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TECHNICAL REPORT
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STUDIES ON FOAM FRACTIONATION AND APPLICATION TO LIPOID MATERIALS

by

Barry L. Karger

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UNITED STATES ARMY
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Food Division
FD-43

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FOREWORD

Better procedures for the separation and identification of lipoidal materials in foods and food-like systems would increase the efficiency of research in many areas of food research. Among the current problems in Food Division where progress would be assisted by improved procedures are studies to establish the mechanism of lipid-protein interactions related to texture and flavor stability in dehydrated foods. Foam fractionation appeared to have promise of useful application in this field. Unlike other separation techniques, its efficiency improves with dilution, making possible good separations of very small amounts of material. Because the separations depend upon small differences in surface activity, it appeared highly probable that good separations could be made not only of the major lipoidal classes, but also of molecular species within each class.

The work covered in this report, performed by Northeastern University under Contract No. DA-19-129-AMC-302(N) (May 1964 - Sept 1965) represents development of improved techniques for foam fraction and preliminarily investigation into their application to the separation of the major classes of lipoids. The investigator was Dr. Barry L. Karger, Associate Professor in the Department of Chemistry.

The U. S. Army Natick Laboratories Project Officer was Albert S. Henick and the Alternate Project Officer was Dr. William L. Porter, both of Food Chemistry Branch, Food Division.

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ABSTRACT

A simplified apparatus has been developed for the recovery and concentration of ionic species by foam fractionation. The process involves total reflux by thermal breakage of foam at the top of the column. Mechanical breakage can also be used when heat sensitive materials are used. The system has been applied to several dyes initially and then to the successful recovery of phospholipids and trace concentrations of salts of fatty acids.

Solvent sublation has also been investigated as a selective separation technique. Exploratory studies indicate that the extraction process is kinetically controlled and that time might therefore be an effective separation parameter.

FOAM FRACTIONATION

Introduction.

The technique of foam fractionation for the separation of substances has been known for a long time (1). Foam separation takes advantage of the surface activity of certain solutes at a gas liquid interface. When a solution is foamed, the active components collect at the surface or foam layer, which can then be removed and broken to give a rich liquid product. An excellent review of the whole field can be found in an article by Rubin and Gaden (2)

Initially only surface active substances which formed stable foams were separated by foam fractionation, and the applications were therefore somewhat limited. More recently it has been found that even non-surface active compounds can be separated by this technique. For example, metal ions have been separated by adding to the solution a foaming agent which can complex the metal ions and carry them into the foam (3). Karger and Rogers (4) have separated organic compounds which do not form stable foams by themselves. They showed that in the case of an ionic solute, the component could be concentrated most effectively by using an ionic foaming agent of opposite charge.

A major aspect of the work carried on under this contract has been the establishment of an effective system for the concentration and recovery of dilute concentrations of ionic solutes from aqueous solutions by foam fractionation. For the most part studies have been made with methyl orange (MO) and protonated 1-naphthylamine as test solutes because of the simplicity of analysis; information obtained with these compounds could then be applied to the concentration and recovery of lipoid materials.

Foam fractionation is a particularly good method for recovery

problems of ionic, non-surface active solutes due to the fact that the technique becomes more effective at low concentrations as seen from the Gibbs adsorption equation. In other words quantitative removal and accumulation of solutes in the foam should be easily achieved.

Lemlich and Lavi (5) have shown that the enrichment of surfactant increases considerably with the increase of external reflux. Total reflux, in which the foam is broken and returned as liquid to the top of the foam column, has been tested by Schnepf and Kevorkian (6) and also by Brunner and Lemlich (7); in both cases considerably higher enrichments were obtained. Rogers and Olver (8) have pointed out that the increased enrichment of a solute in the foam may be due not only to reflux but also to drainage of bulk liquid from the foam. In our experiments the conditions have been designed to increase both drainage and reflux and thus recovery.

When gas is passed through a solution of a surface active agent, a foam is produced which can then travel up the column. The foam consists of films of bulk liquid and surface active species adsorbed at the gas liquid interface (2). Bulk liquid drains countercurrent to the rising foam, thus thinning the film at the top of the foam. This drainage is a factor in the concentration of the surface active agent at the top.

The thinning of the film can eventually lead to the breakage of the bubbles at the top. When this breakage occurs, the surface active agent can then be adsorbed at the gas liquid interface of the rising layers of bubbles. Interchange can occur between the more surface active and the less surface active species to produce a concentration of the most surface active agent at the top of the foam column. This phenomenon is called internal reflux. It should be noted that drainage can also cause interchange of surface active species, and thus reflux, due to the fact that the bulk liquid does contain some of the surface active species.

In order to produce high recovery in foam fractionation, conditions

should be devised to increase drainage and reflux This increase can best be made by breaking the foam artificially at the top of the column either thermally or mechanically; however, thermal breakage is often more convenient Essentially the principle involved is to prevent foam from rising out of the column by breakage at the top during the reflux period. After this total reflux period the breaker must be removed so that foam can go out of the column and be collected. In thermal breakage this removal can be easily achieved by switching off the heater whereas in mechanical breakage removal may not be as easy. Also, in many types of mechanical breakage there is a possibility of trappage of foam or liquid in the breaker. However, when components are thermally unstable at the foam breakage temperature, the mechanical breaker is preferable.

Heating Tape Apparatus.

Initial experiments with total reflux involved the use of a heating tape for thermal breakage For this work the recovery of protonated 1-naphthylamine, which does not form a stable foam, was investigated. An oppositely charged surfactant, sodium lauryl sulfate, was used to produce the foam and carry the organic solute into the foam column.

A. Experimental

Figure 1 shows the apparatus used in this work. In each run 300 ml. of solution were pipetted into the column. Nitrogen gas was passed through a saturator (to prevent spurious evaporation effects) and entered the solution through a coarse porous glass frit. The flow was adjusted to 30 ml. per minute by means of a calibrated rotameter. A heating tape (Briskeat 1/2" x 4', 192 watts) controlled by variac was wound near the top of the column, and the temperature in the column was maintained at about 105 C. The foam rose to the top and broke in the heated section,

the liquid flowing down as reflux. A small condenser was fitted at the top of the column to prevent any vapors from escaping. Reflux time began at the moment foam reached the heated section. After the reflux period the heater was switched off, and the condenser was removed from the top of the column and replaced by the collector. The collector was also heated by a similar heating tape and fitted with a condenser to prevent any vapors from escaping. The gas flow was increased to 60-70 ml per minute, and 3 ml of the collapsed foam were collected in a graduate cylinder. The solutions used in the experiments were 2×10^{-3}M sodium lauryl sulfate and 10^{-4}M 1-naphthylamine adjusted to pH 2 with HCl. Sodium lauryl sulfate was recrystallized from a water acetone mixture, 1-naphthylamine from toluene, and both were dried in a vacuum desiccator.

The concentration of the surface active agent, sodium lauryl sulfate, (2×10^{-3}M) was at the point just prior to the critical micelle concentration as measured on the Du Nuoy tensiometer. This concentration results in the greatest foam stability. If higher concentrations are used, micelles would form which would adversely affect recovery and foam stability. If lower concentrations of surfactant are used, the foam column is less stable and less reproducible and it may become necessary to add surfactant during the run in order to maintain the foam column. It is worth noting that in these studies the concern is not removal of foaming agent but only using it to remove solute and produce an enlarged gas-liquid interface.

