Separation by dielectric distribution

Billy Charleston Black II

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Billy Charleston Black II

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>REVIEW OF LITERATURE</strong></td>
<td>3</td>
</tr>
<tr>
<td>Dielectrophoresis</td>
<td>3</td>
</tr>
<tr>
<td>The Size and Structure of Phosphatide Micelles</td>
<td>11</td>
</tr>
<tr>
<td><strong>EXPERIMENTAL</strong></td>
<td>14</td>
</tr>
<tr>
<td>Description and Operation of Dielectric Distribution Apparatuses</td>
<td>14</td>
</tr>
<tr>
<td>Materials Investigated and Analytical Procedures</td>
<td>25</td>
</tr>
<tr>
<td><strong>THEORY</strong></td>
<td>31</td>
</tr>
<tr>
<td>The Efficiency of Separation</td>
<td>31</td>
</tr>
<tr>
<td>Derivation of General Distribution Equations</td>
<td>33</td>
</tr>
<tr>
<td><strong>RESULTS AND DISCUSSION</strong></td>
<td>50</td>
</tr>
<tr>
<td>Batch Dielectric Distribution Apparatus</td>
<td>50</td>
</tr>
<tr>
<td>Continuous Flow Dielectric Distribution Apparatus</td>
<td>68</td>
</tr>
<tr>
<td>Simple Parallel Plate Apparatus</td>
<td>75</td>
</tr>
<tr>
<td>Parallel Plate Stack Apparatus</td>
<td>76</td>
</tr>
<tr>
<td><strong>SUMMARY</strong></td>
<td>80</td>
</tr>
<tr>
<td><strong>LITERATURE CITED</strong></td>
<td>83</td>
</tr>
<tr>
<td><strong>ACKNOWLEDGMENTS</strong></td>
<td>85</td>
</tr>
</tbody>
</table>
INTRODUCTION

Small particles suspended in a medium of different dielectric constant may be concentrated by their movement in a nonuniform electric field. Such motion is called dielectrophoresis. The more polar material in the suspension moves toward regions of high field intensity and less polar material moves toward regions of low field intensity. This leads to a new distribution of the material in the field.

This effect (dielectrophoresis) was first postulated a number of years ago by a German worker, Muller (14). Later, in this country, Pohl (16) observed this phenomenon when he suspended an organic polymer (polyvinyl chloride) in a liquid of low dielectric constant and exposed the mixture to a nonuniform electric field. Since that time Loesche and Hultschig (13), Pohl (18, 17), and Pohl and Schwar (20, 21) have studied this effect. They concluded the effect would not be appreciable for particles of molecular size but the effect would be quite large for particles of 1 to 2 μm or larger.

There are a number of methods which may be used to separate very small particles (chromatography, distillation, partition, etc.). As the particle size increases these methods become impractical for various reasons. Density separation (centrifugation) and screening (filtration) are essentially the only methods available to work with large particles.
Dielectric distribution should be useful in the same range of particle sizes where density separations and filtration are employed and should supplement these methods.

The objective of this study was to investigate the use of this phenomenon, dielectric distribution, for the analytical and preparative separation of various materials with special emphasis on the separation of phosphatides from soybean miscella.
REVIEW OF LITERATURE

Dielectrophoresis

The effects of a strong nonuniform electric field on solutions and suspensions have received only little attention in the past. In 1938 Muller (14) predicted that suspended particles should move in a liquid of different dielectric constant when exposed to nonuniform fields. He calculated that such an effect should be observable by means of capacity changes in a cylindrical condenser. He also concluded that the effect would not be appreciable for particles of molecular size.

Bates (3) in 1950 disclosed a technique for precipitating sludge from petroleum electrostatically in a cylindrical condenser. He found that sludge formed by boron trifluoride treatment is removed by applying an alternating current with a potential gradient of at least 5,000 v./cm. for about one minute. This phenomenon seems to be dielectrophoresis. The sludge collected on the central electrode. There was an optimum temperature range between which this process must be carried out. For lubricating oils the optimum temperature range was found to be 15-35° C. No precipitation would occur below 0° C. or above 60° C. Bates found that sludges formed by treatment with sulfuric acid could not be removed.
In 1951 Pohl (16) studied the motion of suspensoid particles, relative to the solvent, resulting from polarization produced in an inhomogeneous electric field. He defined this relative motion as "dielectrophoresis". Pohl noted that this phenomenon was analogous to the related phenomenon of electrophoresis, in which motion of charged suspensoid particles is produced by the action of an electrostatic field. Pohl also noted that this phenomenon was distinctly different from electrophoresis in that it does not require a net permanent charge on the particle. In dielectrophoresis the particles move under the influence of the dipoles induced by the electric field. With dielectrophoresis one can use either AC or DC fields whereas one must use only DC fields with an electrophoretic process. Pohl found that when the polarizability of the suspensoid is greater than the solvent, the asymmetric field forces accelerate the suspensoid particles relative to the solvent, giving rise to an increased concentration of the suspensoid near the regions of high field strength. The suspensoid particles are then more prone to collision and coagulation because of the concentration per unit volume, so they precipitated in the regions of high field strength. Pohl also used a cylindrical condenser to generate the asymmetric field and derived equations relating the velocity of dielectrophoresis to particle size, field strength, apparatus dimension, solvent viscosity and difference in dielectric constants.
In 1954 Debye et al. (4, 5) and Barber et al. (2) made some investigations on materials with high dielectric constants suspended in media of low dielectric constant in inhomogeneous electrical fields. Two types of apparatuses were used in these investigations: 1) a cylindrical condenser with a central fine wire as the center electrode and 2) a stack of about 60 razor blades with sharp edges uniformly spaced with microscope cover glasses which served as one electrode and directly opposite this a brass plate which served as the other.

Debye et al. (5) used both of the above described apparatuses in their investigations. They used a 1½ polystyrene (mol. wt. 600,000) in cyclohexane and found that the polystyrene would accumulate in the region of highest field strength.

Debye et al. (4) used the cylindrical condenser apparatus in their "high-frequency dielectric method" for molecular weight determination. Here again a polymer was suspended in a liquid of low dielectric constant. When a high field was applied the polymers concentrated around the center electrode forming a "polymer atmosphere" having what they called "a Boltzmann distribution corresponding to a potential energy, $V = \alpha \frac{1}{2} E^2$". The condenser containing the above described structure was made a part of the circuit whose oscillation frequency could be measured. The change in oscillation frequency that occurred when the potential was applied was measured. Conclusions could be drawn about the distribution of mobilities and
and subsequently about the molecular weight of structures of the polymer from the way in which the change in frequency occurred.

Barber et al. (2) used the razor blade stack apparatus in their "field-induced diffraction method" for determining molecular weight. They placed the entire apparatus in a polymer solution and applied a strong electric field; here again the "Boltzmann atmosphere" of polymer was found where the field was strongest, around the edges of the blades. Light diffraction through the apparatus was measured before and after the field was applied. From this data they could make conclusions about the molecular weight.

In 1955 Loesche and Hultschig (13) made a thorough study of the behavior of dielectrics in an inhomogeneous field. They also extended Muller's (14) mathematical treatment of this phenomenon for cylindrical condensers. They derived equations to predict the rate at which equilibrium between dielectrophoresis and back diffusion of the suspensoid would be attained and the capacity changes which would accompany dielectrophoresis. There was considerable discrepancy between their predictions and their experimental results. They attributed this to the approximations necessary in deriving their equations.

In 1958 Pohl (18) made a more comprehensive study of some of the effects of nonuniform electric fields. He stated that in practice, the study of the effects of a nonuniform electric
field is made complex by many competing events: conduction, thermal convection, diffusion, and the accumulation of permanent charges on the particles. Pohl used both the batch and continuous dielectrophoretic separators in this experiment. Both separators were of the cylindrical condenser type. They contained a center and a peripheral vent to collect separate fractions. The only difference was the batch separator only separated one condenser's volume at a time while the suspension flowed through the continuous separator. Pohl also gave a more rigorous derivation of his equation to predict the relative velocity of motion of particles.

Up to this point the work reported on the phenomenon of dielectrophoresis was essentially qualitative except for that of Loesche and Hultschig (13). In 1959 Pohl and Schwar (20) studied some factors which affect the separation yields. Their apparatus consisted of a cylindrical cell of Pyrex glass as the outer electrode and an insulated supported wire as an inner electrode. In some cases the inner surface of the glass cylinder was coated with graphite to act as an outer electrode. Polyvinyl chloride powder with particle sizes of 213 μ, 163 μ, and 90 μ, suspended in CCl₄:CH₂, 1:1 v/v mixture was used in this study.

