25 ± 5	0.138	-1
						Average	± 1.3

It will be noted that the forces, and hence the constant k, are about one-third those calculated for SDS. This discrepancy is probably due to the choice of concentration in equation (3). Since the value of $\frac{\partial \gamma}{\partial c}$ for SDDS is 2.3 times that for SDS in the corresponding concentration regions, the surface concentration is 2.3 times that of SDS at the same concentration. Thus the effective value of c in determining the charge density may be a function of $\frac{\partial \gamma}{\partial c}$, so that the force of repulsion for .015% SDDS may actually be greater than that for .05% SDS.

In Table 12, the close packing concentration for .005% SDDS was calculated by successive approximations with equation (9). Using the value for $\frac{\partial \gamma}{\partial c}$ of 2.2×10^3, the first approximation gives a close packing concentration of .021%, which corresponds to the higher $\frac{\partial \gamma}{\partial c}$ of 1.4×10^4. Using this value in (9) with the same c_o, the final close packing concentration becomes .006%.

3. <u>From .001 to .005% SDDS</u>

It is apparent from Fig. XI that the deemulsification in this region follows the same general law that was found for SDS between .002 and .015%. Table 13 gives the data needed for equation (14).

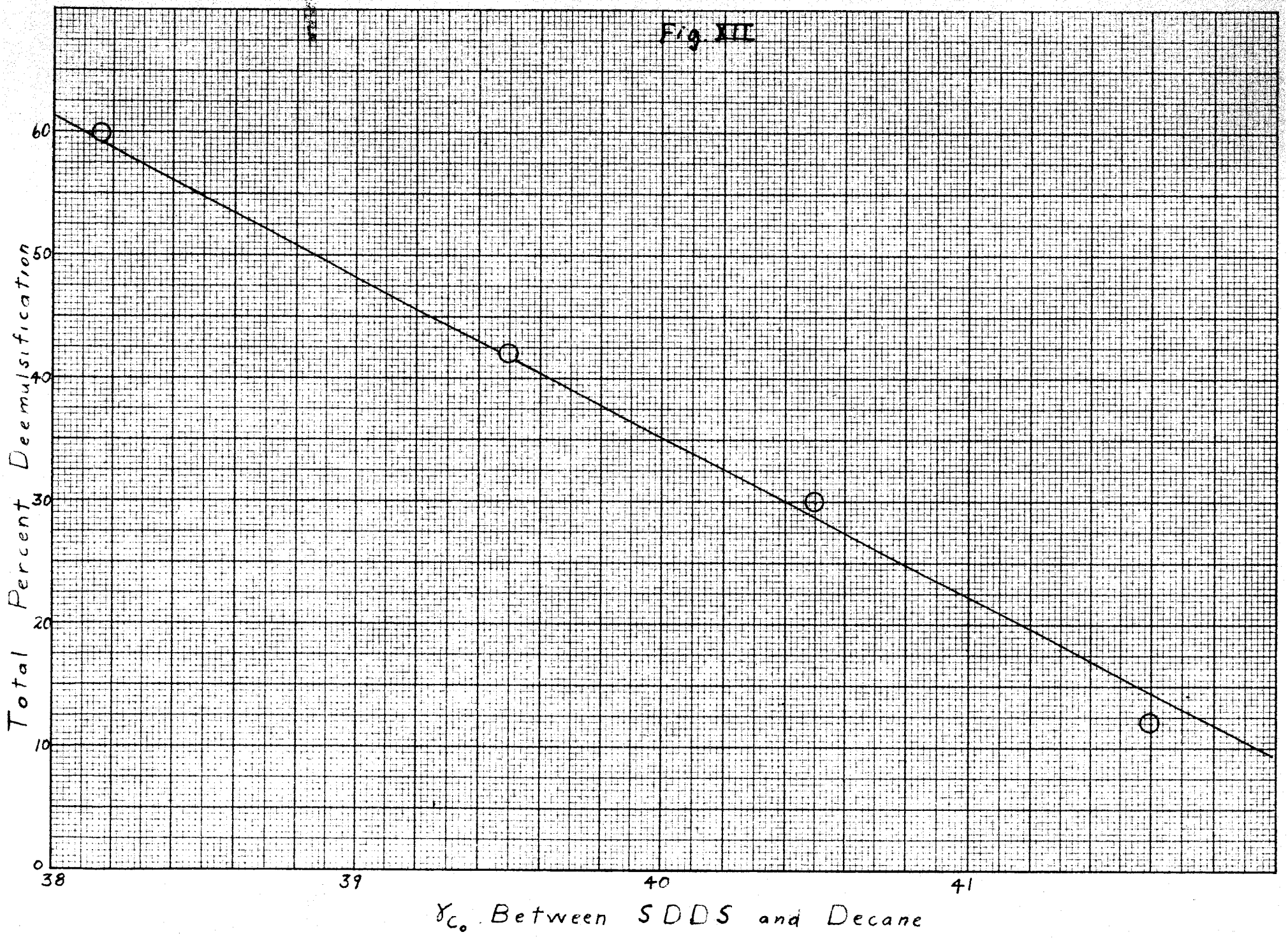


Table 13

Initial Concentration SDDS in %	Interfacial Tension in dynes/cm.	Total % Deemulsification (TD)	Deviation
0.001	41.6 ± .3	12 ± 3	-2
0.002	40.5 ± .2	30 ± 3	2
0.003	39.5 ± .2	42 ± 3	0
0.005	38.2 ± .2	60	0

Average ± 1

A plot of total deemulsification against the interfacial tensions given in column 2 of Table 13 is found in Fig. XII. The slope of this line is -13.3 as compared to -13.5 for SDS in Fig. X. The difference is well within the uncertainty of both the interfacial tension measurements and the deemulsification readings. The equation obtained by substitution in (14) is:

$$TD_{(.001-.005\%\ SDDS)} = -13.3\left(\gamma_{ow} + \gamma_{ow}\cos\theta - 7.5\right) \quad (14b)$$

The deviations in column 4 of Table 13 are calculated from the theoretical deemulsification obtained from this equation.

According to equation (14b), a 180° contact angle is approached as the concentration of SDDS increases, and a 145° angle is obtained when the initial concentration approaches 0. This is the same range that was found for SDS.

b. Effect of Volume Percentage Decane

The following data were obtained using a 28.6% decane emulsion. This has exactly twice as much decane

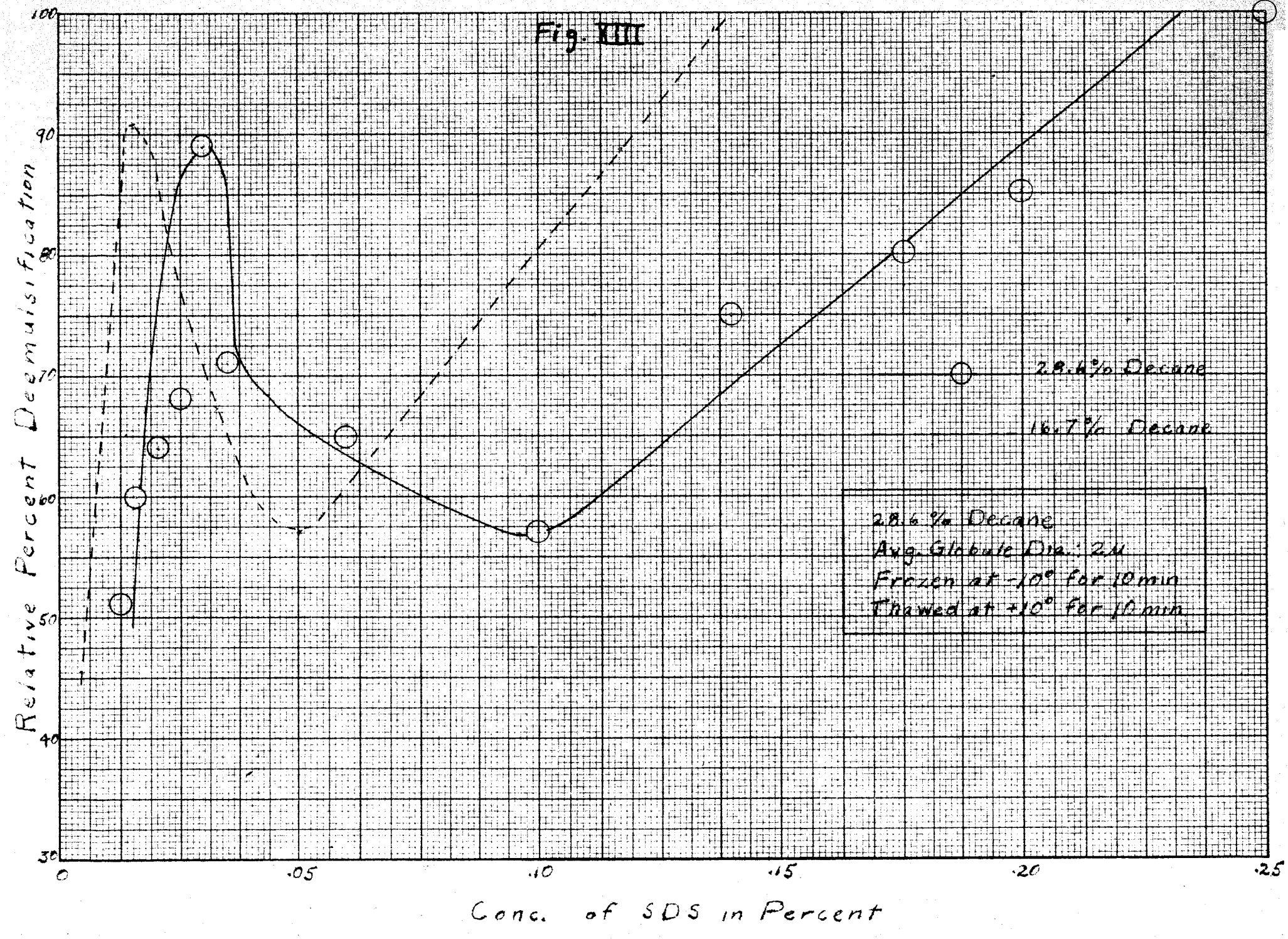
per unit volume of aqueous phase as does the 16.7% emulsion.

Table 14

Total Volume: 6 ml.
28.6% Decane
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Concentration SDS in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.005	43 ± 10	68 ± 16
0.01	46 ± 10	73 ± 16
0.0125	32 ± 6	51 ± 10
0.015	38 ± 7	60 ± 10
0.02	40 ± 5	64 ± 8
0.025	43 ± 5	68 ± 5
0.03	56 ± 3	89 ± 5
0.035	45 ± 3	71 ± 5
0.06	41 ± 4	65 ± 6
0.10	36 ± 5	57 ± 8
0.14	48 ± 3	75 ± 5
0.175	50 ± 5	80 ± 8
0.20	58 ± 3	91 ± 5
0.25	63 ± 8	100 ± 3

The poor reproducibility of the value at low concentrations was probably because it was difficult to get a uniform particle size with emulsions of 28.6% decane at these concentrations. The .005% sample showed an average



diameter of 3 microns with many as large as 5 and 6, while the .015% sample gave the typical distribution and particle size found with the other emulsions. A variation of 50% in the specific surface, which is found with .005%, will give a corresponding variation in bulk concentration, which in turn affects the deemulsification.

It will be noted that the general shape of the curve is similar to that of the 16.7% emulsion. The data are plotted in Fig. XIII. The dotted curve represents the values for 16.7% decane.

The relative deemulsification used here is with respect to the 63% maximum, instead of 60 with 16.7%. It is to be expected that with a larger percentage dispersed phase, a smaller proportion will be protected between the broad crystal faces which have a limited capacity.

1. From .10% to .25% SDS

For an initially 28.6% decane emulsion concentrated to its close packing ratio of 74%, the aqueous phase contains emulsifying agent 7 times the concentration before the start of freezing. The total surface per liter of solution at close packing is the same as that for 16.7%: 5.7×10^7 $cm.^2$. The close packing concentrations may then be calculated from equation (9). Using equation (10a), the following table was obtained:

Table 15

Initial Concentration SDS in %	C_{cp}	% RD	$28 + 122C_{cp}$	Deviation
0.10	0.21	57 ± 7	56	1
0.14	0.29	75 ± 5	66	9
0.175	0.38	80 ± 8	77	3
0.20	0.42	85 ± 5	80	5
0.25	0.52	100	92	8
				Average +5

The average deviation of the observed values is less than the average precision of the measurements: 6%. The constant positive deviation indicates that some other factor is playing a part. More coalescence may occur before the fall in ζ than with 16.7%.

Since the ratio of the concentrations at close packing for the two volume percentages of 16.7% and 28.6% is as 1:2, the corresponding percentages demulsification should occur at initial concentrations whose ratio is 1:2. Thus the minimum is at .10% for 28.6% and at .05% for 16.7% decane.

2. From .03 to .10% SDS

Table 16 was obtained by applying the same calculations to this concentration range as to the region from .015 to .05% SDS with 16.7% decane.