The concentration of 1-naphthylamine in the foamate was determined spectrophotometrically after the 3 ml of the collected liquid were diluted to the required volume with HCl at pH2. The spectrophotometer used was a Hitachi Perkin-Elmer Model 139. The wavelength for maximum absorbance was 277.5 mμ and the extinction coefficient 5.8×10^{3}. It

was determined that sodium lauryl sulfate did not interfere with the analysis at this wavelength.

The amount of sodium lauryl sulfate collected in the 3 ml was determined as sulfate by the wet oxidation method of Du Bose and Holland. (9) The surface tension determinations were made with a Fisher Model 19 Du Nuoy Tensiometer.

B. Results and Discussion

For the recovery measure of $\frac{\text{wt. collected}}{\text{wt. original}} \times 100$ the results with thermal breakage are shown in Figure 2. It can be immediately seen that after a reflux period of one hour, recovery is complete in the 3 ml of the collected liquid. This result shows the high recovery possibilities of ionic solutes at low concentrations by foam fractionation when drainage and reflux are emphasized. It can be seen that the 1-naphthylamine represents only 14 ppm. in the solution. In these experiments the collected product contains both the surfactant and the solute. If the goal is to obtain the pure solute, it may be done by a relatively easy extraction or the use of an ion exchanger to remove the surfactant as will be shown later.

At zero reflux time, about 40% of the solute is recovered. This 40% recovery represents initial adsorption, internal reflux, and drainage since the foam takes about 15 minutes to reach the top of the heated section of the column. Further, when recovery is complete, the system reaches a time invariant situation for the 1-naphthylamine. This situation is not necessarily a steady state, for nearly all the solute is at the top of the foam and thus no more solute is being adsorbed in the foam layer from the solution. In order to have a true steady state it would be necessary to have a balancing of addition and removal of solute in the bulk solution. Schnepf et al. (3) have broken the foam and recycled it continuously into the bulk solution until no change occurred in the system.

From a theoretical standpoint it is helpful to produce such a steady state, but if one wishes to recover components completely it does not seem necessary to recycle.

During the longer reflux periods a solid was observed at the top of the foam column because of the high concentration. This solid may be either the salt 1-naphthylamine hydrochloride or the surfactant-solute complex; both species are stable at the temperature of the heated section of the column (105°). It is possible to skim off the solid; however, a more efficient and reproducible method would be to use the method described in the experiments.

It was decided to test whether 3 ml were necessary to collect all the 1-naphthylamine. Thus runs were made with a reflux period of one hour in which 1 ml fractions were collected in succession up to 5 ml. The results indicated very poor reproducibility in the 1st., 2nd., and 3rd. ml due to the fact that the carry over of solid and the dissolved 1-naphthylamine could not be maintained at the same rate each time. However, it was found that in a total volume of 3 ml essentially all the material was collected.

Analysis of the sodium lauryl sulfate in the collected volume was also made in a few cases. During a one hour reflux period, roughly 10% recovery of the surfactant could be made in the 3 ml. There was not a significant difference between the cases in which 10^{-4}M 1-naphthylamine was present and those in which it was not present. In order to produce a higher recovery of the surfactant, it would be necessary to collect a much larger volume of foam because of the higher concentration of the surfactant. Thus the technique of thermal breakage can be an aid in recovery and concentration not only for solutes, but also for the foaming agents themselves.

In their production of a steady state, Schnepf et al. (3) have defined an enrichment ratio as: Concentration in collected foam/Concentration in the remaining bulk solution. With this measure the enrichment ratio goes from 68 at zero reflux to infinity at complete recovery in the experiments of this paper. It can be seen that when there is complete recovery, the enrichment ratio is not a good measure of the concentrating effect, as has been previously noted by Brunner and Lemlich (7) However, if a concentration ratio defined as Concentration of collected foam/ Concentration of the original solution is used for the 1-naphthylamine, some measure of the concentrating effect can be obtained With this concentration ratio, the results in this work go from 40 at zero reflux to 100 at complete recovery. If a volume smaller than 3 ml is collected, the concentration ratio would be higher.

These initial studies indicate that total reflux can increase recovery and concentration in the foam of ionic species which do not form stable foams by themselves. The use of the heating tape to provide thermal breakage of the foam for reflux and collection does however present several problems. In the first place it can be seen in Figure 2 that reproducibility was poor, especially at low reflux times. This lack of reproducibility may be due to internal reflux. Also after the reflux period when the heating tape was removed, a finite time was necessary for the heating zone to cool to room temperature. Thus the reflux period could not be closely reproduced, because rising foam was under partial reflux while the heating zone cooled.

A second problem resulted from the fact that the column walls were at a higher temperature than the middle of the column. Excessive drainage and evaporation occurred along these walls, so that in certain cases, a solid, which was difficult to remove, formed on the walls. This result

was especially true for the slightly surface active solutes which could not form stable foams by themselves. Thus recoveries of such species as methyl orange could not be made high, even though the removal of the dye from the bulk solution was complete.

The second part of this work involved the development of a new apparatus for total reflux with thermal breakage which did not present the problems described above.

Friedrichs Condenser Apparatus.

A. Experimental

The improved apparatus for more controlled recovery by foam fractionation is shown in Figure 3. The funnel foam column and 15 mm coarse glass frit were similar to those used in the previous study. It was decided, however, to reduce the column proper from 90 cm. down to 23 cm. The foam was thermally broken by passing steam through a Friedrichs condenser attached to the column proper. When the reflux period was concluded, the Friedrichs condenser was rapdily cooled with tap water and the gas flow rate was increased. The foam passed from the condenser into an adapter and thence into the foam breaker section. The foam breaker consisted of a spinning wire basket similar to that described by Rubin. (10) The liquid from the collapsed foam was collected by a glass funnel and allowed to fall into a 10 ml. graduated cylinder. Since solvent evaporation was minimal during total reflux, a cold condenser was not used during the reflux period.

In a given run, a 150 ml solution of solute was pipetted into the funnel foam column section. The required amount of surfactant was then dissolved in this solution. Nitrogen gas was passed through a water

saturator (to prevent spurious evaporation effects) and enter d the solution through the coarse porous glass frit. The nitrogen flow rate was established at 42 ml/min for the initial foam rise and reflux period and then was increased to 60 ml/min for collection purposes. The flow rate was measured upstream from the foam column by means of a soap bubble flow meter. Unless otherwise specified the volume of collapsed foam collected was 4 ml.

Methyl orange and the cationic surfactant, hexadecyltrimethylammonium bromide (Matheson, Coleman and Bell-Technical Grade) were purified by crystallization from an acetone-water solvent mixture. The concentration of collected fractions of methyl orange was determined colorimetrically with a Beckman DU2 spectrophotometer. The solution was first adjusted to pH 1 to prevent interference from the surfactant. The wavelength maximum at pH1 is 504 mμ with an extinction coefficient of 4.53×10^4. The analysis of hexadecyltrimethylammonium bromide (HDT) consisted of the two phase titration procedure of Cross (11) using sodium tetraphenyl boron as titrant.

B. Results and Discussion

1. Recovery of 10^{-5}M Methyl Orange

Methyl orange could not be successfully recovered with the heating tape method; however, using 10^{-5}M methyl orange (MO) and 7×10^{-4}M hexadecyltrimethylammonium bromide (HDT) at pH 10 Figure 4 shows that methyl orange can be recovered with the Friedrichs condenser apparatus and that the total reflux is a definite aid to enrichment and recovery. (Note that total time from the start of nitrogen flow is plotted in this figure.)