First they studied the effect of voltage on precipitation yield. Precipitation yield is the percentage of polar material
(polyvinyl chloride) attracted to the center electrode and collected from the central vent when the apparatus is drained. At low voltages the yield was low. It increased rapidly with voltage until a plateau was reached. As the voltage was raised further the yield increased only a little more, then a critical voltage was reached at which point the polar material sloughs off the inner electrode. They also studied the effects of particle size, cell diameter, central electrode diameter and amount of central electrode insulation on the yield and slough-off voltage. They found that the slough-off voltage was inversely proportional to the central electrode diameter and varied with the thickness of insulation; the thicker the insulation the higher the slough-off voltage.

Next they studied the effect of direct vs. alternating voltage on the yield and slough-off voltage using several different particle sizes. They found that the yield and slough-off voltages were essentially the same for either alternating or direct voltage. The findings agreed with the theory of dielectrophoresis proposed by Pohl (16) in an earlier publication. He attributed the slough-off effect to the accumulation of charges on the particles from contact with the central electrode.

In 1959 Seelig et al. (23) reported a technique for mixing liquids in an electrostatic field. They found that liquids having different dielectric properties could be mixed intimately
in an inhomogeneous electrostatic field. The mixing of iso-octane with a number of polar liquids was investigated using a glass electrostatic cell. The bottom electrode was a pool of mercury and the upper electrode was of the brush type. They used a transformer capable of delivering 25,000 v. at 0.0001 amp. Isooctane could be mixed excellently with nitrophenol, pyridine, ethyl acetate, isopropyl alcohol, and aniline using a voltage of 5,000-8,000 v. This phenomenon seems to be the exact reverse or inverse of dielectrophoresis. This technique for mixing liquids worked very well if the dense polar liquid was introduced on the bottom electrode and if the nonpolar liquid was introduced at the upper electrode. This technique did not work if the order of introduction of the liquids was reversed.

In 1960 Pohl and Schwar (21) made further studies of batch methods of particle separations by nonuniform electric fields. They found that the yield of precipitated solids increased with applied voltage in cylindrical cells until the slough-off voltage was reached. They also found that the yield decreased with increase of volume fraction of suspended solids in the range of 1% to 50% v/v. With particles of a given size, the yield was directly dependent on the dielectric constant, while moisture in the particles had only little effect on the yield.

Pohl and Schwar (21) stated that the current flow during
the process was observed to range up to about 20 μA, and this indicated that a new method of conduction takes place with the particles present. They suggested that this was due to ionic charging of the particles. The particles then aided current flow and energy consumption (dielectric loss) by rotating.

In 1960 Pohl (17) reported a simplified theory of the behavior of suspended polymer particles in a real liquid dielectric. He believed that in a real dielectric, the initial attraction to the central electrode felt by all particles due to the nonuniform field and its polarizing induction is gradually overcome by the repulsive effects of charge accumulated on the particles due to ionic conduction in the liquid. He calculated the "reversal time" for the particle precipitation on the inner electrode. The reversal time for a typical system was about three hours and he thought this value was reasonable.

Pohl and Plymale (19) in 1960 reported a dielectrophoretic method for separating solid and liquid mixtures with different dielectric constants. This process was a continuous one and they could use either alternating or direct current fields. They listed osmotic, gravitational, dielectrophoretic, and electrophoretic forces as acting on the particles when subjected to this process. The electrophoretic forces, caused by the electric field on the excess charges on the particles, and the dielectrophoretic forces, caused by the nonuniform field on both field polarized neutral particles and the current induced
dipoles on the particle surface, were thought to be the major contributing forces. Pohl and Plymale also reported that there is an optimum voltage range between which the process must take place if there is to be appreciable separation. They used a zircon-rutile mixture to demonstrate the usefulness of this process. This mixture is difficult to separate and cannot be separated by magnetic or density methods. This mixture was resolved into its individual components under dielectrophoretic conditions.

Plonsey and Collin (15) mentioned that a dielectric experiences a force in an electric field and calculated this force for certain simple cases.

The Size and Structure of Phosphatide Micelles

Elworthy (7) in 1959 studied the formation of phosphatide micelles in benzene by an osmotic pressure technique. He used lecithin as the model phosphatide. He noted that small micelles appeared even at very low concentrations, and there is a critical micelle concentration at which aggregation of small into large micelles begins. He also studied the equilibrium between the two types of micelles. Elworthy found that the critical micelle concentration of lecithin in benzene was 0.73 grams per liter using the osmotic pressure technique. He also found that the micellar weight of a solution of lecithin in benzene at this critical concentration was 3,180 at 25° C. and 1,830 at 40° C.
At concentrations above 10 g./l. the micellar weights were 57,000 at 25° C. and 43,000 at 40° C. If one assumes a molecular weight of lecithin of 788 then the larger micelles contained about 73 molecules at 25° C. and the smaller micelles (formed at the critical concentration) contained about 40 molecules at 25° C.

Later in 1959 Elworthy (8) studied the size and structure of phosphatide micelles in benzene solution through the use of diffusion and viscosity studies. Here again Elworthy used lecithin as the model phosphatide. His viscosity studies showed that large micelles were asymmetric, and treatment of ellipsoids gave axial ratios of about 2:1. The final molecular weights for the large and the small micelles agreed with those obtained from osmotic data. He concluded that it was quite probable that the polar head groups of the large micelles were turned inwards from the benzene, and the hydrocarbon chains of the fatty acids protrude outwards. Also there were two general possibilities for arrangements of molecules in the micelles: first, as a laminar micelle in which the head groups are arranged as in a sandwich and second, as a spherical micelle where the head groups are arranged to cover the surface of a sphere.

Elworthy and McIntosh (9) in 1961 investigated micelle formation by lecithin in several aliphatic alcohols using light scattering and viscosity techniques. They used methanol,
ethanol, butanol, and hexanol as solvents in these investigations. Micelles were present in all solvents; the micellar weights increased with increase in chain length of the aliphatic alcohols. From this one can see that as the polarity of the solvent decreased the micellar size increased. They also noted that temperature affected the size of the micelles; a lower temperature gave a larger micellar size. From their viscosity measurements they gained an idea of the shape of the micelles. They concluded that the micelles had a laminar structure.
**EXPERIMENTAL**

Description and Operation of Dielectric Distribution Apparatuses

**Batch cylindrical condenser**

Figure 1 shows a schematic diagram of the batch dielectric distribution apparatus. It consisted of a Pyrex glass cylinder 1.31 cm. in diameter and 12 cm. long with an insulated center metal electrode 0.31 cm. in diameter and metal foil on the outside of the cylinder as the peripheral electrode. A potential difference was applied between the outside and inside electrodes. The field strength increased from the peripheral to the center electrode, thus giving a nonuniform field.

This apparatus was connected to a high voltage Jefferson Electric Transformer (Jefferson Electric Company, Bellwood, Illinois). The primary terminals of the high voltage transformer were connected to a variable transformer which could adjust the input into the high voltage transformer from 0 to 120 v. at 60 cps. The variable transformer was calibrated by measuring the voltage from the high voltage transformer with a voltmeter. The variable transformer had to be recalibrated for each particular apparatus.

The material to be separated through dielectric distribution is put in the apparatus at inlet "A". Once the apparatus is filled to capacity the desired voltage is applied for a
Figure 1. Schematic diagram of the batch dielectric distribution apparatus
A INLET
B CENTER ELECTRODE
C INSULATION
D PERIPHERAL ELECTRODE
E TO TRANSFORMER
F BARRIER
G PERIPHERAL OUTLET
H CENTER OUTLET
definite period of time. The material is distributed from center to periphery according to its dielectric constant. The material with the highest dielectric constant (the more polar material) is attracted to the place of highest field strength, which is around the center electrode. The material with the lower dielectric constant moves toward the periphery of the cylinder where the field is weakest. When equilibrium is attained, the fractions are drained through the central and peripheral outlets, "G" and "H". The barrier "F" divides the central fraction from the peripheral fraction. The two fractions are drained so their ratio is proportional to the volumes on the inside and outside of the barrier. The contents of each fraction are analyzed.