Table 16

Initial Concentration SDS in %	Concentration Close Packing (C_{cp}) in %	$F_R \times 10^4$ in dynes	Relative Demulsification (RD) in %	$(RD)(F_R)$	Deviation
0.03	0.072	5.31	89 ± 5	0.475	-8
0.035	0.084	6.80	71 ± 5	0.461	-5
0.060	0.126	7.80	65 ± 6	0.506	-1
0.100	0.210	8.98	57 ± 8	0.511	0
				Average	± 3.5

The average deviation is less than the error in the measurements. However, as was the case with the .015% value for 16.7%, the high deviation for .03% is probably due to the effect of spreading coefficient. The deviationsin column 6 are calculated on the basis of equation (12a). The average k for these measurements excluding the first is .493 as compared with .516 for 16.7% decane.

3. From .005 to .03% SDS

The wide errors obtained for concentrations below .03% do not permit a quantitative treatment, but qualitatively it is seen that the predicted fall in deemulsification does occur. The maximum at .03% corresponds with that at .015% for 16.7% decane, in that it occurs at double the concentration. We have seen that the close packing concentration is one half that for 16.7% in this case.

The following results were obtained with higher volume percentages of decane:

Table 17

Total Volume: 6 ml.
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Volume % Decane	Concentration SDS in %	Total % De-emulsification	Close Packing Concentration in %
40	0.10	58± 5	0.123
50	0.10	64± 5	0.085

The volume of decane in the bulk layer after thaw-

ing increased steadily over a period of one hour, reaching the totals shown in column 3 of Table 17. After twenty minutes they were 48 and 55% respectively.

From the close packing concentrations we note that the ratio of the two deemulsifications is the same as that for the same close packing concentrations with 28.6% decane: 58/64 = .91, 65/71 = .92. Since the maximum obtainable deemulsification for these volume percentages decane was not determined, an exact comparison of the actual values cannot be made. The ratios indicate that the same relationships with the force of repulsion are applicable.

c. Effect of nature of emulsifying agent

1. Hexadecyl benzyl dimethyl ammonium chloride (HBDAC)

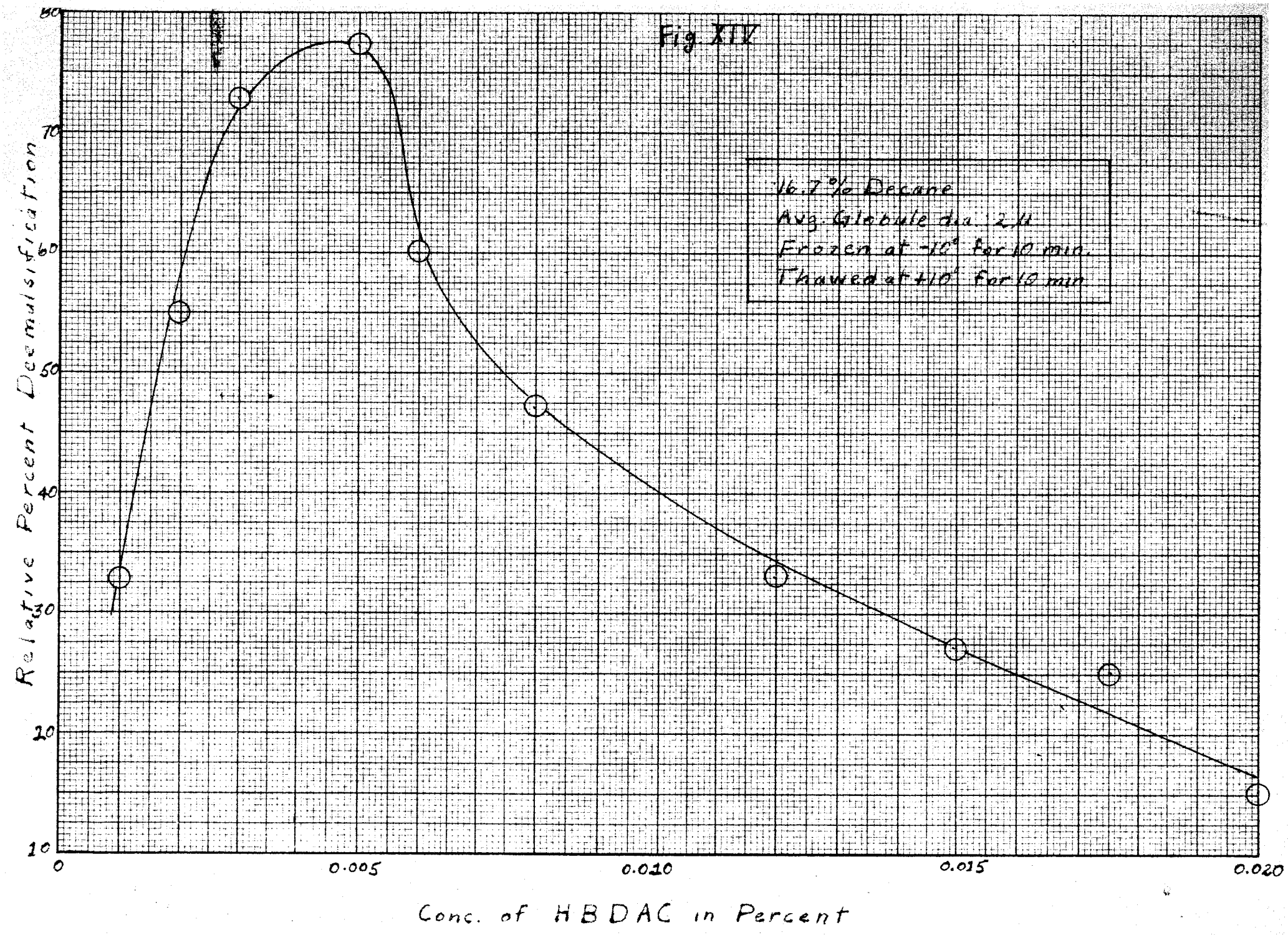
Hexadecyl benzyl dimethyl ammonium chloride was used as a cationic surface active agent. In addition to bearing a positive charge, it differs from SDS and SDDS in that it lowers the interfacial tension between decane and water to a much greater extent, due to the sixteen carbon paraffin chain. The data obtained are given in Table 18. The values listed are the average of three separate determinations. A total time of one hour was required to reach a constant volume of decane at the surface after thawing, as compared with 20 minutes for the other two emulsifying agents. The significance of column 4 is explained below.

Table 18

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Concentration HBDAC in %	Total % Deemulsification	Relative % Deemulsification	C_o-.004%	Deviation
0.001	17 ± 6	28 ± 10		
0.002	30 ± 5	50 ± 8		
0.003	41 ± 5	68 ± 8		
0.005	43 ± 3	72 ± 5	14	-1
0.006	33 ± 5	55 ± 8	11	-2
0.008	25 ± 5	42 ± 8	8.0	0
0.012	17 ± 6	28 ± 10	5.5	-1
0.015	13 ± 5	22 ± 8	4.0	1
0.0175	12 ± 5	20 ± 8	3.0	4
0.02	6 ± 3	10 ± 5	2.0	0
0.04	$\ll$2		Average	± 1
0.10	0			

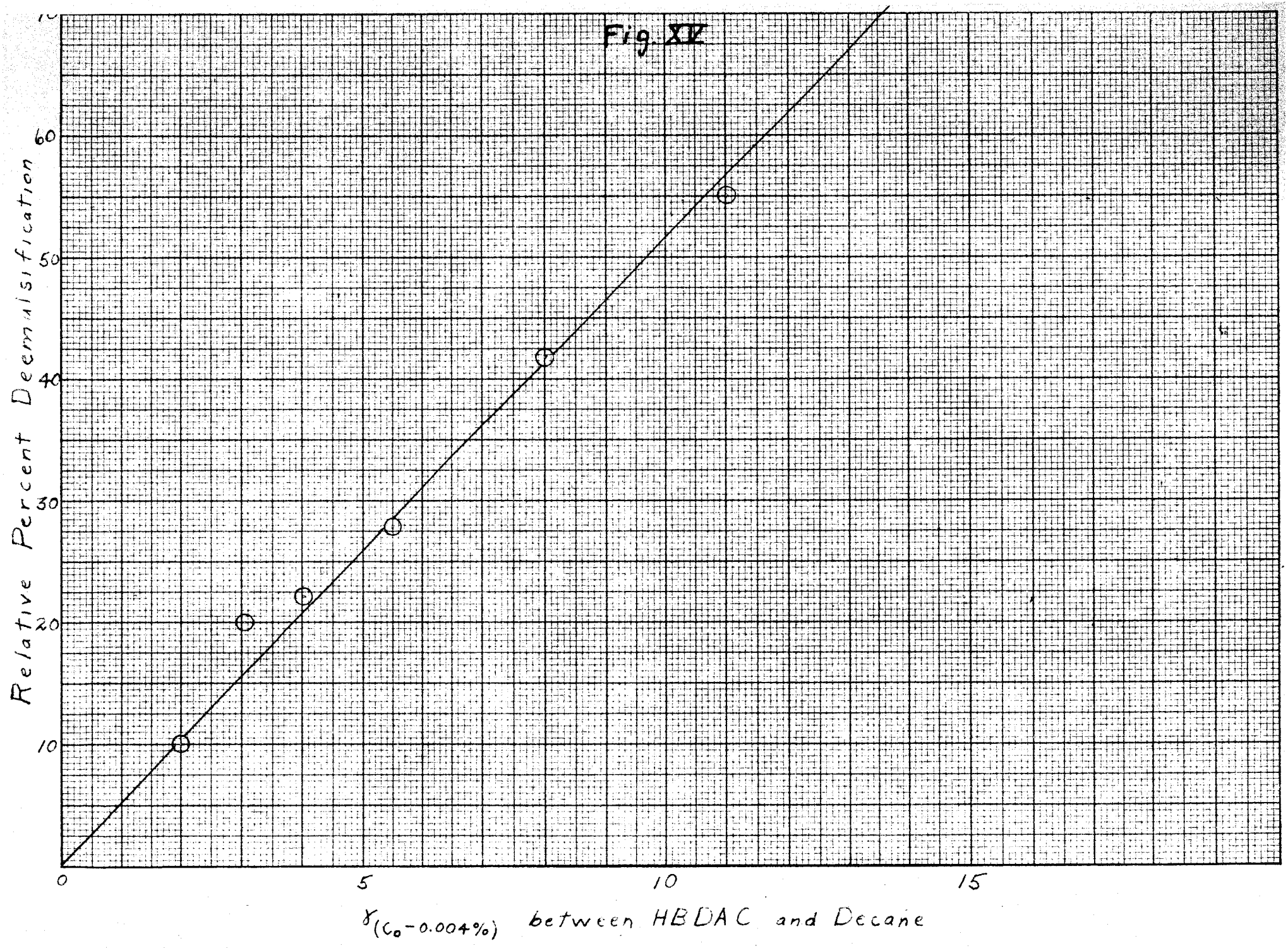
These values were unaltered by allowing the samples to stand overnight. The attainment of equilibrium could be hastened by periodic stirring after thawing. It was noted that within fifteen minutes after thawing a cream layer developed below the bulk layer, usually occupying a volume of 1 ml. in a 5 ml. sample. A particle size count showed



globules with a complete range of sizes, in contrast with the SDS emulsions, where the remaining emulsion had a similar size distribution as the original.

The data is plotted in Fig. XIV, where the ordinate is the relative deemulsification, and the abscissa is the percentage of HBDAC.

An analysis of the curve shows that the behavior of this emulsifying agent is decidedly different from that of SDS and SDDS. The deemulsification decreases toward 0 as the concentration is increased, while it increases with concentration for the anionic surface active agents. In the latter cases a maximum amount of deemulsification occurred if the zeta potential fell below .08 volts. Here, however, the potential is always below .08 volts, so that we may expect that coalescence would occur at the maximum possible rate during freezing. In other words, the force of the growing ice crystals is always greater than the repulsive force between the globules. This will lead to establishment of close contact between the close packed globules. The rate of coalescence will now depend on the extent to which the total surface energy can be reduced by decrease of mutual surface, and hence on the interfacial tension. With the two anionic agents studied the interfacial tension never falls below 15 dynes/cm. for a saturated solution. Consequently at this value coalescence is almost



instantaneous with respect to the rate of freezing. In the case of HBDAC, on the other hand, the interfacial tension at close packing may be near 1 dyne/cm., where spontaneous emulsification takes place on stirring. Hence the rate of coalescence will be extremely low.

The calculation of the interfacial tension at close packing and during coalescence is difficult. Application of equation (9) with successive approximations gives a lower concentration on each approximation until the region of constant $\frac{\partial \gamma}{\partial c}$ below .0005% is reached. Since the slope changes more rapidly than the concentration, evaluation of C_o from a given $\frac{\partial \gamma}{\partial c}$ and C_{final} gives an increasing C_o as C_{final} is decreased. In any case, the concentration will increase during coalescence.