Approximately 80% of the MO is recovered within a one hour total reflux period and after this period there is a slow rise in enrichment

with time up to 92% recovery in a 3 hour total reflux period. It is not convenient to operate beyond 3 hours because the foam column cannot be maintained. The slow rise in recovery for long reflux times and the fact that 100% is not recovered is not caused by slow removal of MO from the solution. To prove this point, 100 ml of bulk solution were evaporated down to 5 ml after a 90 minute reflux period, and analysis revealed no detectable MO. The slow increase and lack of 100% recovery may be due rather to the slow removal of adsorbed MO from the glass surfaces.

A 10^{-4}M 1-naphthylamine solution with 10^{-3}M sodium lauryl sulfate at pH 2 was next tested. As with the heating tape method, essentially complete recovery occurred after a one hour reflux period. This result indicates that the incomplete recovery of methyl orange is due to the solute itself and that complete recoveries are possible with the apparatus of Figure 3. It should be again pointed out that MO cannot be recovered in high yield with the heating tape set-up.

The reproducibility was found to be considerably better with the Friedrichs condenser method than with the heating tape method. While reproducibility for the heating tape method was 20% at low reflux times, the Friedrichs condenser experiments showed a reproducibility of 5%. The errors probably arise from the inability to collect exactly 4 ml each time, the lack of reproducible bubble size from run to run, internal reflux while the foam is rising in the column, and the colorimetric analysis. Considering the possible sources of error, the 5% reproducibility figure is certainly quite acceptable.

The use of the Friedrich's condenser is a definite improvement over the heating tape apparatus for several reasons. In the first place during reflux, heat is applied internally over a wide portion of the foam column rather than at the outer walls. Thus it is possible to apply less

heat to break the foam and the problem of zones of excessive drainage and evaporation is then decreased. Solid adsorption on the glass walls is lessened. Surface-active solutes can therefore be recovered with this technique. Secondly, after the total reflux period, the reflux zone is rapidly cooled by passing cold tap water through the condenser. The reflux period is more closely defined and this result produces more reproducible data for this technique than for the heating tape method, especially for short reflux periods. Of course for long reflux periods both techniques are quite reproducible.

2. Concentrating Effect

The total reflux foam fractionation technique which has been described can be used for concentrating ionic solutes as well as recovering them. A solution of 10^{-5}M MO and $7x10^{-4}$M HDT at pH 10 was foamed with total reflux for 1 1/2 hours. The collapsed foam after reflux was collected in 1/2 ml samples up to 4 ml rather than one 4 ml sample and the results of this experiment are shown in Table I. In this table the enrichment factor, E, is equal to

$$E = \frac{\text{concentration of MO in collected foam}}{\text{concentration in original}}$$

It can be seen that a 200 fold enrichment of methyl orange has been effected in the first 1/2 ml. This enrichment factor should be compared with an E value of 10 for MO obtained an 1/2 ml samples in a previous publication (4). Thus the total reflux technique can be a very effective method for concentration as well as recovery.

Table I points out some other interesting points. There is a rapid decrease in solute concentration as the 4 ml are collected with 94% of the total material collected in the first ml. It is apparent that in the reflux zone methyl orange is highly concentrated and that the collection

process causes a dilution. Indeed it was necessary to collect 4 ml so that some of the collapsed foam could wash methyl orange from the collector funnel into the graduated cylinder. With suitable modification of the collection apparatus, it may be possible to effect the recovery in volumes smaller than 4 ml.

The data in Table I show that the concentrating effect is based to a large extent on the ratio of the volume of starting material to that collected. Thus a continuous feed of sample (without surfactant) into a foam column operating under total reflux could be used. The residual liquid could be drained off in a manner amply described by others. (12). The solute which is to be concentrated would remain at the top of the foam column and bulk liquid travel into the residual pot. If the solute became too concentrated at the top of the column, feed and total reflux may be temporarily stopped and the concentrated foam portion collected. With this procedure large volumes of samples could be easily concentrated 10^3 and perhaps 10^4 or higher. Thus continuous foam fractionation with total reflux could become an effective means of concentration for trace ionic species in aqueous solution.

3. Effect of Concentration of Solution on Rate of Recovery

Since removal becomes more efficient as concentration of solute decreases, it is expected that for any given reflux period before total removal, the diluter the initial concentration of solute the higher should be the recovery. A solution of $5x10^{-7}$M MO and $7x10^{-4}$M HDT at pH 10 was foamed for various reflux periods, and the results are compared with that of a $1x10^{-5}$M MO solution in Table II. It can be seen that the % R is larger at all reflux times for the lower concentrated material. It is further seen that essentially all of the $5x10^{-7}$M MO is recovered in 1 1/2 hours reflux. It is quite clear that adsorption on glass walls is

decreased as the initial solute concentration is decreased. It is further worth noting that $5x10^{-7}$M solution of MO represents an impurity concentration of only 0.17 ppm, a very small concentration.

4. Modification of Apparatus for More Rapid Removal and Recovery

In all the experiments reported so far considerable time was expended to produce high % recoveries. For example, it took one hour of total reflux to recover 80% of 10^{-5}M methyl orange. In an effort to decrease reflux time, the 15 mm. porous glass frit of the apparatus in Figure 3 was replaced by a 35 mm. porous medium glass frit. For a given gas volume, it was visually noted that more and smaller gas bubbles were produced for the medium frit. A 35 mm fine porous glass frit was also tested but later abandoned because of the excessive pressures necessary to force gas through the frit.

A comparison of % R for the two frits as a function of total reflux time is shown in Table III for a flow rate of 30 ml/mm.* In this table, $1x10^{-5}$M MO and $1x10^{-3}$M HDT at pH 10 were used as the test mixture. It is clearly seen that a much more rapid recovery is possible with the medium frit. The result is even more striking from the standpoint that the % R is greater for the medium frit than the coarse frit in 3/4 the collected volume. The improved speed of recovery for the medium frit is due to the increased rate of removal of methyl orange from the solution as a result of the greater gas-liquid surface area and the greater amount of bulk liquid entrained in the foam.

It should be noted that while the medium frit is advantageous in concentration and recovery problems, the narrow diameter coarse frit is

* To assist in foam breakage of the wet foam produced by this frit asbestoes insulation was placed around the Friedrich's condenser.

probably better suited for the separation of solutes. In separation it is desired to remove selectively one component relative to another from the bulk solution. A small number of large size bubbles would allow more selective adsorption because of decrease in gas-liquid interface and would carry up less entrapped bulk liquid than a large number of small sized bubbles.

5. Isolation of Solute from Surfactant in the Foamate

The product collected in the collapsed foam contains solute and excess surfactant and a further experiment must therefore be performed to recover pure solute. This separation is most conveniently carried out by an ion-exchange process in which the surfactant is retained on an ion-exchange resin.

The isolation of pure solute from surfactant was tested with a solution of 5×10^{-4}M methyl orange and 7×10^{-3}M HDT at pH 10. One gram of Amberlite IR 120 CP (Rohm and Haas) porosity resin in the hydrogen form was first converted to the sodium form with 6 M NaOH. The separation of solute from surfactant was then carried out in a batch process by mixing 3 ml of solution with the one gram of resin. After equilibrium the solution was decanted and the resin was washed, to give a final volume of 10 ml. Analysis of the final solution revealed all the methyl orange and no detectable HDT. Thus ion-exchange is a simple and effective method for isolation of solute from surfactant in the foamate.