Continuous cylindrical condenser

The continuous dielectric distribution apparatus shown in Figure 2 was similar to the batch apparatus in that a cylindrical condenser was used to create the nonuniform field. The distribution of polar and nonpolar materials was the same. The diameter of the cylinder in the continuous apparatus was smaller (0.8 cm. in diameter) than in the batch apparatus while the center electrode diameter was the same, thus decreasing the gap between the two. The time required for a mixture to come to equilibrium decreases with the fourth power of the radius of the cylinder according to Pohl (18); therefore, the equilibrium time
Figure 2. Schematic diagram of the continuous dielectric distribution apparatus
A INLET
B CENTER ELECTRODE
C INSULATION
D PERIPHERAL ELECTRODE
E TO TRANSFORMER
F BARRIER
G PERIPHERAL OUTLET
H CENTRAL OUTLET
was much shorter with the continuous apparatus than with the batch apparatus. The column's length here was 78 cm. as compared to 12 cm. for the batch apparatus. The barrier and outlets were similar to those of the batch apparatus. The flow rate was controlled through the use of small delivery tubes drawn to the desired length and diameter. The desired volume of either fraction could be collected and analyzed.

**Plate stack**

A schematic diagram of the plate stack apparatus is shown in Figure 3. The principle of separation using the plate stack condenser is similar to that of the cylindrical condensers. The polar material tends to move to the region of high field between the plates. This condenser was prepared by stacking plates that were 12 mm. in diameter 1 mm. apart. There were 60 plates in the stack and this plate stack was put into a plexiglas cylinder that was 15 mm. inside diameter. The odd numbered plates were connected and the even numbered plates were connected. The connecting wires were insulated to avoid short circuiting. One set of plates was connected to the high voltage terminal of the AC transformer to give an electric field between plates. There was an opening in the top of the condenser to allow the mixture to be separated to enter. The polar material was held between the plates by the electric field while the nonpolar material passed through the condenser.
Figure 3. Schematic diagram of the plate stack apparatus
and was collected through the outlet at the bottom. Successive fractions of uniform volume size (25 ml.) were collected and analyzed. From the analysis one can determine the extent of the separation and capacity of such a condenser.

**Parallel plate**

Figure 1 shows a schematic diagram of a column between two large parallel plates. This apparatus was constructed by using two copper plates, 1 mm. thick, 9.5 cm. x 9.5 cm. clamped parallel to each other 7 mm. apart. The two plates were held 7 mm. apart by clamping 7 mm. rubber stoppers between them. The clamps were also insulated with rubber. The plates were insulated by covering them with sheets of Parafilm. A 6 mm. Pyrex glass tube was fixed between the two plates. One of the plates was grounded while the other was connected to the high voltage terminal of an AC transformer so as to have an electric field between the two plates. The column was partially filled with nonpolar solvent and a mixture of polar and nonpolar material was then put in the top of the column. This mixture moves toward the bottom of the column due to gravity. The voltage is adjusted so the more polar material is retained when it attempts to pass through this field while the less polar material moves through. Fractions can be collected for analysis, that is, the material that passes through the electric field can be collected as one fraction and the material that is retained can be collected as a second fraction.
Figure 4. Schematic diagram of parallel plate apparatus
Materials Investigated and Analytical Procedures

A number of systems were used in an effort to demonstrate that the dielectric distribution effect exists and also to show the usefulness of such a process. These systems contained more polar and less polar components. The analytical procedures that were used to measure the amount of separation obtained by this effect together with the materials used are described below.

**Soybean miscella**

The soybean miscella was prepared from Iowa Hawkeye 1962 soybeans obtained from the Agronomy Department at Iowa State University, Ames, Iowa. These soybeans were crushed with a coffee grinder and then dried in an oven at a temperature of 82° C. for 60 min. with occasional stirring (1). The soybean oil was extracted from the soybean meal with Skellysolve B by using a batch counter-current solvent extraction method. When the extraction process was complete, the soybean miscella was filtered and the concentration was adjusted to the desired percentage of oil by addition of Skellysolve B or by evaporation of Skellysolve B under nitrogen.

**Phosphatide analysis**

The procedure used to measure the phosphatide was a total phosphorous determination. Definite volumes of fractions from
the central and peripheral vents were collected in small Kjeldahl flasks. Glass beads (5 mm. in diameter) were put in the flasks and the Skellysolve B was evaporated on a hot plate. Then 1 ml. of concentrated nitric acid was added and the flasks were heated until initial oxidation was completed. The flasks were cooled and 1 ml. of 70% perchloric acid/0.2 g. fat was added. Next the flasks were put under perchloric fume heads such as described by Diehl and Smith (6). The flasks were heated with a microburner until heavy white fumes were evolved and the digest was clear. This indicated that the digestion was complete.

The excess perchloric acid could be rapidly evaporated by either of the following methods: 1) By packing Pyrex wool filtering fiber in the space between the fume head and the neck of the flask and heating. 2) By using a separate fume head pierced by a piece of glass tubing which extended into the neck of the Kjeldahl flask. The current of air drawn through the tube quickly evaporated the acid as the flask was heated. Pyrex wool was again packed in the space between the fume head and the neck of the flask. The digested material was transferred to 25 ml. glass stoppered volumetric flasks and the analysis was completed by Fontaine's (10) colorimetric phosphorous determination.

The reagents for the colorimetric determination were prepared as follows:
1. Sulfuric acid solution was prepared by mixing 27.4 ml. of concentrated sulfuric acid (97.3%, specific gravity 1.84) with distilled water and bringing the total volume to 1 l.

2. Sodium molybdate solution was prepared by dissolving 75 g. of sodium molybdate (phosphate free) in 1 l. of distilled water.

3. Stannous chloride stock solution was prepared by dissolving 10 g. of stannous chloride (reagent grade) in 25 ml. of concentrated hydrochloric acid and the solution was stored in a glass-stoppered brown bottle. This solution should not be kept longer than four weeks. To prepare the dilute solution used in the analysis, 1 ml. of stock solution was added to 200 ml. of distilled water. A dilute solution was prepared for each set of determinations.

After the digested material was transferred to the 25 ml. glass-stoppered volumetric flask, 5.0 ml. of the sulfuric acid solution, 2.5 ml. of the sodium molybdate solution and sufficient water to bring the volume to approximately 22 ml. were added. It was necessary to shake the mixture at this point in order to avoid the appearance of a premature blue color upon the addition of the reducing agent. Next 2.5 ml. of the dilute stannous chloride solution was added and again the contents of the flask were mixed. The loosely stoppered flask was placed in boiling water for 20 min. to develop the color. Then the
flasks were cooled to room temperature and the volume adjusted to 25 ml. Approximately 4 ml of the solution were transferred to a cuvette and the absorbency was measured with a Beckman DU spectrophotometer at 820 nm against a blank receiving identical treatment. A standard curve for phosphate was prepared by using known quantities of anhydrous potassium dihydrogen phosphate. The calibration curve needs to be determined only once.

After the amount of phosphorous in each fraction was determined, the amount of phosphatide could be approximated by assuming a molecular weight for the phosphatide.

**Thin-layer chromatographic analysis**

Thin-layer chromatography was used for a rough quantitative analysis of phosphatide types. The procedure of Rouser et al. (22) was used. Samples from both fractions (central and peripheral) were spotted on silica gel plates and eluted with a solvent system composed of chloroform/methanol 2/1 plus 20 ml. water/liter. A dilute alkaline solution of Rhodamine 6 G was sprayed on the chromatographic plates and the plates were viewed under an ultraviolet light to detect the components.

**Bacterial spore and vegetative cells mixture**

A crude unclean mixture of vegetative and spore cells was prepared according to the method of Walker et al. (24). An aqueous suspensoid of the mixture was homogenized in a cell
homogenizer. This mixture was freeze dried.

Fractions from the crude mixture obtained after dielectric distribution were observed under a phase microscope to determine the percentage of spores and vegetative cells in each fraction.

**Bacterial spore cells**

Quantities of *Bacillus megaterium* 1-A 28 and *Bacillus polymyxa* 1-A 39 were purified by the procedure of Walker *et al.* (24). An aqueous suspension of the purified spores was freeze dried and suspended in benzene-carbon tetrachloride (2:5:1 v/v). A turbidity measurement was made using a Beckman DU spectrophotometer at 475 m\(\mu\) to determine the concentration.