The sharp rise of deemulsification between .006% and .005% indicates that a sharp change of interfacial tension occurs in that region, either when the droplets are close packed, or during coalescence. Such a rapid change in interfacial tension occurs at about .001%. Taking the effective concentration as .004% less than the initial value, the figures in column 4 were obtained. These are plotted in Fig. XV. From the slope we have the following empirical equation:

$$\%RD = 5.19\gamma_{C_o} - .004\% \qquad (15)$$

From column 6 it is seen that the deviations are less than

the average errors of the measurements. The fact that the straight line obtained intersects the origin indicates that the relationship probably has some theoretical basis. The deviations in column 5 of Table 18 are in terms of equation (15).

The concentration of HBDAC will increase as freezing progresses, due to the release of HBDAC into the bulk solutions as a result of coalescence to give a smaller surface area. This will lower the interfacial tension and therefore decrease the rate of coalescence. In addition, the low interfacial tension will increase the deformability of the droplets under the influence of the ice force, which in turn will decrease in the volume of the aqueous phase between the close packed globules. Such a decrease in volume also increases the concentration. The entire process should, therefore, tend to slow down as freezing progresses. An attempt was made to verify this by microscopic observations, but no conclusive results were obtained.

The values below .005% conform to the qualitative picture developed for SDS and SDDS at low concentrations. the wide range of values for a single concentration are probably due to particle size variation as in the case of 28.6% decane with SDS. It was found that if about half of the decane was thoroughly emulsified first, the second portion added later remained as macroscopically visible particles. Apparently the first portion had adsorbed most

of the HBDAC so that the bulk concentration was close to 0. The results indicate that the initial concentrations correspond with interfacial tensions near that of a pure water-decane system. A value of about 43 dynes was seen to be required for non-spreading of decane on water. Extrapolation of the interfacial tension curve in Fig. VIII shows that this value would be obtained with about .00002% HBDAC, or with most of it adsorbed from solution in an initially .002% solution. Application of successive approximations to equation (9) yields this general result, although the precision of the slope at low concentrations does not enable an accurate calculation to be made.

Microscopic observations with .003, .002, and .001% HBDAC showed the same adherence and spreading as with SDS below .015%.

2. Dodecyl amine hydrochloride (DAH)

The results obtained with this substance are as follows:

Table 19

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2-3 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Table 19 (Continued)

Concentration DAH in %	Total % Deemulsification (TD)	Relative % Deemulsification (RD)
0.002	49 ± 3	81 ± 5
0.005	60	100
0.01	60	100
0.05	60	100
0.15	60	100

The .002% emulsion broke slowly on standing, both before and after freezing.

Since DAH is a positively charged substance, the electrokinetic potential imparted by it is about .04 volts lower than the corresponding negatively charged paraffin chain. Thus for all the concentrations studied, the potential will never be above .08, which is.03 volts less than the maximumfound for SDDS. Consequently, coalescence should proceed at the maximum possible rate as outlined previously. Assuming that its surface active properties closely approximate those of SDDS, we find that the interfacial tension will not go below 15 dynes, and hence there will be no reduction in the rate of coalescence from this cause. These considerations explain the maximum deemulsification obtained above .002%. At .002% it is probable that the interfacial tension had reached the point for the spreading coefficient to determine the deemulsification. This concentration corresponds to .0025% SDDS in terms of molarity, and the

deemulsification for SDDS here is 40%. The value therefore roughly conforms to the predicted quantity.

The 60% maximum obtained here is further evidence that it is due to mechanical factors, since the physico-chemical properties of SDS and DAH are widely different.

The pH of a .15% solution of DAH was 3.7 and was 5.8 at .01% (4×10^{-4}N). In order to eliminate the possibility of pH effect, sufficient pure dodecyl amine base was added to bring the pH of a .01% solution to 7.1. This gave a turbid solution due to the excess insoluble amine. Identical results were obtained for a series of concentrations as were found for the unneutralized amine hydrochloride. The pH of the aqueous phase had dropped to 5.8 with the .01% sample after thawing due to the extraction of the excess amine by the decane.

3. Antarox-400

Antarox-400 is a non-ionic polyethylene glycol insoluble in decane. A series of concentrations were tried, from .001% to .10%. No deemulsification occurred with any of these. The emulsions formed at .001% A-400 creamed very rapidly before freezing but showed no signs of breaking on standing, either before or after freezing. These results can be attributed to the extremely low interfacial tension and the formation of a tough, elastic film on each globule. The zeta potential of a non-ionic system is generally below .10 volts, so that this factor is ruled out.

A 65 volume percent decane emulsion in .1% Antarox-400 gave a 32% deemulsification of freezing and thawing in the standard manner. This emulsion reaches its close packing ratio shortly after freezing begins, which extends the time over which the globules are in close contact under the force of the ice crystals. In addition, since there is more decane than water, the decane will tend to form the continuous phase when the water is being frozen out. This concentrated emulsion showed no signs of instability when saturated with sodium chloride.

It was noted that a trace of A-400 completely prevented deemulsification of SDS emulsions.

d. Effect of nature of dispersed phase

An emulsion of Nujol in .1% SDS was used to determine whether the viscosity of the dispersed phase has any influence on deemulsification. It was found that 45% of the Nujol was deemulsified on freezing and thawing under the standard conditions. This is exactly the same value obtained for decane in .1% SDS. At $0^{\circ}C$ Nujol is too viscous to flow from a 1.5 cm. diameter test tube.

This result shows that once the repulsive force has been reduced below a critical value, coalescence results regardless of the viscosity of the droplets. It is important to note that Nujol consists of long chain hydrocarbons, and is therefore of the same chemical nature as decane.

Several exploratory experiments were made with toluene as a dispersed phase. The curve for deemulsification against concentration of SDS was shifted, so that the minimum was at .3% in contrast with the .05% minimum with decane. The shape of the curve was altered as well. Investigation of the interfacial tension curve showed a similar shift in the point at which the slope changed. Precise measurements of the interfacial tension was difficult, however, due to the mutual solubility of toluene and water. The interfacial tension fell over a long period of time, and the toluene became cloudy if held at 0°C in contact with water. The deemulsification results were attributed to the solubility and the difference in surface properties; probably the zeta potential differs from that of the decane-SDS solution system as well. No further work was done due to the complications arising from the mutual solubility of the phases; toluene dissolves .2 gms. of water at 20°C per 100 ml.

e. Effect of addition of electrolyte

Table 20 gives the effect of sodium chloride and calcium sulphate on the relative deemulsification of a .075% SDS emulsion. The significance of columns four, five, and six are explained below.

Table 20

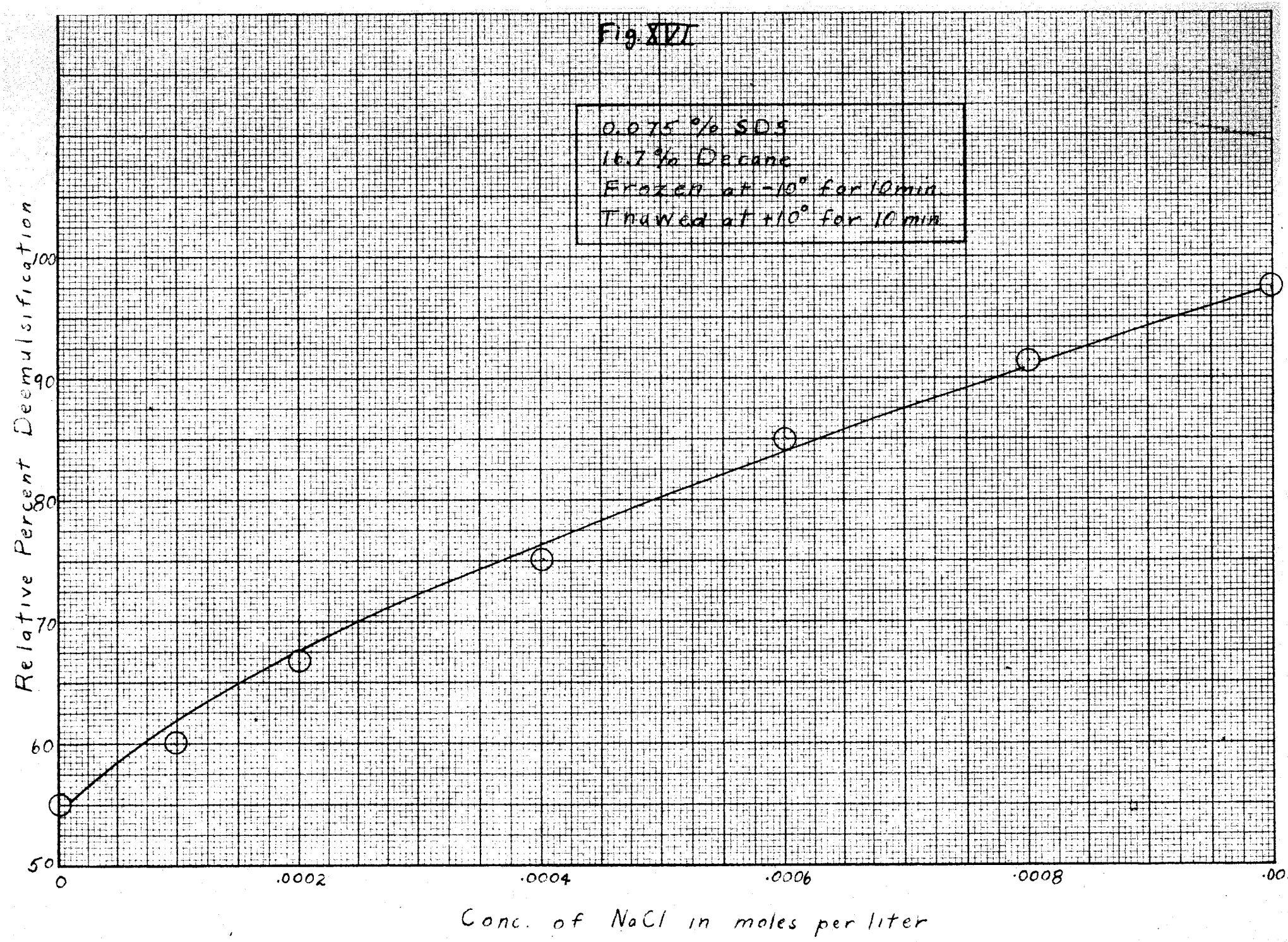
Table 20

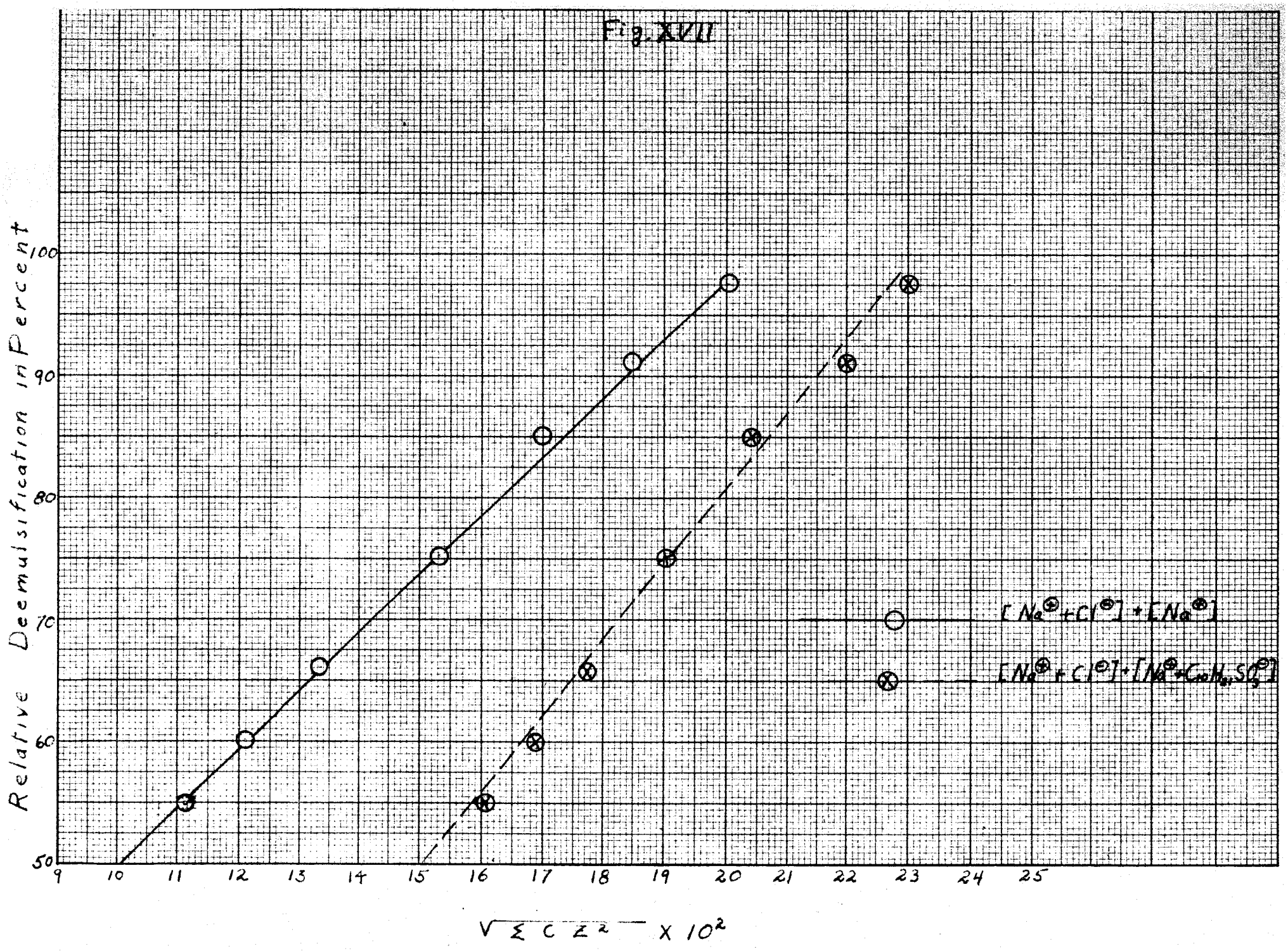
Total Volume: 5 ml.
16.7% Decane
.075% SDS
Average Globule Diameter: 2 microns
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Concentration NaCl in moles per liter	Relative De-emulsification (RD) in %	Zeta Potential in volts	$\sqrt{\sum c_1 z^2 \times 10^2}$	$\sqrt{\sum c_2 z^2 \times 10^2}$	Deviation
0	55 ± 5	0.094 ± 0.004	16.0	11.3	0
0.0001	60 ± 5	0.094 ± 0.004	16.9	12.1	1
0.0002	66 ± 5		17.7	13.7	-1
0.0004	75 ± 5	0.094 ± 0.004	19.0	15.6	-1
0.0006	85 ± 5		20.7	17.0	2
0.0008	91 ± 5		22.0	18.9	-2
0.001	98 ± 5	0.091 ± 0.004	23.2	20.1	-1
0.010	100	0.091 ± 0.004			
				Average	± 1.3%