6. Conclusion

From the results presented here it is quite clear that foam fractionation with total reflux should be a valuable aid in concentration and recovery of certain lipoid materials, especially those which are ionic. Some lipoid materials such as phospholipids are heat sensitive and thermal breakage of the foam is thus not convenient. Studies were under-

taken to design an apparatus for total reflux to be used with these thermally labile species and this design will now be presented.

Recovery of Phospholipids.

For the recovery of phospholipids by foam fractionation under total reflux it was decided to use a mechanical breaker system. Initial attempts at total reflux involved placing a series of spinning wire baskets and/or wire plates in the top of the column. Unfortunately, instead of breaking the foam, the wire baskets and plates whipped the foam into small bubbles with considerable liquid holdup, a result completely opposite to that desired. It thus seemed clear that for successful mechanical breakage, it is necessary to have an arrangement similar to the foam breaker section in Figure 3. In this set-up it is not the cutting action of the spinning wire basket which causes foam breakage but rather the foam being forced against the vertical sides of the basket by centrifugal force.

A. Experimental

The mechanical breaker as shown in Figure 5 was thus devised to be used for heat sensitive molecules. The foam travels out of the column up the 11 mm tubing into the spinning wire mesh basket where it is broken. The collapsed foam then drips back into the column at a controlled rate by means of a three way stopcock. The stopcock also serves to direct the liquid into a graduated cylinder when collection is desired. Since the liquid from the foam may be in the collector funnel for a substantial time, a plexiglass cover was placed atop the glass funnel to prevent evaporation by air convection from the spinning wire basket. Also to increase rate of recovery, the medium frit was used with this apparatus.

By suitable regulation of the three way stopcock it is possible to

maintain any reflux ratio desired. In the heating method the reflux must always be total. Thus the mechanical breakage apparatus may find use in separation of several solutes along with recovery of heat sensitive molecules.

The experimental design for mechanical breakage does not differ greatly from the designs of Lemlich and his co-workers. In one case Brunner and Lemlich (7) pump the collapsed foam back into the top of the foam column. In a second case Lemlich and Lavi (5) gravity feed a portion of the collapsed foam into the center of the column. In our apparatus, the volume of the foam in the 11 mm tubing is small relative to the foam volume in the column proper. Also the foam in the tubing is somewhat drier than in the column proper because of the drainage that will occur as the foam travels from the column proper into the 11 mm tubing. Thus return of collapsed liquid is certainly close to the top of the foam column in Figure 5 as is the case in thermal breakage and in the Brunner-Lemlich work.

The phospholipid test solution in most cases was 10^{-5}M vegetable lecithin. No prior purification step was taken before use. Analysis of the phospholipid resembled closely the procedure outlined by Bartlett (13) in which the phosphorous content in a sample is determined colorimetrically.

B. Results and Discussion

Preliminary studies with the mechanical breaker total reflux apparatus were first made with 10^{-5}M MO and 10^{-3}M HDT at pH 10. Recoveries comparable to those with the heating tape were obtained but the apparatus required a slightly larger collection volume.

The phospholipid selected for study was vegetable lecithin and a representative structure is shown in Figure 6. While the R group may

vary in general from C_{12} to C_{18}, both saturated and unsaturated, the usual R is derived from stearic acid (C_{18}). It can be seen that the molecule is zwitterionic at neutral pH. For successful removal and recovery one must either use a zwitterionic surfactant or alter the pH to try to neutralize one of the charges. The latter course was chosen in this work. Since hydrolysis occurs quite readily in basic media, it was decided to decrease pH to neutralize the phosphate anion and use as surfactant sodium lauryl sulfate (anionic).

The results of a pH study for vegetable lecithin at constant reflux time are shown in Table IV. It can be seen that there is a definite improvement in recovery as the acidity is increased. This result is expected for protonation of the phosphate group would eliminate the repulsion factor. Note that at pH of 1 a substantial portion of the lecithin is recovered in 10 ml. It was decided to use pH 1 for a study of the effect of total reflux rather than go to more acidic pH's because the phospholipid might decompose and the increased acidity might affect foam stability.

A test solution of 10^{-5}M vegetable lecithin and $2x10^{-3}$M sodium lauryl sulfate at pH 1 was next used to determine the usefulness of the total reflux apparatus in Figure 5. The effect of reflux time on recovery in 10 ml of collapsed foam is shown in Table V. It can be seen that there is improvement in recovery with reflux time and thus the apparatus described is effective for recovery of heat sensitive molecules. The increased time for a given recovery relative to methyl orange in Figure 4 is probably a reflection of the reflux apparatus and of the lecithin itself. The removal of lecithin from the bulk is probably more difficult.

Exploratory Studies on the Recovery of Trace Concentrations of Palmitic Acid

Since the total reflux technique has been shown to be capable of recovering small quantities of methyl orange, it was decided to test the technique on the recovery of trace concentrations of fatty acid which contained a C_{14} fatty acid tracer. Other workers have removed labelled metal ions by foam fractionation at the trace concentration range. For example Ito and Shinoda (14) removed Sr^{90} and ca^{45} with sodium dodecyl sulfate. However, to our knowledge, no work has been reported on the removal and recovery of trace concentration of organic compounds.

Initial experiments in the recovery of palmitic acid were performed with the apparatus in Figure 3. Solutions of $8x10^{-8}$M and $8x10^{-9}$M palmitic acid with $7x10^{-4}$M HDT at pH 10 were made up. The solutions were refluxed for one hour at a flow rate of 30 ml/min after which time 4 ml of collapsed foam were collected. The results of these experiments are shown in Table VI A. Analysis involves combustion of the sample with the Van Slyke reagent, trappage of $C^{14}O_2$ in an ion chamber, and readout on an electrometer.

Examination of the table reveals that for a trace concentration of 20 ppb palmitic acid, 53% of the acid can be recovered with 1 hour reflux. At the 2 ppb level we still have substantial recovery and concentration; however because of the extremely low concentration the analysis of the collected foamate for the 2 ppb solution is difficult to get exact. Therefore the 38% recovery should be understood to give an indication of recovery and not be an exact value.

Finally it was decided to run a trace concentration of palmitic acid with the apparatus in Figure 5. The reason for using this apparatus was two-fold: (1) increase the rate of removal and recovery of the solute

by means of the medium porous frit and (2) prevent any thermal decomposition of the solute-surfactant complex. For this experiment a 0.2 ppm sample of tagged palmitic acid was used and the results are shown in Table VI B. It can be seen that within the experimental error of the analytical procedure essentially all the palmitic acid is recovered with 75 min reflux time. Thus foam fractionation with total reflux can recover and concentrate species at the trace concentration level.

SOLVENT SUBLATION

Solvent sublation, as initially introduced by Sebba (15) was devised as an auxilliary technique to ion flotation, for use when persistent foams occurred in the flotation process. In solvent sublation, gas bubbles generated in solution are used to extract material from an aqueous phase to an immiscible non-aqueous phase. The aqueous phase initially contains the mixture of solutes (in most cases ionic) to be separated and a surface active agent. The surface active agent can be adsorbed at the gas-liquid interface, or if the surfactant is of opposite charge from the solute, a surfactant-solute complex may be formed and adsorbed at the interface. In this latter case the solute can be extracted into the non-aqueous phase.