**Oil emulsion**

The oil emulsion was prepared by mixing 4.05 ml. of mineral oil (specific gravity 0.926) and 0.5 ml. of s-tetrachloroethane (specific gravity 1.6) so as to give a final mixture with a specific gravity of one. A solution with the desired percentage of oil was prepared by emulsifying the oil mixture with water in a Waring blender. Koldex (R. G. Moench and Co., Inc., 89 Terminal Ave., Clark, New Jersey) was used as an emulsifying agent. The concentration was determined by measuring the absorbency at 475 m\(\mu\) with a Beckman DU spectrophotometer.
Homogenized milk

Fresh homogenized milk was obtained from the Iowa State University Dairy Industry Plant. The desired dilute solution of milk was prepared by adding the appropriate amount of distilled water. The milk was analyzed for fat by the Mojonnier (11) test. Turbidity measurements were made on the milk fractions with a Beckman DU spectrophotometer at 475 µm.
THEORY

The Efficiency of Separation

The amount of separation for the cylindrical cell was expressed in terms of percent efficiency as shown by the following derivation.

Let the volume inside the barrier (Refer to Figure 1.) be compartment "1" and let the volume outside the barrier be compartment "2". Then $P_1$ is the amount of polar material in compartment "1" at equilibrium and similarly $P_2$ is the amount of polar material in compartment "2" at equilibrium. The total polar material ($P_T$) is $P_1 + P_2$. Let $w_1$ be the weight fraction of polar material initially in compartment "1" and $w_2$ be the weight fraction of polar material initially in compartment "2". Note that $w_1 + w_2 = 1$ and $w_1 = 1 - w_2$.

Efficiency is defined as the actual gain of polar material in compartment divided by the maximum possible gain. The actual gain is $(P_1/(P_1 + P_2)) - w_1$ and the maximum possible gain is $1 - w_1$, therefore

$$E = \frac{P_1}{P_1 + P_2} - \frac{w_1}{1 - w_1} x 100$$

and
E = \frac{P_1}{P_1 + P_2} \cdot \frac{1 - w_1}{w_2} \times 100 \quad 2

Now \( w_1 \) and \( w_2 \) are equal to the volume fraction inside and outside the barrier, respectively, and may be calculated. In the apparatuses used \( w_1 \) was 0.25 and \( w_2 \) was 0.75 so

\[ E = \frac{\frac{1}{3} P_1/P_T - 1}{3} \times 100 \quad 3 \]

The efficiency was defined in this way so that it would be 100% if all the polar material was inside the barrier and zero if the polar material concentration was the same on both sides of the barrier.

In a similar fashion an equation can be derived for the efficiency in terms of the nonpolar material so that it will be 100% if all of the nonpolar material is outside the barrier and zero if the nonpolar material concentration is the same on both sides of the barrier. Then the following results:

\[ E = \frac{N_o/N_T - w_2}{w_1} \times 100 \quad 4 \]

where

- \( E \) = percent efficiency,
- \( N_o \) = amount of nonpolar material outside the barrier,
- \( N_T \) = total amount of nonpolar material,
- \( w_1 \) = weight fraction inside the barrier, and
- \( w_2 \) = weight fraction outside the barrier.
Derivation of General Distribution Equations

A general description of the principles of separation and operation of the dielectric distribution apparatus was given in the experimental section. A more thorough examination of the above mentioned factors will be considered here.

The distribution was considered for the case of a cylindrical condenser. The central insulated electrode was connected to the alternating voltage source while the outside or peripheral electrode was connected to the ground. The strength increased from the peripheral to the center of the condenser, thus giving a nonuniform electric field. Two cases were considered to demonstrate the effect of dielectric distribution: First, where the polar material is the limiting constituent and accumulates at the center electrode; second, where the nonpolar material is the limiting constituent and accumulates at the periphery.

The force that a particle experiences is affected by the polarizability of the particle, the electric field, and the change in field with distance.

\[
\text{Force} = \alpha F \frac{dF}{dx} \tag{5}
\]

where

\[
\begin{align*}
\text{Force} &= \text{the force felt by the particle}, \\
F &= \text{field}, \\
\frac{dF}{dx} &= \text{the change in field with distance}, \text{ and} \\
\alpha &= \text{the polarizability of the particle}.
\end{align*}
\]
Previous authors, Pohl (16) and Loesche and Hultschig (13) have derived equations for the force on a particle and the velocity with which the particle moves when placed in a nonuniform electric field in cylindrical condensers. They assumed that the particles will tend to move toward the inner or outer electrode according to whether they are more or less polar than the suspending medium, respectively, until they reach equilibrium with the counter osmotic force which will arise from the concentration change. This is an oversimplification, because as the particles move, they contain a significant fraction of the total dielectric value of the system. Equilibrium will be reached when \( \frac{dF}{dx} = 0 \), for then, according to Equation 1, the force will be zero. The previous derivation is valid only for the initial velocity of motion.

The field for a cylindrical condenser is defined by the following equation.

\[
F = \frac{Q}{2\pi l \varepsilon r_c}
\]

where

- \( Q \) = charge on the condenser,
- \( l \) = length of the condenser,
- \( \varepsilon \) = dielectric constant,
- \( r_c \) = radius of the condenser, and

\( \frac{dF}{dr_c} = 0 \) when \( \varepsilon = k/r \).

If field \( F \) vs. radius \( r \) is plotted for a constant value of \( \varepsilon \), the curve will look like the one shown in Figure 5.
Figure 5. A plot of field vs. radius for a cylindrical condenser with $\varepsilon = k$.
Note from Figure 5:

\[ r_0 = 0, \]
\[ r_1 = \text{the radius of the center electrode plus insulation}, \]
\[ r_b = \text{radius of barrier}, \text{ and} \]
\[ r_2 = \text{radius of the glass cylinder}. \]

If particles are allowed to move in the field so that \( \varepsilon = k/r \), then the field vs. radius curve in Figure 5 changes to the curve shown in Figure 6.

If one assumes the dielectric constant of a mixture is a linear function of the fraction of the constituents (127, p. 2641), then

\[ \varepsilon = P \varepsilon_p + (1 - P) \varepsilon_n \]

where \( P = \text{the fraction of polar material}. \)

As stated before, if there are enough polar particles the particles will assume a distribution that makes the field constant across the condenser, this is when \( dF/dx = 0 \). If there are not enough polar particles to do this, then the equilibrium will be reached when \( dF/dx = 0 \) as far out from the center electrode as is possible. A similar situation will exist when the nonpolar particles are the limiting constituent. If this concentration of polar material is high enough (very high), the pure polar material will accumulate to a boundary that will be called \( r_y \). Between \( r_1 \) and \( r_y \) \( \varepsilon = \varepsilon_p \), the constant for pure polar material. From \( r_y \) to \( r_2 \) the material will be distributed
Figure 6. A plot of field vs. radius for a cylindrical condenser with $\frac{1}{\epsilon} = k/r$.
so that $dF/dr = 0$. A plot of the concentration of polar constituent vs. radius (Figure 7) illustrates this case.

Figure 8 shows the profile that the polar material "P" makes when it assumes a distribution in a nonuniform field. From Figure 8 the value for $r_x$ can be defined. It is the point at which this curve intersects the r-axis; it can vary from $r_1$ to $r_2$. If there is a small quantity of polar material in the system, $r_x$ is usually less than $r_2$ (curve J), but if the quantity of polar material becomes large, then $r_x = r_2$ (curve L). If the quantity of polar material is very large then a boundary is formed as is shown in Figure 7.