Table 20 (Continued)

Concentration $CaSO_4$ in moles per liter	Relative De-emulsification (RD) in %	Zeta Potential in volts	$\sqrt{\Sigma C_1 Z^2 \times 10^2}$	$\sqrt{\Sigma C_2 Z^2 \times 10^2}$	Deviation
0.0002	89 ± 5	0.092 ± 0.004	22.0	18.9	-3





A plot of the relative percent deemulsification of column 2 against the sodium chloride concentration is found in Fig. XVI.

Since it was found previously that the concentration conditions at close packing determine the deemulsification, those found here must be calculated to obtain a quantitative relationship for the results. Using equation (9), we know that the SDS concentration at close packing is 4.2 times that at the start of freezing. This gives .315% for an initially .075% SDS emulsion or .0129N. Assuming that the sodium chloride is not appreciably adsorbed during freezing, its concentration is 14 times that of the unfrozen sample. Taking the .0004N NaCl emulsion as an example, we find that the close packing concentration is .0057N. Here the zeta potential of a .075% SDS emulsion is not significantly different from the case where no inert electrolyte has been added. It was also found that the zeta potential of a .5% SDS emulsion was unaffected by NaCl concentrations up to .02N. Consequently, if the electrokinetic potential at close packing and during coalescence is similar to that of the unfrozen emulsion, the explanation of the electrolyte effect must lie in some other factor.

Eilers and Korff[37] have pointed out that the addition of small amounts of electrolyte to colloidal systems often causes instability without affecting the measured zeta potential. They attribute this to the effect of the

electrolyte on the energy required to bring two particles together against the action of their electrostatic fields. Their equation for this energy is:

$$E = \frac{B \zeta^2}{10^{7.364}\sqrt{\Sigma c z^2}} \qquad (16)$$

where E is the energy, B , a constant, ζ, the zeta potential, c, the concentration of a given ion, and z, its valence. At constant ζ, the energy is inversely proportional to $\sqrt{\Sigma c z^2}$. It is important to note that this equation was derived for non-surface active electrolytes.

The extent of deemulsification should be inversely proportional to the energy E, and hence directly proportional to $\sqrt{\Sigma c z^2}$. The values of $\sqrt{\Sigma c z^2}$ taking into account all the ions present are tabulated in column four of Table 20. A sample calculation is as follows:

C_o NaCl = 4×10^{-4}N

C_{cp} NaCl = 5.7×10^{-3}N

$C_{Na^{\oplus}}(1)^2 + C_{Cl^{\ominus}}(1)^2 = 11.4 \times 10^{-3}$

C_o SDS = 3.1×10^{-3}N

C_{cp} SDS = 12.9×10^{-3}N

$C_{Na^{\oplus}}(1)^2 + C_{C_{10}H_{21}SO_3^{\ominus}}(1)^2 = 25.8 \times 10^{-3}$

$\sqrt{\Sigma c_i z^2} = 19.0 \times 10^{-2}$

The values in column four are plotted as the abscissae in Fig. XVII. The ordinate is the relative deemulsification.

It will be noted that this plot is linear while Fig. XVI is not. Taking the slope of this line and calculating the RD intercept we have:

$$R.D. = 6100\sqrt{\Sigma C_1 Z^2} - 41 \qquad (17)$$

The fact that this line gives a relative deemulsification of -41 when the concentration is 0 indicates that considering both sodium and decyl sulfonate ions is not valid, since the anion is surface active. The values calculated for the sodium ions only of the SDS are listed as $\sqrt{\Sigma C_1 Z^2}$ in column five of Table 20. A plot of the relative deemulsification against these values is given in Fig. XVII. Here the ordinate intercept is calculated to be -3, which is within experimental error of the origin. This gives the equation:

$$R.D. = 4900\sqrt{\Sigma C_1 Z^2} \qquad (18)$$

The deviations from the experimental data of the values calculated by this equation are given in column six of Table 20. The average deviation is less than the error of the measurements.

Applying either equation (17) or (18) to the data for calcium sulphate the calculated relative deemulsification is 92%, while the observed value is 89%. The method therefore applies to widely different types of electrolytes.

A .005% SDS emulsion showed no increase in deemulsification in the presence of .0002N calcium sulphate. Both

the control and electrolyte samples gave 28% absolute deemulsification directly after thawing. However, the calcium sulphate sample broke completely on standing overnight, while the control was still stable. This is a further indication that where the decane wets ice better than the SDS solution, fewer droplets are subject to deemulsification. The rapid breaking with $CaSO_4$ on standing shows that the energy of repulsion was lowered due to lowered zeta potential or the aforementioned effect, and therefore the maximum amount of decane subject to deemulsification by being squeezed into the narrow intercrystalline zones is 28%, as compared with 60% for higher concentrations. The results were reproducible for lower concentrations of calcium sulphate and for various sodium chloride concentrations.

Interfacial tension is not a factor in electrolyte effect. The interfacial tension of a .075% SDS solution against decane at 0°C was unchanged in the presence of .01N NaCl.

Another factor that would play a part with high electrolyte concentrations is the freezing point of the aqueous phase during the last stages of freezing. In the case of sodium chloride, an initially .001N solution will leave .017% of the water unfrozen at the eutectic point of -17.8°C. Thus at a final freezing temperature of -10°C, about .03% of the water will still be liquid, and about .3% at -1°C. Even this last figure represents the water present when more

than 50% of the close packed emulsion has been frozen, so that it could not be a factor in the deemulsification of 100% of the decane in a given intercrystalline zone. Calcium sulphate has a solubility of .2 gms./100 at 0°C, which is less than that of SDS. The effect here would therefore be completely negligible.

The addition of sodium chloride was found to have no effect on the deemulsification with .008% HBDAC. Concentrations .0001, .001, .01, and .02N NaCl all gave a final value of 42% relative deemulsification, which was the same as the control. Similar results were obtained with .005% HBDAC where the control had a RD of 72%. It was noted, however, that the time required to attain a constant height of continuous decane phase after thawing was 5 minutes for .02N NaCl as compared with one hour without inert electrolyte. The zeta potential of concentrations likely to be found during coalescence of these emulsions are given below:

Table 21

Temperature: 0°C

Concentration HBDAC (%)	Concentration NaCl (N)	Zeta Potential in volts
0.01	0	0.054 ± 0.004
	0.05	0.008 ± 0.004
	0.09	-0.01 ± 0.004

No attempt was made to reproduce these values for the zeta potential. In the freezing of an initially .01N

NaCl emulsion of this type, the zeta potential will pass through 0 and reverse itself, but nevertheless, the amount of deemulsification is unaffected. It will be noted that the molar concentration of .01% HBDAC is 1/200 of that of the sodium chloride when the latter is at .05N. The great zeta potential effect is therefore to be expected. The emulsions prepared for the zeta potential measurements were extremely unstable unless highly diluted.

These results further support the previous conclusion that the interfacial tension alone determines the rate of coalescence of the droplets for HBDAC. When the zeta potential is below about .12 volts, coalescence takes place as fast as possible; this is in accord with observations made by Powis[38] - coagulation of hydrophobic sols is independent of the zeta potential below a critical potential. This critical value is .03 volts where only brownian movement causes contacts between globules, and is apparently about .08 volts when the droplets are forced together by growing ice crystals.

These considerations of critical potential explain the more rapid attainment of equilibrium after thawing with sodium chloride. When only HBDAC is present, coalescence of large droplets to form a bulk phase is slow, due to the low interfacial tension and the zeta potential of .05 volts. When this potential is lowered by NaCl to .03 volts, the rate of coalescence will be greatly increased.

The interfacial tension was found to be unaffected by the concentrations of sodium chloride used.

Microscopic observations on the freezing of a .01N NaCl concentration in a .5% SDS emulsion showed distinct clump formation after thawing. Apparently the zeta potential was brought near the critical value. These clumps were observed to coalesce at once, giving one large globule from about 25 small ones. This supports our assumption as to the autocatalytic nature of the coalescence process at low zeta potential.

f. Effect of initial particle size distribution

Clayton[39], in his Theory of Emulsions, states that

> "The general problem of the effects of freezing on prepared emulsions remains open to investigation, particularly in relation to the initial particle size distribution."

Table 22

Total Volume: 5 ml.
16.7% Decane
Frozen for 10 min. at -10°C
Thawed for 10 min. at 10°C

Concentration SDS in %	Average Diameter per Droplet in μ	Average Volume in μ^3	Number of Droplets per ml. Decane	Total Deemulsification in %
0.50	1	2	6.4×10^{11}	63 ± 3
0.50	2	5	1.5×10^{11}	48 ± 3
0.50	5	27	0.27×10^{11}	8 ± 3
0.15	2	5	1.5×10^{11}	60 ± 3
0.15	5	43	0.22×10^{11}	10 ± 3

The last value was unaffected in the presence of .002N NaCl.

It will be noted that the percentage deemulsification decreases as particle size increases, but not in direct proportion to any of the quantities listed here. Other workers have attributed this effect to the clumping of smaller sized droplets; droplets in clumps are supposed to be more susceptible to coalescence. However, no clumps were seen on microscopic examination of the above emulsions. All the droplets in the smallest particle size sample were in brownian motion.

The explanation of these results is readily seen from microscopic observations on freezing. The crowding of globules into the narrow intercrystalline zones during the last stages of freezing is dependent on their ability to flow freely between the growing ice crystals. It was noted that large droplets are entrapped during the early stages of freezing and do not flow to these zones, where deemulsification will occur. Droplets of one micron diameter will be able to move freely when those of 2 micron diameter are already partly engulfed by ice. Thus the overall effect of large particle size is the same as that found where decane wets ice better than water.

It is important to note that the largest particle sized sample with .15% SDS gives a much higher final concentration of SDS due to the smaller surface. However,

other data has shown that for all concentrations above .15%, the deemulsification remains at the maximum with standard particle size.

g. Effect of the amount of water frozen

Walker noted that the amount of coagulation increased very rapidly as freezing neared completion. Our data indicates similar results. The values for percentage water frozen in Table 19 were obtained by taking the average of the rise and fall of the mercury column on freezing and thawing respectively. The .5% SDS values were obtained with the Eastman decane.

Table 23

A general conclusion that can be drawn from these data is that deemulsification does not begin until about 70% of the water is frozen in a cylindrical tube, at least for low volume percentage dispersed phase. Interpretation of the actual values obtained is complicated by the fact that while the overall amount frozen may be 70%, the percentage of water frozen near the periphery of the tube will undoubtedly be higher, so that globules might be completely engulfed by ice in one portion, while still free in another. In any case, no coalescence in a given region should occur until the close packing ratio for spheres is reached. This corresponds to 93% of the water frozen in that region for a 16.7% decane emulsion.

Table 23

Average Globule Diameter: 2 microns
Frozen at -10°C
Thawed at 10°C
Total Volume: 5 ml.

Concentration SDS	Initial Volume % Decane	% Frozen	Total % Demulsification (TD)	TD at 100% Frozen	% of TD at 100% Frozen
0.50	16.7	30 ± 7	0	48	0
0.50	16.7	70 ± 7	25 ± 3	48	52
0.10	16.7	25 ± 7	0	45	0
0.10	16.7	70 ± 7	20 ± 3	45	42
0.10	40.0	76 ± 7	15 ± 3	45	33
0.10	50.0	30 ± 7	0	50	0
0.10	50.0	40 ± 7	10 ± 3	50	20
0.10	50.0	70 ± 7	23 ± 3	50	46

The values in column 6 of Table 23 represent the percentage of the final deemulsification that was obtained on partial freezing.