A. Experimental

The complete apparatus is illustrated in Figure 7 . Nitrogen gas travels through the presaturator into a coiled 1/4" copper tubing column packed loosely with glass wool. The purpose of the glass wool is to trap any droplets of distilled water carried along by the stream of N_2. The gas next flows through a 1/4" nupro needle valve and the 63 BUL Moore flow controller to maintain constant gas flow. Finally the gas travels through a 10 ml soap bubble flow meter and through the 35 mm frit into the column. The open U-tube manometer upstream from the flow controller serves as the constant upstream pressure reference by the 63 BUL, while the second manometer gives the pressure of the gas entering the column. All connections are flexible tygon except where otherwise indicated.

The general procedure under use involves pipetting 300 ml of aqueous solution into a 45 mm diameter column with sintered glass frit at the

bottom. Twenty-five ml. of pure 2-octanol are then slowly added to avoid any undue agitation of the water-octanol interface. Presaturated nitrogen gas is allowed to pass through the column at the desired flow-rate and for the specified length of time. At the end of the run, portions of both the octanol and aqueous layers are collected and analysed by a Beckman DU2 spectrophotometer in the visible region. The solutes being used in this exploratory work are methyl orange (MO) and rhodamine B (RB), and the surfactant is hexadecyltrimethylammonium bromide (HDT), for the simplicity of analysis.

After various non-aqueous solvents were tested, 2-octanol was selected. Solvents of very low polarity, such as benzene and cyclohexane, produced emulsions, while low molecular weight alcohols, such as butanol, were significantly soluble in water and evaporated too rapidly. The 2-octanol seemed to have the required polarity and immiscibility with water to be the most effective solvent tested.

B. Results and Discussion

The results are presented in terms of an extraction coefficient, $E = \frac{\text{conc. (octanol)}}{\text{Conc. (water)}}$, in lieu of the more familiar distribution coefficient, K. This modification is based on the fact that the separation method proposed depends on kinetic factors and as such E is time dependent, while K, which is obtained at partition equilibrium, is not. Thus, a clear distinction must be made between the two coefficients.

1. Separation as a Function of Time

In the first series of experiments the effect of the surfactant on the extraction of the single dyes was studied. For a solution of 10^{-5}M MO at pH 10.5 and no HDT, MO could not be detected in the octanol phase, even after a three hour bubbling period. However, when a solution of 10^{-5}M MO and 10^{-5}M HDT at pH 10.5 was tested, MO could be readily extracted into octanol as shown in a plot of E_{MO} vs. bubbling time

(Figure 8A). Spectrophotometric experiments revealed a peak shift for MO in the aqueous phase when HDT was added (466mμ → 425mμ), indicative of strong HDT-MO interaction. A surfactant-dye complex thus appears to form in the aqueous phase, and this complex is believed to be extracted into the octanol.

It can be seen in Figure 8A, that there is an initial rapid increase in the extraction coefficient followed by a more gradual increase; however, even after a three hour period MO is still being removed from the aqueous phase. It is thus clear that the extraction process is kinetically controlled. To a great extent the flow of mass is unidirectional (from the aqueous phase to the octanol phase), and this factor is certainly responsible in part for the kinetically controlled process.

The effect of surfactant on the extraction of RB was next studied. Table VII presents the results of this study for the solution 10^{-5}M RB and 10^{-5}M HDT at pH 10.5. Nitrogen was allowed to flow through the system for 30 min. and 180 min.; for both extraction times it can be seen that the amount of RB extracted decreases with the addition of surfactant, a trend opposite to that observed for MO. Examination of the visible spectrum of an aqueous solution of RB at pH 10.5 reveals no peak shift on addition of HDT, a result which suggests that surfactant-dye interaction is weak.

Figure 9 shows the structure of MO and a resonance contributor of RB in basic media. It can be seen that several major factors cause RB to interact less strongly than MO with HDT. In the first place in alkaline solution RB is zwitterionic whereas MO is anionic. Thus the RB-HDT interaction will have a charge repulsion factor superimposed on the charge attraction factor. Secondly the functional group on RB is less accessible for interaction than that on MO because of the bulky groups surrounding the carboxylate anion.

Since the rate of extraction of RB is depressed on addition of HDT and the dye-surfactant interaction is very weak, the mechanism of the kinetically controlled extraction of the dye must differ from that of MO. RB is somewhat surface active, and it can thus be extracted into octanol by itself. However, when HDT is present, a competition for the adsorption sites at the gas-liquid interfaces may occur between the surfactant and dye, causing the decrease in the rate of extraction of RB. Figure 8B presents a plot of the extraction ratio for 10^{-5}M RB and 10^{-5}M HDT at pH 10.5. It can be seen in this figure that initially RB extracts at a much slower rate than MO. This result would be expected from the above arguments. In Figure 8B the rate of extraction appears to be increasing for RB with time. In terms of the competition mechanism, this result would indicate that as HDT is depleted from the aqueous phase, RB should be able to compete more effectively for adsorption sites and thus extract more rapidly.

The separation of the mixture-10^{-5}M RB and 10^{-5}M MO - with 10^{-5}M HDT at pH 10.5 was next examined. The results of this study are shown in Table VIII It can be seen in this table that the separation factor, $\phi = E_{MO}/E_{RB}$, is time dependent, being quite large initially and decreasing with time. The results of this kinetic separation are expected from the single solute studies. It is further interesting to note in Table VIII and Figure 8 that the E values at any given time for the solutes alone and in the mixture are found to be roughly similar. Since no competition for extraction between MO and RB appears to occur with 1/2 equivalent of surfactant, different extraction mechanisms must operate for the two dyes.

Many of the extraction procedures currently available are based on solute differences in partition behavior at equilibrium. In these

procedures, short separation times usually produce lower separation factors than longer times, because equilibrium is not attained at the short times However, the separation of MO from RB by solvent sublation is considerably better at shorter times as seen in Table VIII. Herein may lie the potential of solvent sublation. Because of the kinetic processes occurring in sublation, time may be used as an effective parameter in the development of selective separations.

2. Comparison of coarse and medium frits

The data in Table IX show some of the results obtained with a coarse and medium pyrex 35 mm frit. Attempts were made to use a 35 mm fine frit; however this was unsuccessful because of the high pressure necessary to force the gas through the frit. In comparing the E values of methyl orange for the coarse and medium frit it can be seen that the medium frit is able to extract almost 3 times as much methyl orange into the octanol layer. Since the flow rate and the time of gas passage is the same in both cases, the volume of gas is constant. Therefore the medium frit is producing more surface area for the given volume of gas and thus is extracting more material. This result is entirely reasonable for the medium frit would be expected to produce smaller bubbles.

In a comparison of the separation factors (ϕ) for the two frits with MO and RB it can be seen that while the medium produces a higher ϕ, the increase is not great. This result arises from the fact that while the amount of MO extracted into the octanol layer has increased with the medium frit, the amount of RB has also increased to approximately the same extent, producing roughly the same separation.

From these results it would appear that gas bubble size is important in terms of the quantity of material extracted but not in terms of separation. This conclusion is being checked by other methods.