If one takes into account the variation of $\varepsilon$ with "r" then the field is equal to some factor "C" as shown below:

$$F = C = \frac{Q}{2\pi \varepsilon_0 r} = \frac{Q}{2\pi \varepsilon_0 \varepsilon_n r_x}$$

for the case when the polar constituent is limiting where $a = 1$ if $r_x < r_2$ and $a \geq 1$ if $r_x = r_2$. $\varepsilon_n$ is constant for the nonpolar constituent and the dielectric constant at any point is as follows:

$$\varepsilon = \frac{a \varepsilon_n r_x}{r}$$

In Figure 8 a profile of the concentration of polar particles vs. "r" is given. Since this exists in the cylindrical condenser, one can imagine a plot of concentration vs. "r" in three dimensions with "r" extending symmetrically along
Figure 7. A plot of the concentration of polar material vs. radius of condenser
Figure 8. A plot of polar material vs. radius of condenser
the x and y co-ordinates and the concentration plotted in the z direction. Such a plot would form a tent shaped surface such as should be obtained by rotating the plot in Figure 8 around the "r_0" axis for 360°. The integral under this surface will represent the total amount of polar material, P_T. If one calls the volume under this surface from P_y to P_x, P_I, then

\[ P_1 = \int_{P_x}^{P_y} \pi r^2 \, dp \]  

If \( \epsilon \) in Equation 7 is substituted in Equation 9

\[ P \epsilon_p + (1 - P) \epsilon_n = \frac{a \epsilon_n r_x}{r} \]  

Solving for \( r \) and squaring

\[ r^2 = \frac{a^2 \epsilon_n^2 r_x^2}{(P(\epsilon_p - \epsilon_n) + n)^2} \]  

This value for \( r^2 \) is substituted in Equation 10 and integrated from \( P_y \) to \( P_x \). \( P_y = 1 \) by definition. If one considers the case where \( r_x = r_2 \) and \( a \geq 1 \), then \( P_2 \) can be obtained from Equation 11.

\[ P_2(\epsilon_p - \epsilon_n) + \epsilon_n = a \epsilon_n \]  

\[ P_2 = \frac{(a - 1) \epsilon_n}{\epsilon_p - \epsilon_n} \]  

and
If \( P_2 > 0 \), i.e. \( a > 1 \), the volume \( \Pi P_2 r_2^2 \) underneath the broken line in Figure 7 must be added, and the volume \( \Pi P y r_1^2 \) must be subtracted because it is filled with the central electrode and is not available to hold polar material. Then

\[
P_T = P_1 + \Pi (r_2^2 P_2 - r_1^2 P_y)
\]

where \( P_T \) is the total amount of polar material in the system.

If the original concentration of polar material in the condenser before dielectric distribution occurs is \( P_1 \), then the total amount of polar material introduced will be

\[
P_T = P_1 \Pi (r_2^2 - r_1^2)
\]

then

\[
P_T = -\frac{\pi a^2 \epsilon_n^2 r_2^2}{\epsilon_p - \epsilon_n} \left( \frac{1}{\epsilon_p} - \frac{1}{a \epsilon_n} \right) - \frac{\Pi r_2^2 (a - 1)}{\epsilon_p - \epsilon_n} - \Pi r_1^2 = \frac{P_1 \Pi (r_2^2 - r_1^2)}{\epsilon_p - \epsilon_n}
\]

Now there are two equations that one can solve for "a" or "r_x". One can solve for \( r_x \) and then extract the square root for the value of \( r_x \). Solving for a

\[
a = \frac{\epsilon_p}{\epsilon_n} \left( \frac{\epsilon_p^2}{\epsilon_n^2} - \frac{\epsilon_p}{\epsilon_n} \left( \frac{P_1 (r_2^2 - r_1^2) + r_1^2}{\epsilon_n^2 - r_1^2} \right)^{\frac{1}{2}} \right)
\]
Similarly one can consider the case where \( r_x < r_2 \) and \( a = 1 \). An equation similar to Equation 18 is obtained which can be solved for \( r_x \) and \( r_y \).

\[
r_x = (P_1(r_2^2 - r_1^2) + r_1^2)^{\frac{1}{2}}(\frac{\epsilon_n}{\epsilon_p})^{\frac{1}{2}}
\]

\[
r_y = \frac{\epsilon_n r_x}{\epsilon_p} (P_1(r_2^2 - r_1^2) + r_1^2)^{\frac{1}{2}}\left(\frac{\epsilon_n}{\epsilon_p}\right)^{\frac{1}{2}}
\]

If \( r_y < r_1 \), that is, there is no pure polar material phase at the inner electrode, one has the case shown in Figure 8. By the same procedure as before

\[
P_1 = \int_{P_x}^{P_1} \Pi r^2 dP = \frac{\pi a \epsilon_n r_x}{\epsilon_p - \epsilon_n} (r_x - r_1)
\]

Then analogous to Equations 17 and 18

\[
P_T = P_1 \Pi (r_2^2 - r_1^2) = \frac{\pi a \epsilon_n r_x}{\epsilon_p - \epsilon_n} (r_x - r_1) + \\
\frac{\pi r_x^2 (a - 1) \epsilon_n}{\epsilon_p - \epsilon_n} - \frac{\pi r_1^2 \epsilon_n (a r_x - r_1)}{(\epsilon_p - \epsilon_n) r_1}
\]

Again if \( r_x = r_2 \), \( a \geq 1 \) and if \( r_x < r_2 \), \( a = 1 \). Equation 24 can be solved for either "a" or \( r_x \) and

\[
a = \frac{r_2^2 - r_1^2}{2(r_2^2 - r_1 r_2)} \left[ 1 + \frac{(\epsilon_p - \epsilon_n) P_1}{\epsilon_n} \right]
\]
From Equation 2
\[ E = \frac{P_I}{P_T} \left( \frac{r_2^2 - r_1^2}{r_2^2 - r_b^2} \right) - \frac{r_b - r_1}{r_2^2 - r_b^2} \]

where \( r_b \) is the radius of the barrier in the cylindrical condenser.

Consider the case where \( r_x < r_2 \) and \( r_x > r_b \), therefore \( a = 1 \). By the same sort of reasoning as before:

\[ P_I = \int_{P_b}^{P_1} \pi r^2 dr - (\pi r_1^2 P_1 + \pi r_b^2 P_b) \]

where

\[ P_I = \text{concentration of polar material at } r \]

\[ P_b = \text{concentration of polar material at the barrier} \]

and after integration and simplification

\[ P_I = \frac{\pi \epsilon_n}{\epsilon_p - \epsilon_n} (2r_x(r_b - r_1) + r_1^2 - r_b^2) \]

By dividing Equation 29 by Equation 17 a ratio of \( P_I/P_T \) is obtained.

\[ \frac{P_I}{P_T} = \frac{\epsilon_n (2r_x(r_b - r_1) + r_2^2 - r_b^2)}{(\epsilon_p - \epsilon_n) P_1(r_2^2 - r_1^2)} \]

By substituting \( r_x \) from Equation 26 in Equation 30
If one knows the value for the ratio \( \frac{\epsilon_n}{\epsilon_p - \epsilon_n} \), the efficiency, \( E \), can be calculated for any given initial polar concentration for a particular cylindrical condenser.

Now consider the case where \( r_x < r_2 \) and \( a \geq 1 \). Starting with Equation 28 one finds:

\[
P_I = \frac{\pi \epsilon_n}{\epsilon_p - \epsilon_n} \left( 2ar_2(r_b - r_1) + r_1^2 - r_b^2 \right)
\]

Equation 25 defines "a" when it is greater than 1. By substituting the value of \( P_I \) that is given in Equation 32 into Equation 27:

\[
E = \frac{\epsilon_n}{\epsilon_p - \epsilon_n} \frac{2ar_2(r_b - r_1) + r_1^2 - r_b^2}{P_I(r_2^2 - r_b^2)} - \frac{r_b^2 - r_1^2}{r_2^2 - r_b^2}
\]

Equation 33 can be used to calculate the part of the efficiency vs. concentration curve when "a" is greater than one; this would be where there is a higher concentration of polar material. Equation 27 can be used with the lower concentration of polar material.

The next thing that was considered was the case where the nonpolar material is limiting, i.e., a small quantity of nonpolar constituent is suspended in a medium of higher dielectric constant. As was mentioned earlier the nonpolar constituent should move to the periphery of the cylinder when this mixture
is exposed to the nonuniform field. If one assumes the dielectric constant of a mixture is a linear function of the fraction of the constituents:

$$\varepsilon = N\varepsilon_n + (1 - N)\varepsilon_p$$

when $N$ is the fraction of nonpolar material.