The data indicate that in general, one half of the frozen emulsion is completely frozen. Thus when 70% of the .1% - 16.7% sample was frozen, 42% of the total deemulsification had occurred, which corresponds within the experimental error to 35% completely frozen. Likewise for the 50% emulsion, 20% of the total was deemulsified when 1/2 x 40 or 20% was completely frozen. For this to occur, the ice crystals would have to extend inward forming a sawtooth pattern, joining each other at a distance of about half their total length back from the point of farthest advance. When the unfrozen liquid was withdrawn from a partially frozen sample, it was found that the cylinder of ice was rough on the inside - a fine wire could be inserted between the crystals. Furthermore, there was no column of free unfrozen emulsion when the water in the sample as a whole was half frozen. Thus the other 50% of the water was occluded between the ice crystals.

Freezing of the first 30% of these emulsions does not give deemulsified oil on thawing. However, after complete freezing has occurred, thawing of the outer portion gives an oil layer immediately. By the cork borer technique it was determined that the outer 10% gave 60% deemulsification after complete freezing, when the overall per-

centage was 45. The explanation of this lies in the crystal structure of the outer region; along the periphery of the tube the crystals oriented themselves parallel to the length, while the next layer was perpendicular. The difference in structure could thus account for the variation in deemulsification.

In order to determine whether any coalescence at all takes place during the first stages of freezing, particle counts were made on the frozen portion of the emulsion after immersion in the freezing bath for a series of times. The number of particles in a ml. of emulsion was determined from the volume of one square on the hemacytometer to be .00025 cc., and the dilution from the original emulsion which was 200 times. The concentration chosen for this work was .15% SDS, since at this point the maximum amount of deemulsification occurs when completely frozen, so we know that the globules in the narrow intercrystalline zones are coalescing at their maximum rate. Twenty squares were counted in each case.

Table 24

Total Volume: 5 ml.
Average Initial Globule Diameter: 2 microns
Frozen at -10°C
Thawed at 10°C

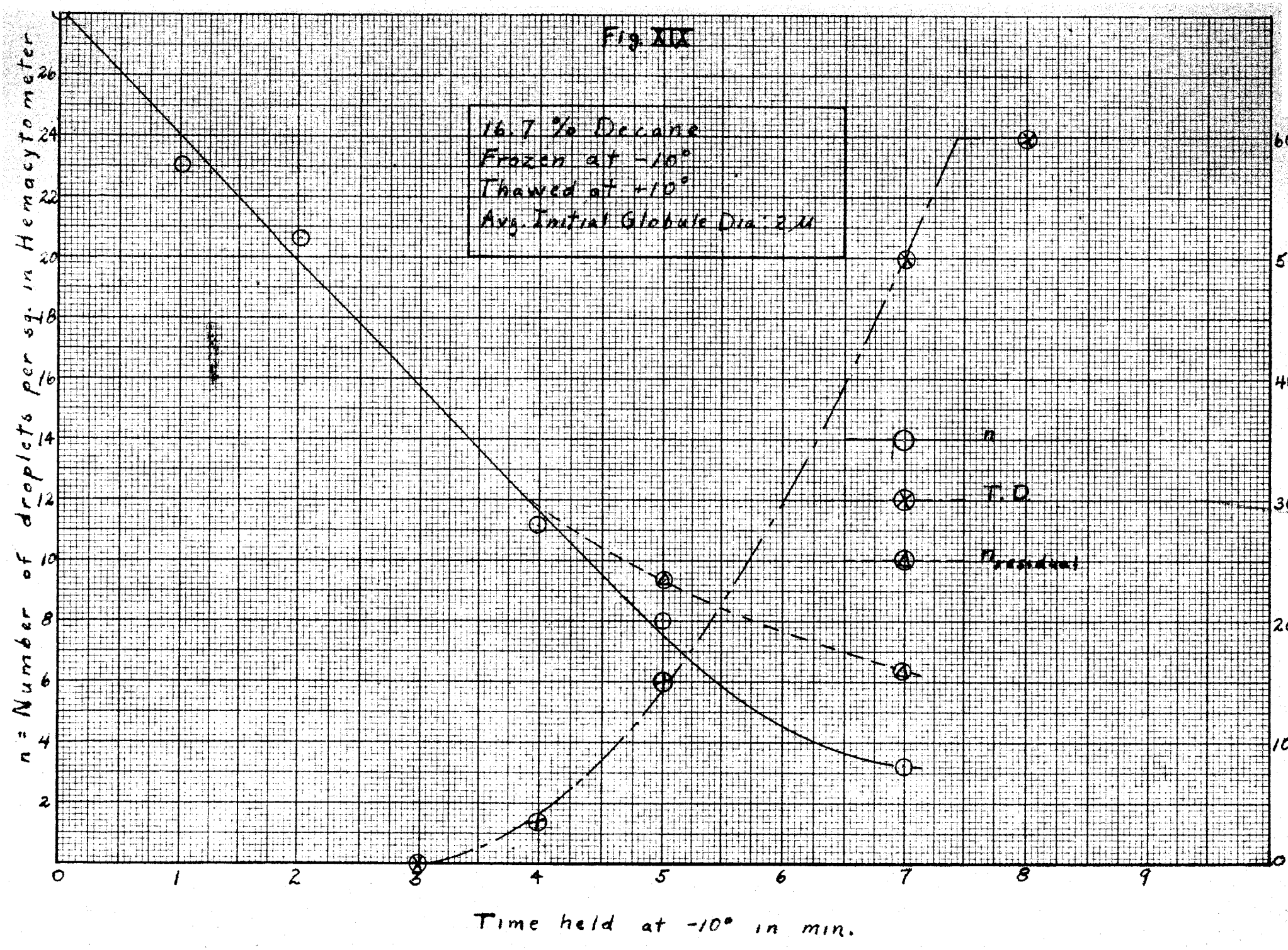


Table 24 (Continued)

Time Held at -10 C in min.	# per Square	# per ml. Decane: Total	# per ml. Decane: Dispersed	TD in %
0	28 ± 1	1.3×10^{11}	1.3×10^{11}	0
1	23 ± 1	1.1×10^{11}	1.1×10^{11}	0
2	21 ± 2	9.8×10^{10}	9.8×10^{10}	0
3	16 ± 1	7.4×10^{10}	7.4×10^{10}	0
4	11 ± 1	5.1×10^{10}	5.3×10^{10}	5
5	8 ± 2	3.7×10^{10}	4.3×10^{10}	15
7	3 ± 1	1.4×10^{10}	2.8×10^{10}	50

These data are plotted in Fig. XIX. The graph obtained for the total number droplets per ml. of decane is linear until 5 minutes is reached. Most of this decrease must be due to the coalescence of droplets between the broad crystal faces which will not ultimately contribute to the bulk decane layer. If the remaining 60% of the decane had reached its close packing ratio, a separate oil layer would have appeared during this time. The slope of this curve gives a value of the rate of coalescence of $dn/dt = 1.9 \times 10^{10}$ droplets coalescing per minute for a sample containing 1 ml. decane. The leveling off of this line is due probably to the fact that the maximum globule diameter obtainable between the broad crystal faces is 10 microns, so that all the globules are enveloped by ice before larger globules can be formed.

The fact that a decrease in the number of droplets occurs before any bulk decane layer is formed, indicates that the droplets between the broad crystal faces are also subject to coalescence. This also shows that it is the thickness of the ice crystals which attain their maximum dimensions first, thus causing coalescence of the globules between the broad faces first.

The fact that deemulsification does not begin until 50% of the water is frozen is in accord with our previous observations. This means that 93% of the water in any narrow intercrystalline zones is not frozen until this time, and over the next two minutes most of the coalescence occurs.

The energy released by coalescence is not sufficient to generate enough heat to affect the freezing of the water. The energy decrease by equation (6) for total coalescence of an emulsion of 2×10^4 cm.^{2}/cm.^{3} decane is about 6×10^5 ergs at an interfacial tension of 30 dynes. This is equivalent to about .015 calories, which is negligible with respect to the heat of fusion of ice.

h. Effect of freezing on residual particle size

The question arises as to how large a droplet must become in order to eventually form a bulk phase. A number of particle size counts were made on partially and completely frozen samples of varying SDS concentration and also on HBDAC emulsions after freezing and thawing. In addition, different rates of freezing were used. Drops of the emulsion were

transferred to microscopic slides immediately after thawing, and at successive intervals after this. In all cases the largest droplets observed were 30 microns in diameter. If a cover slip was pressed against the film of emulsion, the observed diameters increased, due to deformation, and sometimes adherence to the cover slip caused the globules to appear larger. However, no spherical globules were larger than 30 microns diameter, or 14100 cubic microns (1.4×10^{-8} ml.). In many cases a complete range of sizes up to this was noted. This value corresponds with a uniform dispersion containing 7×10^{7} globules per ml. decane. After standing for one half hour, all the globules of diameter larger than 20 microns formed a cream layer directly beneath the bulk decane, and coalesced slowly. The amount of decane giving a bulk layer on thawing is therefore determined by the rate at which these 30 micron globules are formed. In the case of .05% to .14% SDS emulsions, where the rate of freezing has no effect, the rate of coalescence must therefore increase very rapidly when the zeta potential suddenly falls, giving 30 micron droplets immediately. Below this concentration range, where rate of freezing does have an effect, the rate of formation of these large droplets is the main factor. Consequently, such droplets may be formed during the initial stages of coalescence, and become occluded in the ice. Smaller globules toward the center of a given intercrystalline zone are occluded later unchanged, since the zeta potential is higher. Microscopic observations on

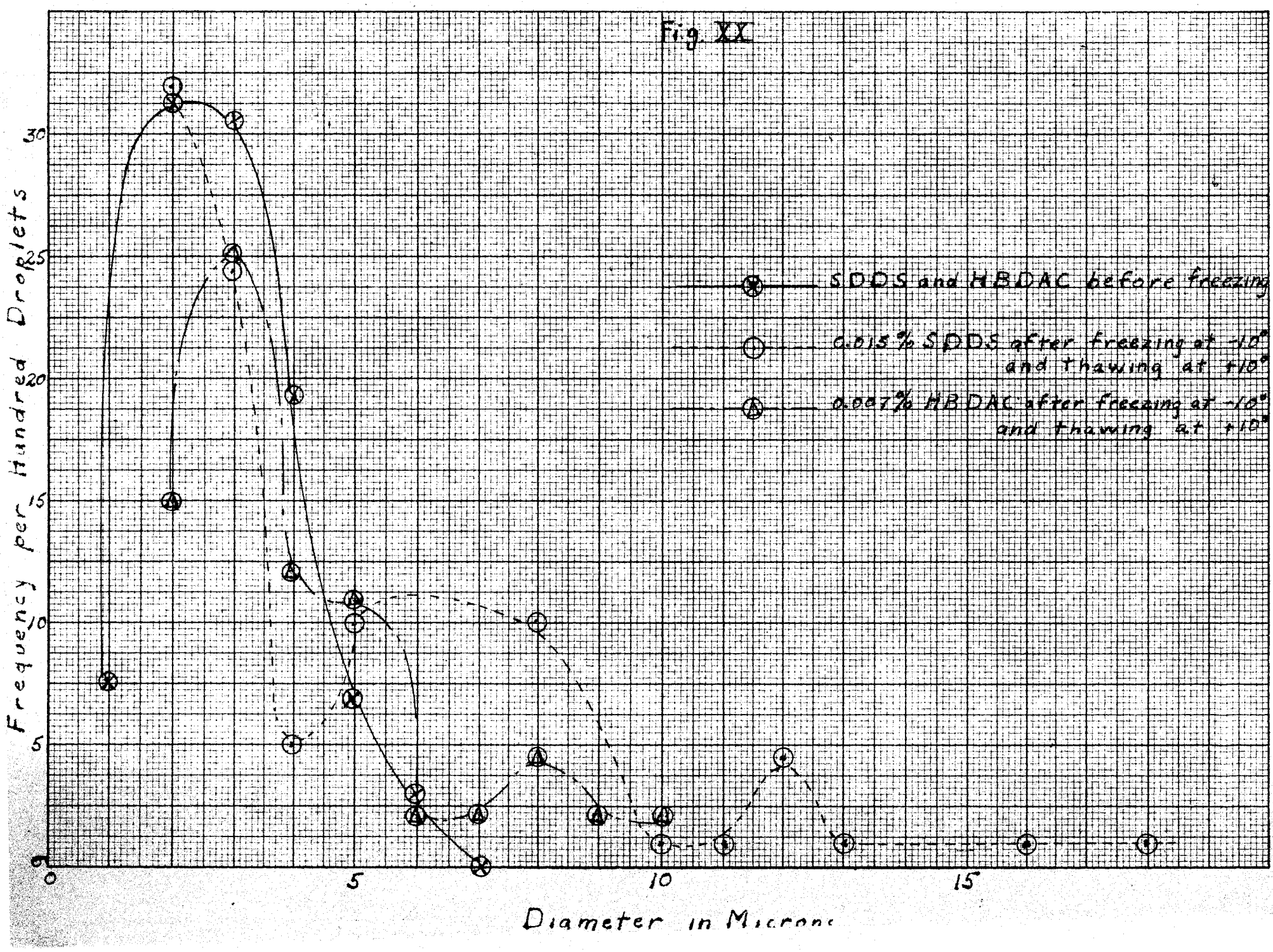
freezing of a .015% SDS emulsion seemed to indicate that this is correct, although it is difficult to tell whether a globule is in the center of a zone or not, due to the hexagonal structure of the ice.