3. Comparison of Solvent Sublation and Liquid-Liquid Extraction

In an effort to determine the differences between the bubbling technique and the mechanical shaking technique used in liquid-liquid extraction, it was decided to run the exact same experiments on each method. Presumably the mechanical shaking technique should produce equilibrium between the two phases, and thus it is possible to ascertain how close to equilibrium the solvent sublation technique comes. The results are reported in Table X.

In the extraction of methyl orange there is very little difference in the E values for mechanical shaking for one hour or bubbling gas for one hour. Note further that even the % of solute extracted is the same in both cases. Thus we are close to equilibrium for solvent sublation with methyl orange in this case. It is worth pointing out that mechanical shaking produces an emulsion in both phases which requires 12 hours standing before it breaks up. This emulsion does not form in the solvent sublation technique.

In the extraction of RB with equimolar HDT, it can be seen that there is substantial difference in the E values for the two techniques. In this particular case we are considerably distant from equilibrium in the solvent sublation technique. Relative to methyl orange the rhodamine B is zwitterionic and this may explain in part the lack of attainment of equilibrium for RB.

Finally the third section of Table X compares bubbling gas with mechanical shaking in regard to separation. For solvent sublation the ϕ is 5.4 while for mechanical shaking the ϕ is 0.26. The solvent sublation technique produces a better separation because of the lack of equilibrium for RB, and also the separation is in reverse order to the liquid-liquid extraction method.

Conclusion

In many of the separation techniques currently available on the analytical scale, recovery of separated fractions decreases as the quantity of solute decreases. Thus in liquid-liquid extraction the ability to extract solutes from an aqueous phase and recover them in a non-aqueous phase is found to decrease as solute concentration is decreased. So also in chromatography, recovery of sample often decreases as sample charge decreases. However, in foam fractionation removal and recovery seems to improve as concentration decreases. Thus the foam technique would appear particularly applicable for recovery of solutes at the trace level of concentration if total reflux is applied.

The technique of batch foam fractionation with total reflux has been developed and applied to the concentration and recovery of low concentrations of lipoid materials in aqueous solution. The method appears to be particularly effective because of its simplicity and high recovery aspects. For this reason it would seem worthwhile investigating further the application of foam fractionation to lipoid materials. One area which time did not permit examination is the application of the technique to fatty acid salt separations. Fatty acid salts are good foamers and thus foam fractionation should find some use in this area.

Solvent sublation has also been investigated in this work. Exploratory studies indicate that the technique holds promise of becoming quite useful in terms of selective separation. The fact that time is a very important factor in the separation process is especially noteworthy. It should further be noted that information gathered on this technique can be applied to foam fractionation, especially in the removal of components from the bulk solution. Certainly solvent sublation offers a promising area for research.

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TABLE I

Enrichment and Recovery of 10^{-5}M Methyl Orange in 1/2 ml. Samples

Sample No.	E	% R
1	210	70
2	31	10
3	5.0	1.7
4	3.6	1.2
5	2.1	0.69
6	1.8	0.60
7	1.5	0.50
8	0.89	0.29

TABLE II

The Effect of Concentration of Methyl Orange on Recovery

Reflux Time	Concentration	% R
0 min	$5x10^{-7}$M	30
	$1x10^{-5}$M	26
30 min	$5x10^{-7}$M	74
	$1x10^{-5}$M	65
60 min	$5x10^{-7}$M	92
	$1x10^{-5}$M	76
90 min	$5x10^{-7}$M	98
	$1x10^{-5}$M	81

TABLE III

Comparison of Medium and Coarse Frits

Frit	Reflux Time	% R
Medium, 35 mm	0	42% (in 3 ml)
Coarse, 15 mm	0	28% (in 4 ml)
Medium, 35 mm	5 min	54% (in 3 ml)
Coarse, 15 mm	5 min	38% (in 4 ml)
Medium, 35 mm	10 min	70% (in 3 ml)
Coarse, 15 mm	10 min	47% (in 4 ml)

TABLE IV

Recovery of Lecithin as a Function of pH

$2x10^{-3}$M sodium lauryl sulfate, 10^{-5}M Lecithin

pH	Reflux Time	% R	Collect ml.
3	120 min	19%	5
2	120 min	30%	5
1	120 min	{51% 22%}	5 5

TABLE V

Recovery of Lecithin as a Function of Total Reflux Time

$2x10^{-3}$M sodium lauryl sulfate, 10^{-5}M Lecithin, pH 1, collect 10 ml.

Reflux Time	% R
0	23%
15 min	31%
30 min	36%
90 min	64%
120 min	73%

TABLE VI

Recovery and Concentration of Trace Palmitic Acid

A. Using apparatus in Figure 3 (coarse frit) collect 4 ml

Concentration	reflux time	% R	E
$8x10^{-8}M$	60 min	53%	20
$8x10^{-9}M$	60 min	38%	14

B. Apparatus in Figure 3 (medium frit), collect 5 ml

$8x10^{-7}M$	75 min	>95%	>28

TABLE VII

The Effect of HDT on the Extraction of RB

Surfactant	Time	$\%RB_{oct}$	E
Absent	30 min.	22.1	3.41
Present	30 min.	6.7	0.90
Absent	180 min.	71.2	29.7
Present	180 min.	44.2	9.5

TABLE VIII

Solvent Sublation of 10^{-5}M MO and 10^{-5} RB with 10^{-5}M HDT

Gas Flow Time	E_{MO}	E_{RB}	$\phi = \frac{E_{MO}}{E_{RB}}$
5 min.	15	ca..03	506
15 min.	26	0.32	56
30 min.	37	1.3	34
60 min.	46	2.7	17
180 min.	56	8.6	6.5

TABLE IX

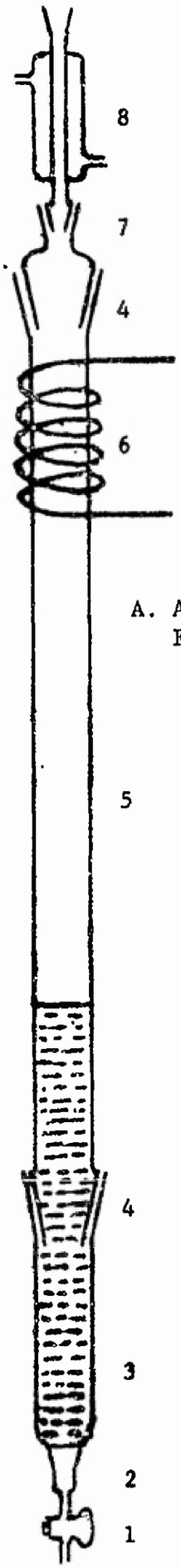
Comparison of Coarse and Medium Frits for Solvent Sublation