Since at equilibrium $\varepsilon$ must be a reciprocal function of $r$ from $r_y$ or $r_1$ to $r_2$

$$\varepsilon = \frac{a\varepsilon_n r_2}{r}$$

where $a = 1$ if $\varepsilon = \varepsilon_n$ at $r_2$ and $N = 1$ at $r_2$. If $N < 1$ at $r_2$, then $a > 1$ and goes to $\varepsilon_p/\varepsilon_n$ for its maximum. By equating Equations 34 and 35 the following results:

$$N(\varepsilon_n - \varepsilon_p) + \varepsilon_p = \frac{a\varepsilon_n r_2}{r}$$

Solving for $r$ and squaring:

$$r^2 = \frac{a^2\varepsilon_n^2 r_2^2}{(N(\varepsilon_n - \varepsilon_p) + \varepsilon_p)^2}$$

The volume representing the total nonpolar material, $N_T$, will be a bowl-shaped figure obtained by rotating the profile in Figure 9 about the $r_0$ axis. The total nonpolar material at equilibrium can be expressed as:

$$N_T = \int_{N_y}^{N^2} \pi(r_2^2 - r^2)\,dN$$
Figure 9. A plot of N vs. r at equilibrium
If the value for \( r^2 \) in Equation 37 is substituted in Equation 38 and if this equation is integrated and simplified the following value for \( N_T \) is arrived at:

\[
N_T = \frac{\pi r_2^2}{\epsilon_n - \epsilon_p} \left( - \frac{a^2 \epsilon_n^2}{\epsilon_p} + 2a \epsilon_n - \epsilon_p \right)
\]  

By definition

\[ N_T = N_1(r_2^2 - r_1^2) \]

where \( N_1 \) is the initial nonpolar material.

If Equations 39 and 40 are equated and solved for "a" the following equation results:

\[ a = \frac{\epsilon_p}{\epsilon_n} \pm \frac{\epsilon_p}{\epsilon_n} \left[ - \frac{N_1(\epsilon_n - \epsilon_p)(r_2^2 - r_1^2)}{\epsilon_p(r_2^2 - r_1^2)} \right]^{1/2} \]

The nonpolar material on the outside of the barrier, \( N_o \), can be calculated in the following manner:

\[ N_o = \int_{N_b}^{N_2} \pi (r_2^2 - r^2) dN + \int_{N_b}^{N_b} \pi (r_2^2 - r_2^2) dN \]

The first term in Equation 42 represents the area under the curve in Figure 9 from \( N_2 \) to \( N_b \) and the second term represents the area under that same curve from \( N_b \) to 0.

When Equation 42 is integrated and simplified

\[ N_o = \frac{\pi r_2^2}{\epsilon_n - \epsilon_p} \left[ 2a \epsilon_n(1 - \frac{r_b^2}{r_b r_2}) - \frac{\epsilon_p(r_2^2 - r_b^2)}{r_2^2} \right] \]

then
\[
N_0 / N_T = \frac{\frac{r_2^2}{\zeta_n - \zeta_p} \left[ 2a \zeta_n(1 - \frac{r_b^2}{r_b r_2}) - \frac{\zeta_p (r_2^2 - r_b^2)}{r_2^2} \right]}{N_1 (r_2^2 - r_1^2)}
\]

If the efficiency, \( E \), is defined as it is in Equation 4, then

\[
E = \frac{N_0 / N_T \left[ \frac{r_2^2 - r_1^2}{r_b^2 - r_1^2} \right] - \frac{r_2^2 - r_b^2}{r_b^2 - r_1^2}}{N_T (r_b^2 - r_1^2)}
\]

Substituting Equation 41 into Equation 44 and putting this into Equation 45 the following results:

\[
E = \frac{\zeta_p}{\zeta_n - \zeta_p} 2r_2 \left[ l - \frac{r_b^2}{r_b r_2} \right] \left[ 1 + \left( \frac{\xi_p - \xi_n}{\xi_p} \frac{r_2^2 - r_1^2}{r_2^2} \right) \right] \frac{1}{r_2^2 - r_b^2}
\]

\[
- \frac{r_2^2 - r_b^2}{N_T (r_b^2 - r_1^2)} - \frac{r_2^2 - r_b^2}{N_T (r_b^2 - r_1^2)}
\]

From the above general equations one can see how well the experimental data fits the theory.
RESULTS AND DISCUSSION

Batch Dielectric Distribution Apparatus

Soybean miscella

In many of the experiments a crude soybean miscella was used to study the phenomenon of dielectric distribution. Soybean oil is composed of phosphatides and neutral fat. When phosphatides are put into a nonpolar solvent such as petroleum ether, a phosphatide micelle structure is formed while the neutral fat forms a true solution. The phosphatide micelle is the more polar material in the soybean miscella and should be concentrated in the place of high field strength.

The batch apparatus, shown in Figure 1 ($r_1 = 1.55 \times 10^{-3} \text{m.}$, $r_b = 3.45 \times 10^{-3} \text{m.}$, $r_2 = 6.55 \times 10^{-3} \text{m.}$, and $l = 1.2 \times 10^{-1} \text{m.}$), was used in making a number of studies. The first was an efficiency vs. voltage study. This study was necessary to determine the voltage at which the maximum efficiency could be obtained. This was done by filling the apparatus with soybean miscella (5.4% soybean oil in Skellysolve B) and applying a definite voltage for $3\frac{1}{2} \text{hr}$. The two fractions (central and peripheral) were collected and analyzed for total phosphorous in the manner described in the experimental section. The efficiency of separation of the phosphatide from the neutral fat was determined through the use of Equation 3. This procedure was repeated and the voltage was increased by 500 v. each time.
The results are shown in Figure 10.

One can see that the efficiency was very low at low voltages and increased rapidly with an increase in voltage until a plateau was reached. The efficiency remains fairly constant with further increase in voltage until a certain point where there is a rapid decrease in efficiency with increase in voltage. The voltage at which there is a decrease in efficiency with increase in voltage has been termed slough-off voltage by Pohl and Schwar (20). They found the slough-off voltage to vary depending on the size of the center electrode, amount and type of insulation, the gap between electrodes, and the size of the particles. Pohl and Schwar (20) attributed slough-off to the capture of net charges by the particles at the central electrode. This causes the particles to repel each other.

Figure 11 shows an efficiency vs. time curve. The three curves were constructed by using three different constant voltages, 2,500 v., 4,000 v., and 5,500 v. A soybean miscella solution (5.4% soybean oil in Skellysolve B) was used in constructing all three curves. Once the apparatus was filled with miscella, the proper voltage was applied for 30 min. then central and peripheral fractions were collected and analyzed by the method already described and the efficiency was calculated. This procedure was repeated and the time increased by 30 min. at each repetition.

There seems to be an induction period (practically no
Figure 10. A plot of efficiency vs. voltage with time constant at 3½ hrs. 5.4% soybean oil in Skellysolve B
TIME 3\frac{1}{2} \text{ hrs.}

[Graph showing efficiency over voltage with time]
Figure 11. A plot of efficiency vs. time (batch cylindrical condenser) with voltages constant at 2,500 v., 4,000 v., and 5,500 v. 5.4% soybean oil in Skellysolve B
efficiency) at first and then the curves rise rapidly and reach a plateau value. The plateau should represent the point at which the change in field with distance becomes zero \((dF/dr = 0)\). This should be where equilibrium is reached and no further motion is needed. All three of the curves start to level off at about 4 hr. time. This does not agree with Pohl's theory \((18)\) which states the velocity of motion is a function of the voltage squared. The length of the induction period seems to be an inverse function of the voltage. There is an increase in the height of the plateau with increase in voltage. The height of the plateau varies between 40-50% efficiency depending upon the voltage used with this particular concentration. The increase in height of plateau with voltage indicates some counter force is opposing the establishment of equilibrium at \(dF/dr = 0\). It seems unlikely that osmotic pressure caused by the higher concentration of particles near the inner electrode can account for the counter force because the phosphatide micelles are too large to have much osmotic effect.

The induction period may represent a change in size, composition, or micellar structure of the particles. Pohl and Schwar \((20)\) reported that the size of the particle has a large effect on the rate that the particle moves to the region of strongest field strength. Clusters may be forming during this induction period and hence the cluster would move at a faster
rate than the smaller micellar particle. There could be also a change in shape of the particle which might affect its polarizability and this would be a factor in the rate of motion. Another explanation is that the phosphatides may exist in separate micelles and resegregate in the electric field; however, it is not clear why the field should induce this effect. There is also the possibility that, as the change in field with distance approaches zero (\(dF/dr \to 0\)) at all points, there may be a drag force on the equilibrium near the periphery where particles move slowly so that only a few particles can pass the barrier until redistribution near the outer electrode occurs.