Particle size distribution of various emulsions before and after freezing are shown in Fig. XX. The particle size distribution of SDS emulsions between .02 and .10% SDS was not measurably altered in a count of 100 droplets if the freezing was carried out at -10°C. However, the total number of droplets had decreased due to the formation of a few large droplets. The increase in particle size of .007% HBDAC and .015% SDDS is attributable to the fact that the repulsive force at close packing in both these cases is less than that for SDS in the range used. The interpretation of these curves will be facilitated by the following table:

Table 25

Diameter of Final Droplet in μ	Number of 2 Micron Droplets Coalesced
5	16
10	125
15	420
20	1000
25	1950
30	3360

These values were obtained from the ratio of the cubes of



the radii of the original 2 micron droplets and the globule of the diameter listed. Thus the one 18 micron droplet with .015% SDDS contains a volume almost equal to all the smaller droplets listed.

A particle size count on a completely frozen .15% SDS emulsion as used in section g showed that the number of 10 micron droplets in a given area in the hemacytometer had increased from 1 to 70, while no droplets larger than 10 microns in diameter were found. The overall particle size distribution was only slightly affected by this, but the percentage of decane in the 10 micron droplets was greatly increased as shown by the ten fold increase in n. Thus the maximum obtainable size for droplets between the broad crystal faces is 10 microns, since coalescence presumably takes place at the maximum rate with .15% SDS.

i. Effect of rate of freezing

Fig. XVIII shows the dilatometer curves for various rates of freezing of the standard emulsion. The ordinate is the height to which the mercury rose. The .5% SDS values were obtained with the Eastman decane.

The data obtained are given in Table 26. All de-emulsification values are ± 3%.

Table 26

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2 microns
Thawed at 10°C for 10 min.

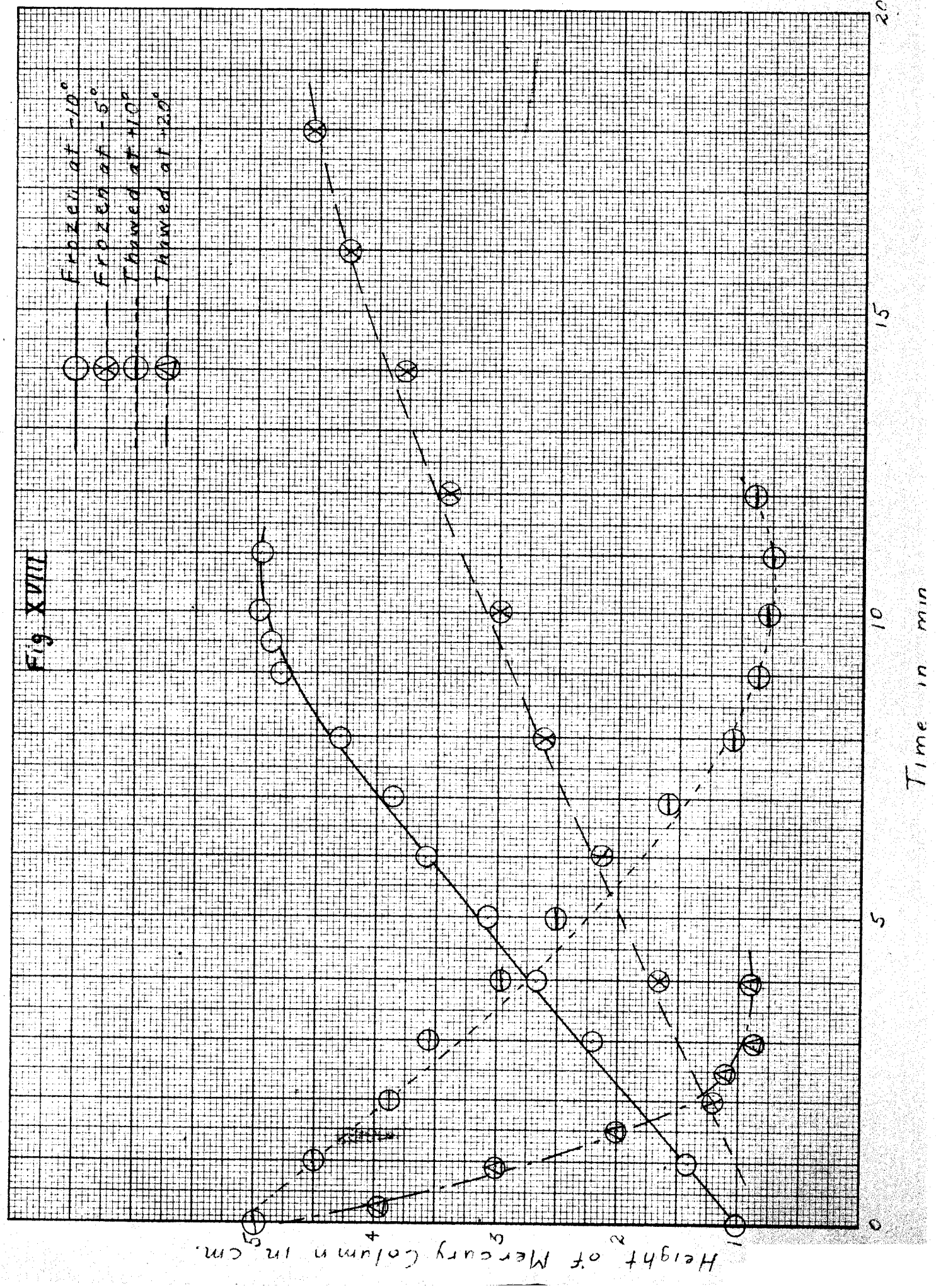


Table 26 (Continued)

Concentration SDS in %	Freezing Time in min.	Freezing Temp. in °C	Total % Demulsification
0.50	90	- 1	48
	42	- 3	47
	13	- 8	47
	10	-10	46
	5	-23	48
	0.2	-29	12
0.15	10	-10	60
	0.2	-29	12
0.125	20	- 5	55
	10	-10	55
	5	-20	55
0.075	20	- 5	33
	10	-10	33
	5	-20	38
0.05	30	- 3	38
	10	-10	36
0.02	30	- 3	60
	10	-10	45
0.0075	10	-10	30
	5	-20	26
0.015% SDDS	30	- 3	50
	10	-10	15
	4	-25	5

Table 26 (Continued)

Concentration	Freezing Time in min.	Freezing Temp. in °C	Total % Deemulsification
0.008% HBDAC	30	- 3	40
	10	-10	20
	4	-24	12

For all the SDS emulsions above .05%, the rate of freezing in test tubes had no significant effect on the deemulsification. This is a strong indication that the rate of coalescence at a zeta potential of .10 volts is so small that no droplets reach a 30 micron diameter before ice envelopes it, even when the rate of freezing is decreased by a factor of 3. When freezing out brings the concentration to the point corresponding to a zeta potential of .08 volts, the rate is increased to give 30 microns globules immediately regardless of the rate of freezing. Other factors, however, may also be operative when the rate of freezing is varied. It is not known whether the ice is capable of exerting the same force when forming at different rates, nor whether surface equilibrium can be maintained at high rates of freezing. In the case of freezing at -3 to -1°C, it was noted that the emulsion became much more concentrated in the center portion of the tube. Rough measurements indicated that the central column of emulsion was 50% decane if uniform throughout. The outer portion of the frozen mass consisted of almost transparent ice with vertical striations; large droplets of de-

emulsified decane were seen at widely separated points in this ice. Consequently the relationship between the ice and decane is changed; despite this the deemulsification remains the same. One would expect that the maximum obtainable deemulsification would be higher on very slow freezing due to a greater chance for droplets to flow to the last zones to freeze, but this was not observed.

A freezing time of .2 minutes was obtained by spreading the emulsion on a copper plate as described in the procedures. The point of complete freezing was estimated visually. The results may be explained in terms of the number of globules per intercrystalline zone. We shall assume that the rate of formation of crystal nuclei is inversely proportional to the total time required for freezing. This would give a total of about 3.5×10^7 crystals in a 5 ml. sample, which would allow only 1/50 of the number of droplets per zone as in the case of freezing at $-10^{\circ}C$. in a test tube. For the latter emulsion, we have calculated that there are 1.1×10^5 globules per zone, but now only 2.2×10^3 can fit. If all these coalesced into one, the final diameter would be 25 microns, which is less than the critical size of 30 microns. In order to verify this, a particle size count was made on the .15% sample after freezing at $-29^{\circ}C$. Only those globules larger than 10 microns in diameter were counted, since these make up by far the greatest portion of the total volume. The average diameter was found to be 21 microns, with many as

large as 30 and 25. This is in good agreement with our calculations, since the assumptions were made on a rough basis. Consequently coalescence may still occur to the greatest extent possible when freezing is almost instantaneous. With the .5% SDS emulsion it was found that rate of thawing and inert electrolyte have no effect on the 12% deemulsification obtained with this very rapid freezing.

Since the shape of the pan in which the emulsion was frozen in the above experiments was different from the standard container, several tests were made to ascertain the effect of shape of the vessel. Freezing slowly at -10°C on this copper surface gave a 48% deemulsification with .5% SDS, as did the freezing in a test tube. Likewise freezing of a .125% SDS emulsion in this manner and in a tilted erlenmeyer flask gave the same deemulsification as in the test tube experiments.

One would expect that in the range of concentration of SDS where rate of freezing has no significant effect on the amount of decane forming a bulk layer, the residual particle size would be increased with very slow freezing. This was found to be the case. .075% SDS emulsions frozen at -10°C and -20°C showed no change in particle size distribution over the original. When frozen at -3°C the average diameter increased to 3 microns, and from the distribution of large droplets, it was calculated that the average droplet present

before freezing participated in about 100 coalescences during freezing and thawing. Therefore the force of repulsion where the zeta potential is .103 volts is insufficient to prevent coalescence during slow freezing.

The increase of 25% in the deemulsification of the .02% SDS sample when the rate of freezing is decreased by a factor of three, indicates that where the deemulsification is determined by the force of repulsion at close packing, the rate of coalescence is comparable to the rate of freezing. This is further supported by the results with .015% SDDS. Here we find that the deemulsification is directly proportional to the freezing time within the limit of experimental error. The .02% values may also be proportional to the freezing time, although the maximum prevents a further rise.

The results with .0075% SDS show that the maximum obtainable deemulsification is found with this concentration, and that the spreading coefficient effect is virtually unaffected by rate of freezing.

The increase of deemulsification with time of freezing for .008% HBDAC is the expected result if we assume that the coalescence at low interfacial tension is a slow process. Thus the rate determining step is coalescence in this case, while adherence is the critical factor where zeta potential and interfacial tension are high. With SDS above .05%, adherence throughout the close packed emulsion may be considered instantaneous with respect to the rate of freezing

when the zeta potential suddenly falls to .08 volts. Coalescence ensues at a very rapid rate at this point where the interfacial tension is above about 10 dynes per cm.

Several experiments were carried out to determine the effect of instantaneous freezing of a thin film of emulsion on the cold stage. The film was allowed to supercool to -10°C, whereupon it solidified spontaneously without visible crystal formation. The polarizing microscope failed to reveal any crystal boundaries; it was assumed that vitreous ice had formed, or else crystals of submicroscopic size were present. It is known[40] that vitreous ice will form from thin films supercooled to -12°C, and from larger volumes when plunged into liquid air. The emulsion droplets were uniformly dispersed throughout the frozen mass, in contrast to the crowding effect seen with slower freezing. Most were rod shaped, although a few retained their spherical form. From the size of these rods it was estimated that each represented about 5 original droplets. On slow thawing no coalescence was observed, and the elongated masses assumed spherical shapes. The final size distribution showed some globules 10 and 15 microns in diameter, indicating a much greater extent of coalescence than was visible during freezing or thawing. A complete range of particle sizes was noted from the unchanged 2 micron diameter to the aforementioned 15 micron size. Slow freezing yielded only very large and very small droplets.

j. Effect of rate of thawing

Typical dilatometer curves for various thawing temperatures and rates are given in Fig. XVIII.

Table 27 gives the data obtained for the effect of rate of thawing. The .5% SDS values were obtained with the Eastman decane.