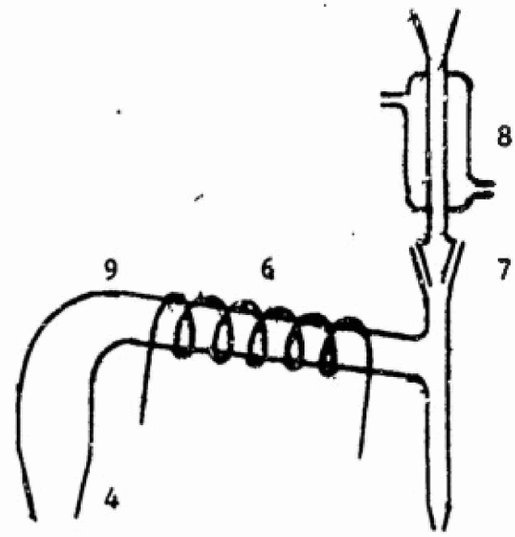
Sample	Fc (ml/min)	Time (min)	Frit	MO		% RB		E	Ø
				Octanol	H_2O	Octanol	H_2O		
10^{-5} M MO 10^{-5} M HDT pH 10	5.0	60	Coarse	37.1	62.6			0.593	
10^{-5} M MO 10^{-5} M HDT pH 10	5.0	60	Medium	62.0	37.3			1.67	
10^{-5} M MO 10^{-5} M RB pH 10 10^{-5} M HDT	5.1	60	Coarse	35.9	63.6	11.5	88.5		4.4
10^{-5} M MO 10^{-5} M RB pH 10 10^{-5} M HDT	4.9	60	Medium	60.1	44.4	21.8	78.2		5.4

TABLE X

Comparison of Solvent Sublation and Liquid - Liquid Extraction

Sample	Technique	Fc	Time	% MO		% RB		E	Ø
				Octanol	H_2O	Octanol	H_2O		
10^{-5} M MO, 10^{-5} M HDT, pH 10	S.S.	5.0	60 min	62.0	37.3			1.67	
10^{-5} M MO, 10^{-5} M HDT, pH 10	L.L.		60 min	60.4	37.8			1.60	
10^{-5} M RB, 10^{-5} M HDT, pH 10	S.S.	5.0	60 min			48.7	51.3	0.95	
10^{-5} M RB, 10^{-5} M HDT, pH 10	L.L.		60 min			84.2	15.8	5.33	
10^{-5} M RB, 10^{-5} M MO, 10^{-5} M HDT, pH 10	S.S.	4.9	60.1 min	60.1	44.4	21.8	78.2		5.4
10^{-5} M RB, 10^{-5} M MO, 10^{-5} M HDT, pH 10	L.L.	4.9	60 min	71.0	34.5	87.8	12.2		0.26





A. Apparatus for Foam Fractionation

B. Apparatus for Foam Collection

1. Two-way stopcock
2. Porous glass frit, coarse, 15 mm., Kimaz, 28280.
3. Funnel foam column section, 36 mm, x 20 mm.
4. 40/50 standard tapered joints
5. Foam column proper, 36 mm. x 90 mm.
6. Heating tape, Briskeat ½" x 4', 192 watts
7. 19/22 standard tapered joints
8. Reflux condenser, Metroware, ME-517-B3
9. Recovery tube, 36 mm. x 27 mm., 75° bend

Figure 1. Apparatus for Foam Fractionation and Collection.

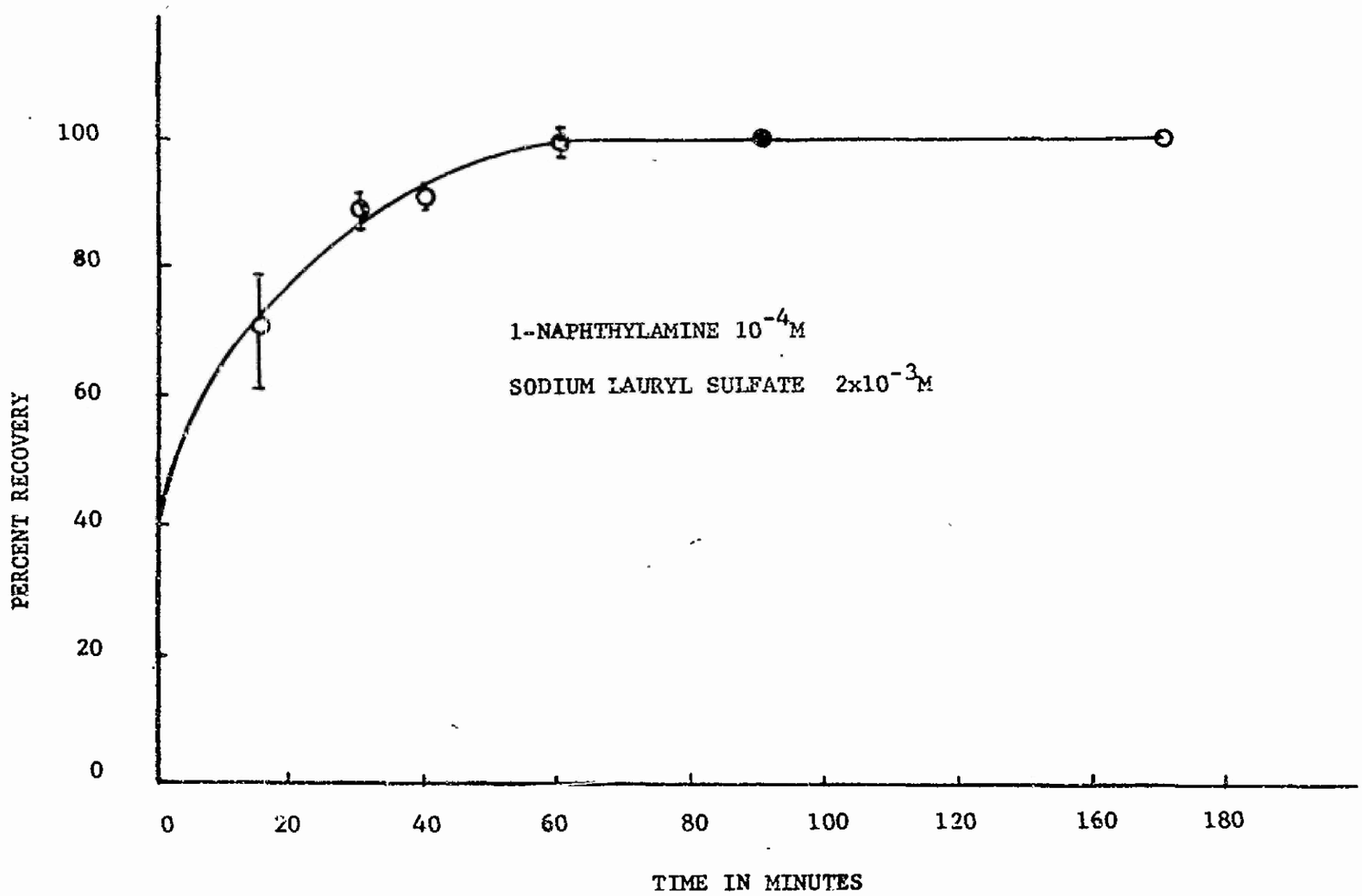
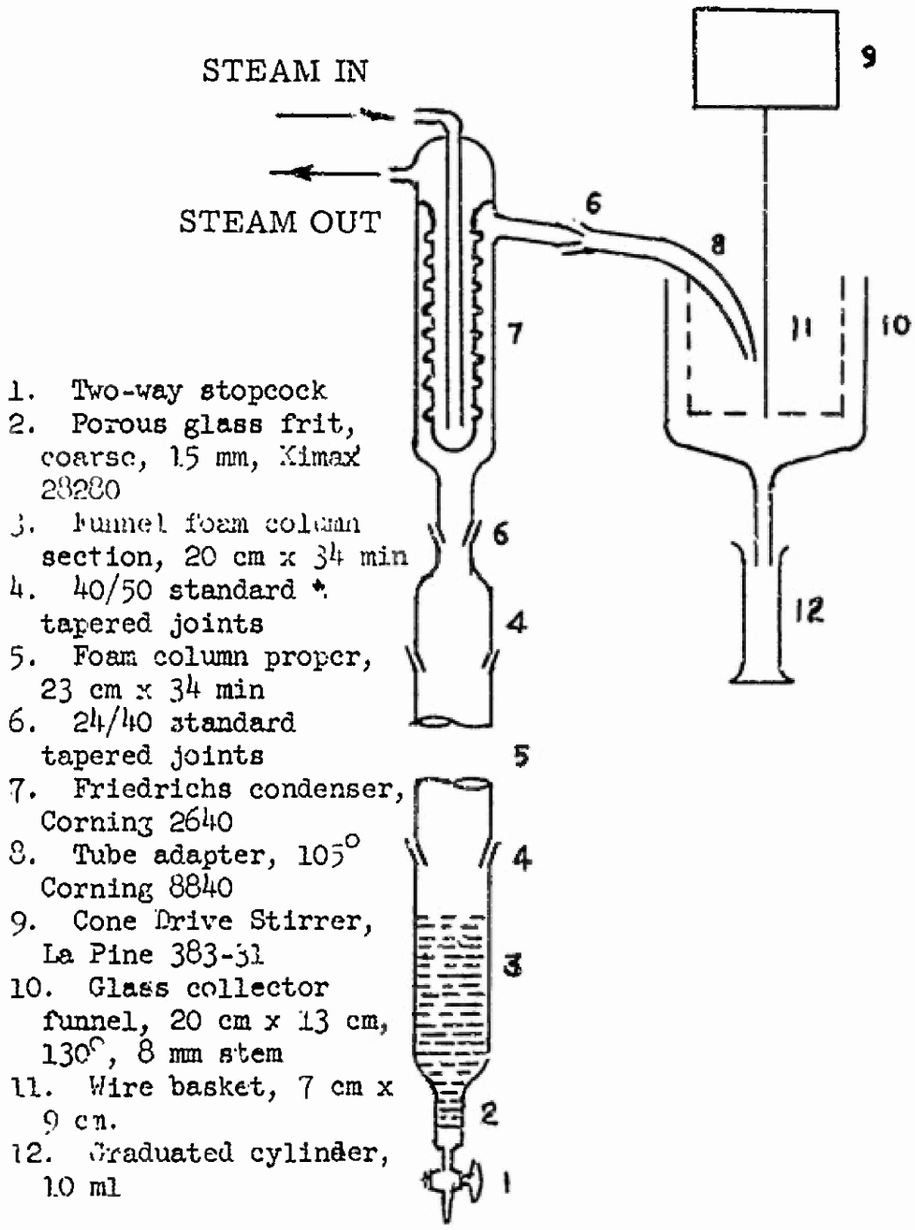