Figure 12 shows efficiency vs. time curves at two concentrations. These experiments were carried out in the same manner as those described earlier. As can be seen from Figure 12 the more dilute solution gives the higher plateau efficiency. Also one will note that the more dilute solution showed more of an induction period than the more concentrated one. The increase in the plateau efficiency with dilution can be accounted for by the theory derived earlier. The longer induction period with decrease in concentration of polar particles could be accounted for by slower formation of the clusters of phosphatides suggested above.

The efficiency vs. concentration studies were conducted to really give the theory presented earlier a thorough test. The
Figure 12. A plot of efficiency vs. time at two concentrations; voltage constant at 4,000 v.
time-voltage studies were necessary in order to select the proper time and voltage to get the maximum efficiency at a given concentration. The time and voltage in this experiment were constant at 3\(\frac{1}{2}\) hr. and 4,000 v., respectively. Figure 13 shows the results of this study. A very low concentration of polar material was used in the first experiment and the concentration was increased for each succeeding experiment. The efficiency was calculated for each experiment and was plotted against the concentration used. The dots represent the experimental data and the curve represents the theoretical values. Values for the phosphatide dielectric constants were calculated from the efficiencies at different concentrations using Equation 30. The theoretical curve was gotten from Equations 31 and 33 using an average of the calculated phosphatide dielectric constant. The experimental results agree well with the theoretical curve calculated in this way, particularly in the region of higher concentration. The value for the dielectric constant for the phosphatide, \(\varepsilon_p = 9,321\) (assuming the phosphatide has a molecular weight of 788), appeared to be unusually high compared to molecules of this structure and size. The ideal thing to do here would have been to measure \(\varepsilon_p\) in the petroleum ether solvent. Unfortunately equipment was not available for measuring \(\varepsilon_p\) at lower frequencies such as 60 cps and this is the frequency that was used in these experiments. Measuring \(\varepsilon_p\) at higher frequencies would be of little value.
Figure 13. A plot of efficiency vs. concentration of phosphatide in soybean miscella at constant time 4 hr. and constant voltage of 4,000 v.
Homogenized milk

Homogenized milk (4.5% fat) was used in an effort to demonstrate that fat could be concentrated at the peripheral electrode of the condenser. The methods described in the experimental section were used to determine the extent of fractionation. The Mojonnier test for fat (11) indicated that there was a tendency for the fat to accumulate at the peripheral electrode, but the separation was barely detectable. The turbidity measurements also indicated that the separation was small. This lack of separation may be because the surface of the fat globules is coated with milk casein and other proteins which give the particles a net charge which causes them to repel each other.

Oil emulsion

Since the milk system failed to demonstrate that nonpolar material could be concentrated at the periphery of this condenser a less complex system was used. This system was an emulsion of mineral oil-tetrachloroethane in water. Again the batch type dielectric distribution apparatus (shown in Figure 1) was used to investigate dielectric distribution with this system. Preliminary voltage studies indicated that 5,000 v. was the most suitable voltage for the oil emulsion system. First the effect of time on the efficiency of separation was measured. A 1% emulsion of oil was used at 5,000 v. The efficiency was calculated using Equation 4. The results are
shown in Figure 14. The curve rises rapidly until a plateau is reached. This curve has the same shape as the corresponding one for phosphatide micelles in petroleum ether.

Next an efficiency vs. concentration study was made at constant voltage using the mineral oil emulsion. The procedures for this experiment were the same as those in the previous studies. Two different times for equilibration were used. The results are shown in Figure 15. The two curves have generally the same shape as the one for the polar material. One hundred percent efficiency was not reached at experimentally feasible concentrations. The longer time (17 hr.) gives a higher efficiency for a given concentration, so evidently \( \frac{17}{2} \) hr. was not long enough for equilibrium to be attained.

Calculations were made to test the validity of the proposed theory. The general shape of the curve is that expected from the theory; however, no positive value of the dielectric constants of the oil particles would give a curve which would fit the experimental points. The use of turbidity to measure the concentration changes in this system where the particle size may be nonuniform may introduce some error, but it is unlikely that it accounts entirely for the failure of the theory.

In the distribution of the phosphatide the theory fits only by assuming a suspiciously high dielectric constant for the phosphatides. In the distribution of the oil particles no reasonable value of the dielectric constants will fit the
Figure 14. A plot of efficiency vs. time. Concentration constant at 1% and voltage constant at 5,000 v.
Figure 15. A plot of efficiency vs. concentration at two different equilibration times at 5,000 v.
TIME CONSTANT 17 hrs.

TIME CONSTANT 4 1/2 hrs.
curve. In both cases the results gave much lower efficiencies than would be expected. Pohl and Schwar (20) have proposed that the dielectrophoretic force is counter balanced by the accumulation of net charge on the particle. This causes the particles to repel each other and at high voltages leads to slough-off. This might account for the lack of separation of milk fat globules and the increase in plateau efficiency with voltage demonstrated in Figure 11 as well as the deviations from theory noted here. However, the evidence for this hypothesis is not entirely convincing. In the experiment on spores with a simple parallel plate condenser that will be described further on, the spores were found to attract rather than repel each other and they formed long chains between the condenser plates. This tendency to form chains should also exist in the cylindrical condenser, and would oppose the movement of the particles to the center by dielectrophoresis. A mathematical expression of this tendency and its interaction with dielectrophoresis has not been derived so far, so it is impossible to say if it will explain the deviations in the theory considered.

Another source of error in the theory is the assumption made in Equations 7 and 34 that the dielectric constant is an additive function of the fraction of its constituents. There
may be considerable deviation from this idealized assumption. In making calculations the weight fraction was used, but approximately the same results would have been obtained with the volume fraction.

**Bacterial spore and vegetative cell mixture**

An aqueous mixture of spore and vegetative cells was used to further demonstrate the dielectric distribution effect in the batch apparatus. Using this aqueous suspension a voltage of 2,000 v. was applied for 30 min. and the fractions were observed under a phase microscope. The results of this observation revealed that the spores had been preferentially attracted to the center electrode and withdrawn from the condenser via the central vent and in a like manner vegetative cells were withdrawn preferentially via the peripheral vent.

**Continuous Flow Dielectric Distribution Apparatus**

All of the data shown thus far were gotten with the batch apparatus. At this point the design of the apparatus was changed so that it could run continuously. The diameter of condenser was decreased because, according to Pohl and Schwar (20) the time that it takes the mixture to come to equilibrium is related to the fourth power of the radius of the condenser. Also the condenser's length was increased so that a faster flow rate could be used. The dimensions were: length 78 cm., \( r_1 = 1.55 \times 10^{-3} \text{ m.} \), \( r_b = 2.0 \times 10^{-3} \text{ m.} \), and \( r_2 = 4.0 \times 10^{-3} \text{ m.} \).
A schematic diagram of this apparatus was shown in Figure 2. An attempt was made to prepare some fairly pure phosphatide in high yield starting with dilute, crude soybean miscella. The flow rate used in this experiment was 1.5 ml./min. The voltage was constant at 5,000 v. and the concentration 1.08% soybean oil in Skellysolve B. The crude soybean oil contained 0.17% phosphatide assuming a molecular weight of 788 for the phosphatide (the value for a typical lecithin molecule). The drain ratio in these experiments was approximately 3:1 (peripheral volume to central volume). The barrier shown in Figure 2 divides the condenser's volume in a 3:1 ratio and it is necessary to maintain the drainage of the two outlets in this same ratio.

Preliminary results, using this particular apparatus, indicated that approximately 95% of the phosphatide would be in the central fraction. About 25% of the total fat should be collected in the central fraction while about 75% of the total fat should be collected in the peripheral fraction with a 3:1 drain ratio (central: peripheral fraction).

From these results the percentage recovery and purity of phosphatide could be calculated at each stage as long as the phosphatide concentration was kept low at each stage. A scheme for purifying the phosphatide was worked out and it is shown in Figure 16. Side 1 and side 2 in the flow diagram correspond to the central and peripheral fractions, respectively. The side 1
Figure 16. A flow diagram for recycling fractions to obtain pure phosphatide from soybean miscella.
fraction was recycled and each succeeding central fraction was recycled until a theoretical percentage of 77.5% of the original fat was obtained. The resulting fractions were analyzed for phosphate and the percentage of phosphatide was calculated. The fraction that had an expected purity of phosphatide of 57.39% was actually found to be about 64% pure. The other fraction rich in phosphatide had an expected 19.21% of the total phosphatide and 0.365% of the total fat. The experimental percent purity was 7.61% phosphatide while the calculated purity of phosphatide was 8.21%. The deviation in the found and predicted purity is mostly due to the real drain ratio being a little greater than 3:1. If one were to combine to two fractions richest in phosphatide they should contain 96.7% of the total phosphatide. They were actually found to contain about 97% of the total phosphatide. A higher purity could be obtained by recycling further. The only limitation is that the concentration of phosphatide in Skellysolve B must be kept low. This experiment demonstrated that phosphatide can be purified in good yield from crude miscella.