Table 27

Total Volume: 5 ml.
16.7% Decane
Average Globule Diameter: 2 microns
Frozen for 10 min. at - 10°C

Concentration SDS in %	Thawing Temp. in °C	Thawing Time in min.	Total % Deemulsification
0.5	3	30	60
	10	11	48 ± 3
	25	4	35 ± 3
	50	2	35 ± 3
0.1	2	40	50 ± 3
	4	20	42 ± 3
	10	10	45 ± 3
	25	4	48 ± 3
	45	2	50 ± 3
0.05	2	40	43 ± 3
	10	10	34 ± 3
	25	4	46 ± 3
	50	2	53 ± 3
0.02	10	10	45 ± 3
	25	4	50 ± 3

Table 27 (Continued)

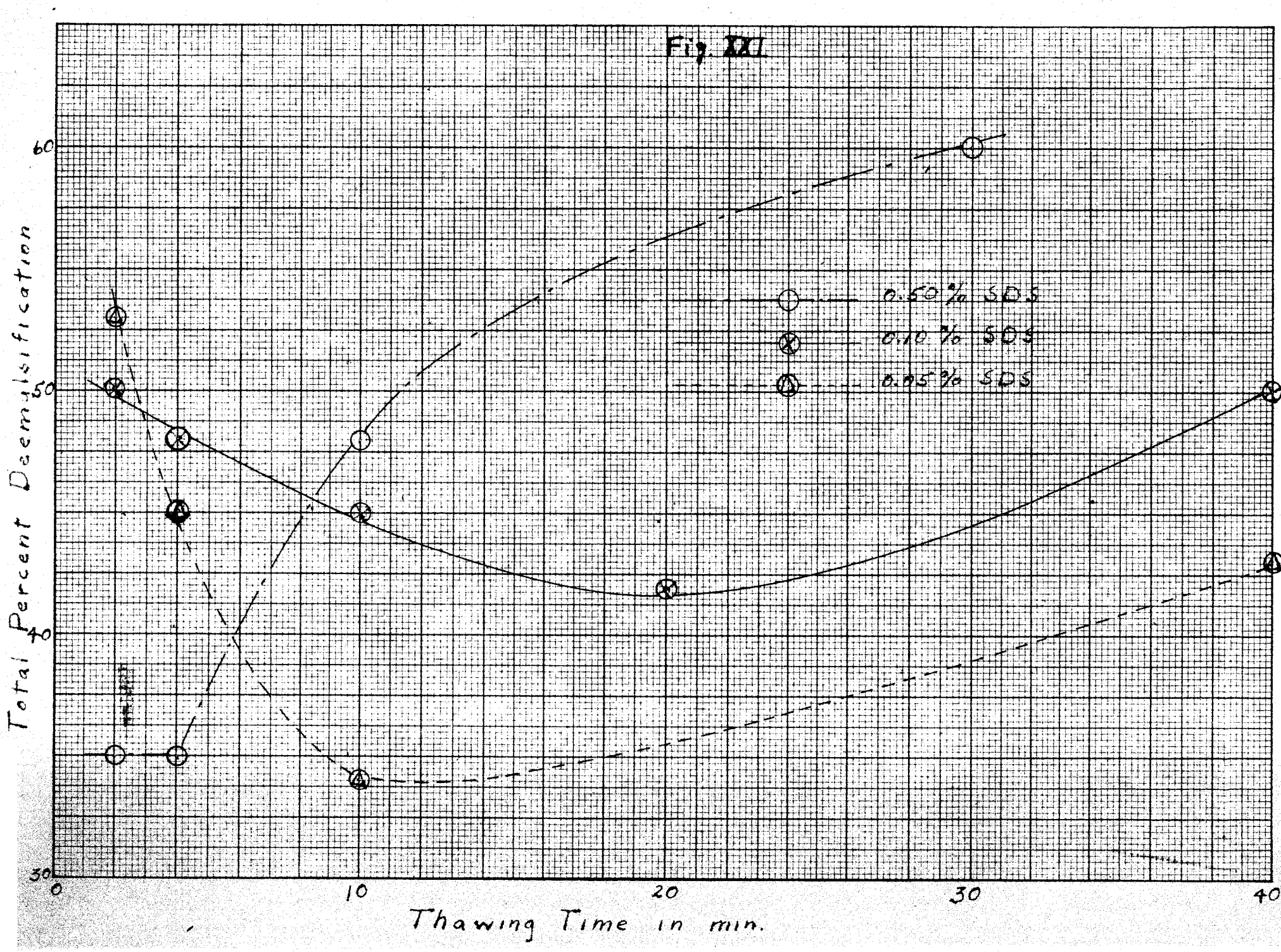
Concentration in %	Thawing Temp. in °C	Thawing Time in min.	Total % Deemulsification
0.008 HBDAC	4	20	25 ± 5
	10	10	25 ± 5
	50	2	30 ± 3

The values for .50% and .10% and .05% SDS are plotted in Fig. XXI. The curves may be explained on the basis of two assumptions:

1) the intercrystalline zones thaw first if their freezing point is lowered by the presence of an appreciable concentration of electrolyte and

2) the rate of coalescence of the droplets after release into the bulk liquid aqueous phase is dependent on the rate of resorption and reorientation of the protective layer of SDS, and on the number of collisions immediately after release.

In the case of a frozen .50% SDS emulsion, the overall concentration in the volume occupied by the close packed globules is 7% or .28N SDS. Some of this is in the form of macroscopically visible crystals. Another portion is still associated with the decane surface and probably precipitated near the interface as microcrystals. Sufficient material is associated with the interface to form at least a monomolecular film as shown by the observations on



the disappearance and reappearance of globules. The intercrystalline zone as a whole will melt at the freezing point of a saturated SDS solution. This was measured experimentally as -.08°C, which is the theoretical value for a uni-univalent electrolyte at .022N. If time is allowed during thawing for a temperature gradient to be set up between the ice surface and the interior of the ice mass, the intercrystalline zones will melt first, assuming the bulk of the ice to be pure water. This will give rise to a situation analogous to that found on freezing: the globules will be pressed against one another in a confined space without the protective action of surrounding ice. Consequently they will tend to coalesce until enough water has melted to relieve the close packed situation, or until sufficient reorientation and resorption of the emulsifying agent has occurred to increase the zeta potential.

Rapid thawing will not allow time for this temperature gradient to be set up, and consequently the droplets will be released directly into the dilute emulsion. With high emulsifier concentration the rate of resorption and reorientation is apparently high enough to prevent coalescence of droplets released in this manner. Consequently the curve for .5% falls as thawing time is decreased, finally reaching a constant minimum value. It is possible that this 35% minimum represents that amount deemulsified on freezing alone.

Where the emulsifier concentration is .1%, the freezing point of the intercrystalline zones will not be reduced to as great an extent as with .5% for two reasons. First, a greater proportion of the SDS is adsorbed on the droplets and hence not available for freezing out. Secondly, a saturated solution will occupy one-fifth the volume of that found for .5%, although the last fraction of water to freeze will be saturated with SDS. Consequently the effect of slow freezing is less pronounced. The time required for resorption and reorientation of a protective film will be longer in the case of .1%. Very rapid thawing will release more droplets per unit time accompanied by turbulance at the point of melting and thus increase the number of effective contacts between droplets susceptible to coalescence. Fig. XXI shows that this effect is more pronounced as the SDS concentration is increased. The increase in deemulsification over the minimum value is double that for .1% in the case of .05% when thawing time is reduced to 2 min. This supports our assumption that rate of resorption is proportional to the emulsifier concentration, since the concentrations are also in the ratio of 1:2. However, a deeper minimum may be present with .05% near 20 minutes.

Microscopic observations bear out these assumptions. With .5% SDS emulsions the intercrystalline zones of a film frozen on a microscope slide melted first, at about -.1°C,

although the temperature could not be read precisely. The droplets flowed and coalesced during this stage, but not after complete melting had occurred. Rapid thawing did not give any appreciable coalescence after melting either. The intercrystalline zones melted first with .1% SDS as well, but not as much flowing and coalescence was observed.

Several samples were stirred while thawing using the wire procedure described. The following results were obtained where the thawing temperature was 5 degrees and the thawing time 10 minutes:

Table 28

Concentration SDS in %	TD stirred in %	TD Unagitated in %	Increase with Stirring in %
0.10	53 ± 3	47 ± 3	6
0.05	50 ± 3	36 ± 3	14
0.005	90 ± 3	30 ± 3	60

TD is the total deemulsification.

Here, as in the rate of thawing experiments, the increase with .05% is about double that for .1%. This is a further indication that the rate of reattainment of a protective electric charge is proportional to the overall concentration. Agitation will tend to cause more collisions between newly released droplets. With .005%, most of the decane present was deemulsified, which is the expected result

by extrapolation of the other two values. A sharp decrease in the total number of droplets decreases the probability of further collisions, so that not all of the dispersed phase was affected.

In general we may conclude that when an emulsion is frozen at -10°C and thawed at 10°C in the manner of our experiments, most of the deemulsification occurs during freezing. The variation of deemulsification with rate of thawing between 0°C and 20°C thawing temperature is within the experimental error for the range of concentration used. In this range the effect of concentration on deemulsification is considerably greater than could be accounted for by thawing effects, and of opposite sign from what would be expected from thawing considerations alone. Thus the deemulsification decreases from .14% to 105% SDS and again from .015% to .002%. Since the rate of resorption decreases as concentration decreases, the contribution of thawing to the decane layer should increase as we go from .14% to .002%. This contribution is apparently negligible on unagitated freezing and thawing, judging from the almost linear decrease below .015%.

The effect of rate of thawing on HBDAC emulsions is seen to be negligible. It is probable that the interfacial tension is reduced to a value approaching that for for equilibrium with the bulk solution at the instant of re-

lease, regardless of the electrokinetic potential. Consequently any collisions are not likely to result in coalescence; only the constant force of growing ice crystals can produce coalescence where interfacial tension is near 1 dyne per cm.

k. Effect of other variables

1) Freezing with stirring

Using a spiral glass stirrer with a diameter slightly smaller than the freezing tube, the following results were obtained:

Concentration SDS in %	TD Stirred	TD Unagitated
0.50	12	48

This shows that the number of globules squeezed in the narrow intercrystalline zone is reduced by the random orientation of the crystals produced by stirring.

2) Time held in frozen state

Concentration SDS in %	Freezing Temp. in °C	Holding Temp. in °C	Time Held in min.	%TD when Thawed Immediately	TD After Holding in %
0.50	-10	-10	60	48	48
0.50	-10	0	60	48	48
0.50	-29(frozen in thin film)	-29	60	12	12

(Continued)

Concentration SDS in %	Freezing Temp. in°C	Holding Temp. in°C	Time Held in min.	%TD when Thawed Immediately	TD After Holding in %
0.075	-10	-10	90	40	40
0.005	-10	-25	30	25	25

These results indicate that once the droplets have become surrounded by ice, no coalescence is possible. Apparently the rate of heat transfer with the .50% sample held at 0°C was insufficient to allow melting of the intercrystalline zone, and ultimately the entire mass, since the melting point was -.08°C.

Summary

1. The system n-decane-aqueous solution of emulsifying agent was studied with respect to interfacial tension, electrokinetic potential, and other physical properties. Sodium decyl sulfonate (SDS) was the principal agent used. Sodium dodecyl sulfonate (SDDS) and hexadecyl benzyl dimethyl ammonium chloride (HBDAC) were also employed.

2. Particle size distribution, bulk emulsifier concentration and stability of the unfrozen emulsions were determined.

3. The sequence of events during the freezing and thawing of an emulsion was studied both microscopically and macroscopically. The structure of the frozen emulsion was also noted.

4. The effect of freezing and thawing under standardized conditions was determined for emulsions of various SDS concentrations and 16.7% decane. A portion of the deemulsification curve obtained was correlated with a sharp fall found in the zeta potential curve. Another portion was correlated with the force of repulsion between the droplets. At low concentrations of emulsifier the deemulsification was dependent on the spreading coefficient of decane at an ice-water interface. The following equations were developed for deemulsification on freezing:

$$RD_{(.05\text{-}.14\%\ SDS)} = k_1(C_{cp} + k_2)$$

$$RD_{(.015\text{-}.05\%\ SDS)} = k_3 / F_R$$

$$TD_{(.002\text{-}.015\%\ SDS)} = k_4\left(\gamma_{wo} - \gamma_{ws}\cos\theta + \frac{100}{k_4}\right)$$

where RD is the relative percent deemulsification, TD the total percent deemulsification, C_{cp} the emulsifier concentration at close packing of the globules, F_R, the force of repulsion between the droplets, γ_{wo}, the interfacial tension between decane and the solution, and θ, the angle of contact between decane and ice. These equations were partially verified for SDDS and 28.6% decane in SDS.

5. HBDAC and dodecyl amine hydrochloride were used as cationic emulsifying agents for comparison with the anionic SDS. The effect of freezing on emulsions stabilized by these substances was explained in terms of the interfacial tension and zeta potential. The following empirical formula was derived for HBDAC:

$$RD_{(.005\text{-}.02\%\ HBDAC)} = k_5\gamma_{(C_o\ -.004\%)}$$

where $\gamma_{C_o\ -.004\%}$ is the interfacial tension at .004% HBDAC less than the initial concentration.

6. The influence of sodium chloride on the deemulsification of a standard SDS emulsion was studied. The data were correlated with the energy of interaction between the droplets. The following equation was obtained:

$$RD = k_6\sqrt{\sum c z^2}$$

where $\sqrt{\sum c z^2}$ is the $\sqrt{\text{sum}}$ of the non surface active ion concentrations times the square of their charge.