Thin layer chromatography was used to determine if there was any fractionation of types of phosphatides in the continuous flow experiments. The results indicated that both the central and peripheral fractions contained the same types of phosphatides. The results also indicated that the central fraction contained a much higher concentration of phosphatides than the
Peripheral fraction in agreement with the phosphorous analysis.

Next an experiment was carried out to demonstrate that the level of phosphatide could be reduced to about 33% of the original level (a common commercial practice) using a concentration of miscella similar to that occurring in the normal refining process. Figure 17 shows a flow diagram for the concentrated miscella indicating the theoretical percentages of fat and phosphatide in each fraction. Preliminary results show that with a 5.4% fat solution about 67% of the total phosphatide would accumulate in the central fraction (side 1) which contained about 75% of the total fat (side 2). The theoretical percentages of total fat were gotten from the fact that drain ratio (peripheral fraction:central fraction) is 3:1. From the flow diagram (Figure 17) one can see that all of the final central fractions were combined and all of the final peripheral fractions were also combined. An analysis was done on each of the two groups of pooled fractions to determine the percentage of phosphatide and neutral fat in each. The theoretical percentage recovery of oil with the reduced concentration of phosphatide was 94.32% and compared quite favorably with the experimental recovery of 93.31%. The level of phosphatide was calculated to be 42.5% of the original level and actually it was reduced to about 39%. The pooled fractions richer in phosphatides could have been recycled further to get an even higher percent recovery. From these results one can see that
Figure 17. A flow diagram for recycling concentrated soybean miscella to separate the phosphatide from the oil.
by recycling the central and peripheral fractions virtually any degree of separation of phosphatide from oil desired could be achieved.

This technique provides a convenient way of separating phosphatides from nonpolar lipids which compares favorably with other techniques from the point of view of time, simplicity of apparatus, yield and gentleness.

Simple Parallel Plate Apparatus

Pure spore cells

Several experiments were done with this apparatus (Figure 4) to further demonstrate the usefulness of dielectric distribution. First the column was filled three-fourths full with a low dielectric organic solvent. Then a suspension of dried bacterial spores was put into the top of the column. The spores would move downward (due to the force of gravity) until they reached the electric field. If the electric field was strong enough the downward motion of all of the spores would be stopped. However, if the field was sufficiently weak some of the spores would be withheld by the field while others would pass through the field. If the spore suspension was introduced slowly one could observe that the first group of cells would migrate preferentially to the wall that was closest to the high voltage plate. Then each succeeding group would migrate to the edge of the previous group until a chain was
formed across the cylinder. Pohl (18) reported in 1958 that he had attempted unsuccessfully to demonstrate the dielectrophoretic effect with a parallel plate apparatus.

**Bacterial spore and vegetative cells mixture**

A mixture of dried bacterial spore and vegetative cells were suspended in a benzene-carbon tetrachloride solvent mixture (2.5:1). The column was filled three-fourths full with the benzene-carbon tetrachloride solvent system, then the spore and vegetative cell mixture was introduced and at the same time a voltage of 3,000 v. was applied. The spore cells were preferentially withheld in the column between the two plates while the other material including the vegetative cells passed through the electric field. The material that passed through the field was collected as fraction one and the other material was collected as fraction two. Both fractions one and two were refractionationed separately and another set of fractions A and B were collected. Fraction 2B was a relatively pure spore fraction. About 90% of the particles were spores. By combining the proper fractions and retractionating it was possible to separate spores from an unclean mixture of spores and vegetable cells.

**Parallel Plate Stack Apparatus**

Soybean miscella was used to demonstrate dielectric distribution with a stack of parallel plate condensers (Figure
3). The polar phosphatide micelles were attracted in and held between the plates while the fat solution passed along the edges of the plates and collected through the outlet. Fractions of 25 ml. (2.8 times the apparatus volume) were collected and analyzed for total quantity of phosphatide. A number of different concentrations of miscella were tried and the lower concentrations gave better results. A concentration of 0.54% soybean oil in Skellysolve B was used to make the study reported in Figure 18. The voltage used was 1,000 v. and the flow rate 0.28 ml./min. The level of phosphatide in the unfract­ionated miscella was designated 100%. As the miscella passed through the condenser, the phosphatide micelles were withheld, thus, the resulting fractions would have a lower level of phosphatide than the feed solution. As can be seen from Figure 18 the quantity of phosphatide in the fractions decreased rapidly to practically nothing at Fraction 4 and remained there until about Fraction 11. The reason for the presence of phosphatide in Fractions 2 and 3 is not clear. These fractions had as much residence time in the apparatus as any. The quantity of phosphatide in the fractions then increased again and finally reached the original concentration. This indicates that the plate stack condenser was filled to capacity with phosphatide. The factors determining the capacity of the plates is not clear. Certainly the plates were not physically full of phos-
Figure 18. A plot of percent original concentration vs. fraction number (fraction size 25 ml.)
phatide. Perhaps phosphatide chains formed at the edges of the plates and hindered the entrance of more particles. Theoretically one could increase the capacity of such a phosphatide removing apparatus by either increasing the number of plates or increasing the diameter of the plates or both. With an arrangement to periodically turn off the current and drain the phosphatide out the plates, the apparatus could operate on a semi-continuous basis.
SUMMARY

Dielectric distribution, a method to separate polar and nonpolar materials, was investigated. Dielectric distribution may be defined as the segregation of material in a nonuniform electric field according to its dielectric constant or polarity. The material moves under the influence of dipoles induced by the electric field. If the suspended material is more polar than the medium in which it is suspended, it will move toward the region of highest field intensity and if the suspended material is less polar than the medium it will move toward the region of lowest field intensity. Four types of apparatuses were used in this investigation: batch cylindrical condenser, continuous cylindrical condenser, parallel plate stack, and simple parallel plates.

A theory was proposed to predict the distribution of material in the cylindrical condenser at equilibrium. The condenser consisted of an insulated metal wire as the center electrode and metal foil around a glass cylinder as the peripheral electrode. The field strength increased from periphery to the center, thus giving a nonuniform field. Two cases were considered to demonstrate the effect of dielectric distribution: first where the polar material is the limiting constituent and accumulates at the center electrode, second, where the nonpolar material is the limiting constituent and accumulates.
at the periphery. The basic assumption in the theory is that as the material moves, the derivative of field with distance changes if the material contributes a significant fraction of the total dielectric value of the system. This change in field with distance becomes less as the material moves and eventually becomes zero at which point equilibrium is reached.

The dielectric distributions of phosphatide micelles in petroleum ether and of an oil emulsion in water were studied using the batch cylindrical apparatus. The inner and outer portions of the cylinder could be drained separately to analyze for the concentration of material in the two portions. The effect of time, voltage, and total particle concentration on the distribution was studied. The proposed theory predicted the general shape of the dielectric distribution, but evidently does not account for all the variables involved.

The continuous cylindrical condenser was used to concentrate soybean phosphatide micelles from crude soybean miscella. The miscella flowed through continuously and the phosphatide which collected in the center was drained separately from the periphery which was less rich in phosphatide. By recycling the inner and peripheral fractions any degree of separation of phosphatide from oil could be achieved.

The parallel plate stack was also used to demonstrate that phosphatides could be removed from the oil using the dielectric distribution technique. The miscella flowed past
the edge of the parallel plates and the phosphatide collected in between the condenser plates. This technique provides a convenient way of separating phosphatides from nonpolar lipids which compares favorably with other techniques from the standpoint of time, simplicity of apparatus, yield, and gentleness.

The simple parallel plate apparatus was used to separate spores from vegetative cells, thus further demonstrating the usefulness of dielectric distribution. Both spore and vegetative cells were retained between the condenser plates and by proper adjustment of the voltage, spores could be retained in preference to vegetative cells.
LITERATURE CITED


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