7. Data was obtained on the effect of varying the initial globule size on deemulsification due to freezing. The results were attributed to effect of globule size on their mobility during the last stages of freezing.

8. Emulsions of various volume percentages decane were partially frozen and the deemulsification noted. The results were interpreted in terms of the structure of the frozen emulsion.

9. The effect of rate of freezing on deemulsification was determined for various SDS, SDDS, and HBDAC concentrations. The results were explained on the basis of the rate of coalescence of the globules as influenced by zeta potential and interfacial tension.

10. Measurements on the effect of rate of thawing were made. These data were explained on the basis of assumptions as to the melting point near the globules and the rate of resorption of a protective membrane during thawing.

Conclusions

1. Coalescence of emulsified oil droplets on freezing of the aqueous phase is due to the crowding action of the growing ice crystals. This gives rise to sufficient force to bring the globules in close contact against the action of their electric fields. The attractive forces then act to cause reduction of mutual surface by coalescence.

2. No coalescence occurs until enough water has frozen to concentrate the globules near their close packing ratio of 74%.

3. During the freezing of a bulk sample of emulsion, the ice crystals reach their maximum thickness first, entrapping about 40% of the globules between the broad crystal faces. These globules coalesce only to a small extent and do not contribute to the bulk layer on thawing. Those droplets pressed between the narrow crystal edges may coalesce completely to form a continuous phase.

4. For emulsions of decane in solutions of greater than .015% sodium decyl sulfonate (SDS) the deemulsification is dependent on the repulsive forces between the globules, and hence on the zeta potential and emulsifying agent concentration.

5. If the zeta potential is below .085 volts, the rate of coalescence on freezing is high enough to give the maximum possible decane layer on thawing for a wide range

of freezing rates. When the zeta potential is above about .085 volts, the extent of coalescence is inversely proportional to the force of repulsion at the close packing ratio of the globules. Coalescence is very slow at a zeta potential of .103 volts above .05% SDS.

6. Where the zeta potential is dependent on a critical orientation of the paraffin chains at the hydrocarbon-solution interface, the decrease in surface concentration produced by the close approach of a second globule apparently shifts the zeta potential to that corresponding to a lower bulk concentration.

7. For emulsions of 16.7% decane and less than .015% SDS, or where the initial interfacial tension is greater than about 40 dynes/cm., the decane wets ice better than it does the solution. The globules therefore adhere to the ice and fail to concentrate in the narrow intercrystalline zones. Since the globules are more isolated, they coalesce to a lesser degreethan with higher SDS concentration. This effect is proportional to the spreading coefficient of decane at a solution-ice interface.

8. The general shape of the deemulsification-emulsifier concentration curve is unaltered by the use of sodium dodecyl sulfonate instead of SDS or by the use of 28.6% decane instead of 16.7%. The observed differences are explicable in terms of the physical properties of the systems involved.

9. If the interfacial tension between decane and the solution is below 10 dynes per centimeter, and the zeta potential below .085 volts, the rate of coalescence on freezing is sufficiently slow for some of the globules to be enveloped unchanged by the ice. The rate of coalescence is approximately proportional to the interfacial tension below 10 dynes/cm. These conditions are found with hexadecyl benzyl dimethyl ammonium chloride (HBDAC) emulsions of decane above .005% emulsifier concentration.

10. The presence of sodium chloride in a SDS-decane emulsion increases the deemulsification although it does not affect the measured zeta potential in the concentration range used. This effect is due to the reduction of energy of interaction as derived by Eilers and Korff. Sodium chloride does not affect HBDAC emulsions, although it does lower the zeta potential.

11. Smaller globules have greater mobility during the last stages of freezing than do larger ones, They therefore tend to flow to the last zones to freeze, becoming subject to coalescence there. Larger globules are entrapped during the early stages of freezing and are thus more isolated and are prevented from coalescing.

12. The extent of deemulsification is approximately proportional to the freezing time where the zeta potential is between .09 and .10 volts. Above and below this range, the rate of coalescence is either too rapid or too slow for

the deemulsification to be affected by the freezing rates used. The deemulsification is likewise dependent on the freezing rate when interfacial tension determines the rate of coalescence, as with HBDAC.

13. Coalescence during thawing may take place either while the globules are still pressed against each other in the intercrystalline zones, or after release into the liquid phase. Where the freezing point of the intercrystalline zones is appreciably lowered by high emulsifier concentration slow thawing will melt these zones first, causing increased deemulsification. Rapid thawing therefore decreases the amount of deemulsification at high emulsifying agent concentration.

14. Frozen emulsions of lower emulsifying agent concentration, where the intercrystalline zones have a melting point close to that of pure water, are less affected by slow thawing. However, the rate of resorption and reorientation of a protective membrane is slower as concentration decreases. Rapid thawing therefore releases the globules before they have regained a protective charge, and thus causes increased deemulsification.

15. The extent of deemulsification on freezing and thawing of an emulsion is independent of the viscosity of the dispersed phase, but is influenced by the chemical nature of the globules.

Special Comments on Previous Work

Comparison of our results with those in the literature is difficult due to the widely different nature of the dispersions used. However, several general points may be considered.

Most of Young's observations on freezing of emulsions on microscope slides were reproduced in the course of our work. However, he stated that reemulsification of coalesced droplets occurred on thawing. Our observations also seemed to show an increase in the number of droplets on thawing as compared with the number visible in the frozen state. Further investigation on very slow thawing showed that when the droplets are close packed and separated by a thin layer of ice, they give the illusion of fewer globules being present. In addition, the thinning of the adsorption membrane as noted by Rochow and Mason also tends to reduce the visibility of the droplets.

Swingle and Snapp found that stirring on freezing and thawing increased the deemulsification. According to our results, only the stirring on thawing had this effect, while agitation during freezing decreases the deemulsification.

Rochow and Mason's observations on the thinning and disappearance of the adsorption membrane were substantiated in our microscopic work. This was manifested by the

apparent disappearance of the droplets between the broad crystal faces as the temperature was lowered. The difference in refractive index between ice and decane is not sufficiently small to account for this, but probably the ice structure merely obscured them. Large droplets were visible under these conditions. Rochow and Mason's results can be explained on the basis of the freezing point of a sodium oleate solution at the concentration found at the globule surface. Assuming the surface was saturated with sodium oleate molecules, the dimensions given by Thomas give a theoretical freezing point of -8.8°C. The authors mentioned found very rapid thinning at -10°C. The theoretical freezing point of a close packed SDS film, where the molecules are smaller than those of sodium oleate, is about -15°C. Our value of -2°C is accounted for by the limited solubility of SDS, which gives a freezing point depression of -.08°C at saturation. In addition, electrostatic repulsion would tend to lower the surface density.

Rochow and Mason concluded that coalescence occurs only on thawing after the temperature has been brought low enough to freeze the adsorption membranes. Our results with varying freezing temperatures indicate that with sodium decyl sulfonate emulsions of decane this is not the case.

The conclusions of Rochow and Mason with regard to the osmotic dehydration of the membrane are open to question. For this to occur, the bulk emulsifier concentration must

be higher than the surface concentration. Since the latter is about 2 molar from the freezing point, it is unlikely that such a concentration could be obtained in the bulk liquid by freezing out of an initially .02N solution. The limited solubility of the soap would prevent this. The whole concept of hydration and "bound water" per se as factors in the stability of colloids has been criticized by Derjaguin, Verwey and Overbeek, and other colloid scientists. These workers have successfully accounted for the stability of a variety of suspensions in terms of the energy of attraction and repulsion alone. High hydration usually accompanies tough film formation and low interfacial tension; these latter factors are probably responsible for the observed stability to freezing. Our results as plotted in Fig. XIX certainly cannot be accounted for by hydration, since this would increase as concentration increases. The result would then be increasing stability to freezing as concentration increases, while the opposite effect was observed over most of the range. That ice force alone can cause coalescence is indicated by the fact that centrifugation caused an oil layer to appear on our standard emulsion. The centrifugal force should not result in dehydration, but will tend to bring the globules in close contact against the action of their electrical fields.

Dahle concluded that highly hydrated globules deflect the formation of ice crystals. This is not supported by our results on the ratio of crystal size to globule

diameter. There are about 10^5 globules per crystal when an emulsion of 2 micron globules is frozen at $-10^{\circ}C$ in a test tube, so that an individual globule could not appreciably affect the formation of an ice crystal.

Doan and Baldwin observed a rapidly increasing percentage coagulation on freezing as the initial fat content of cream was increased. This does not necessarily contradict our results, which showed little effect. The influence of volume percentage dispersed phase was found to be determined by the shape of the zeta potential-emulsifier concentration curve. Such a curve for milk fat particles suspended in a protein solution is undoubtedly different from decane globules in sodium decyl sulfonate solutions.

The observations and conclusions of Walker regarding the freezing of neoprene suspensions were substantiated by our work. The order of protective ability for different types of emulsifying agents was found to apply to decane emulsions as well. The effect of partial freezing was also reproduced. However, he found that the concentration of emulsifying agent did not affect the stability to freezing. He used all the emulsifying agents above their critical micelle concentrations where the zeta potential is usually constant; thus changing the concentration in this region should have no effect. Walker suggested that the mobility of the droplets during the last stages of freezing is an

important factor in determining stability. This was found to be the case in our work where particle size was varied and where decane wet ice better than water.

The results obtained by Gutbier and others on the freezing of hydrophobic suspensions of solids are readily explained on the basis of our hypotheses. In general the electrokinetic potential, and hence the force of repulsion, of such sols is lower than that of emulsions stabilized by surface active agents. In addition, the particles in these sols are much smaller than emulsion droplets; they will all flow to the last zones to freeze and will not be protected between the broad crystal faces. Consequently, complete coagulation under the influence of the ice force is to be expected, unless the zeta potential has been raised by the addition of some protective electrolyte.

Bibliography

1. Newman, J. Phys. Chem. 18, 45 (1914)
2. Vickery, Report of the Food Investigation Board; Year 1928, London, 1929, p. 24
3. Young, Plant Physiology 9, 795 (1934)
4. Swingle and Snapp, U.S. Dep. Agr. Tech. Bull. 253 (1931)
5. Rochow and Mason, Ind. Eng. Chem. 28, 1296 (1936)
6. Holzapfel, Kolloid-Z. 85, 272 (1938)
7. Doan and Baldwin, J. Dairy Sci. 24, 277 (1941)
8. Baldwin and Doan, Ibid. 19, 225 (1936)
9. Webb and Hall, Ibid. 18, 275 (1935)
10. Dahle, Ibid. 24, 245 (1941)
11. Little, Milk Plant Monthly, 37, 42 (1948)
12. Walker, J. Phys. Colloid Chem. 51, 451 (1947)
13. Gabriel, Technical Aspects of Emulsions, London, 1935, p. 146
14. Clayton, Theory of Emulsions The Blakiston Co., Philadelphia, 1943, p. 185
15. Gutbier, Kolloid-Z. 29, 161 (1921)
16. Foote and Saxton, J. Am. Chem. Soc. 38, 588 (1916)
17. Hazel, J. Phys. Colloid Chem. 51, 415 (1947)
18. Beaver, PhD Dissertation Columbia University, 1921
19. Henry, Phil. Mag. 7, 164 (1930)
20. Derjaguin, Trans. Faraday Soc. 36, 203 (1940)
21. Dickinson, Ibid. 46, 48 (1944)
22. Porter, Proc. Roy. Soc. A133, 106 (1933)

23. Verwey and Overbeek, Theory of the Stability of Hydrophobic Colloids, Amsterdam, Elsevier Publishing Co, 1948; p. 160

24. Klevens, J. Phys. Colloid Chem, 52, 130 (1948)

25. Tartar, J. Am. Chem. Soc. 61, 539 (1939)

26. Tartar, Private Communication

27. Walton, Heibert, and Sholtes, J. Colloid Sci. 1, 385 (1946)

28. Deansley and Carleton, J. Phys. Chem. 45, 104 (1941)

29. Rochow and Mason, Ind. Eng. Chem Anal. Ed. 6, 367 (1934)

30. Price and Lewis, Trans. Faraday Soc. 29, 775 (1933)

31. Powney and Wood, Trans. Faraday Soc. 36, 57 (1940)

32. Thomas, Colloid Chemistry, New York, McGraw-Hill Book Co., 1934, p. 247

33. Alexander and Johnson, Colloid Science, Clarendon Press, Oxford, 1949, p. 587

34. Michaels and Hauser, J. Phys. Colloid Chem. 55, 405 (1951)

35. Kalb, Centr. Mineral. Geol. 1921, 129 (CA 15, 3803 (1921))

36. Adam, Physics and Chemistry of Surfaces, London, Oxford University Press, 1930, p. 187

37. Eilers and Korff, Trans. Faraday Soc. 36, 239 (1940)

38. Powis, Z. Physik. Chem. 89, 186 (1914)

39. Clayton, loc. cit., p. 185

40. McIntosh and Edson, J. Am. Chem. Soc. 38, 613 (1916)