Figure 2. Recovery of 1-naphthylamine as a function of reflux time.



1. Two-way stopcock
2. Porous glass frit, coarse, 15 mm, Ximax 28280
3. Funnel foam column section, 20 cm x 34 min
4. 40/50 standard tapered joints
5. Foam column proper, 23 cm x 34 min
6. 24/40 standard tapered joints
7. Friedrichs condenser, Corning 2640
8. Tube adapter, 105° Corning 8840
9. Cone Drive Stirrer, La Pine 383-31
10. Glass collector funnel, 20 cm x 13 cm, 130°, 8 mm stem
11. Wire basket, 7 cm x 9 cm.
12. Graduated cylinder, 10 ml

Figure 3. Apparatus for Foam Fractionation with Total Reflux.

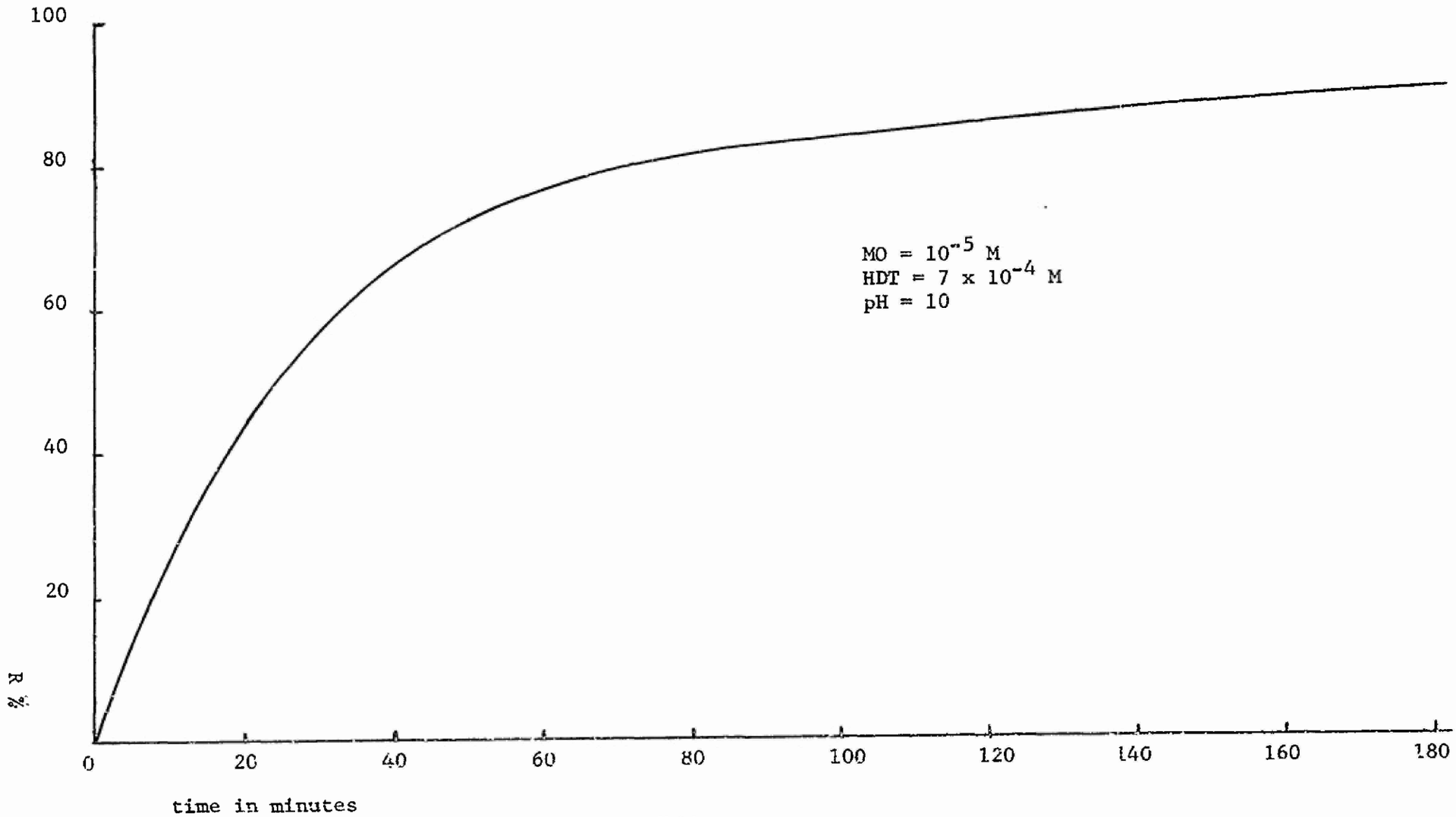
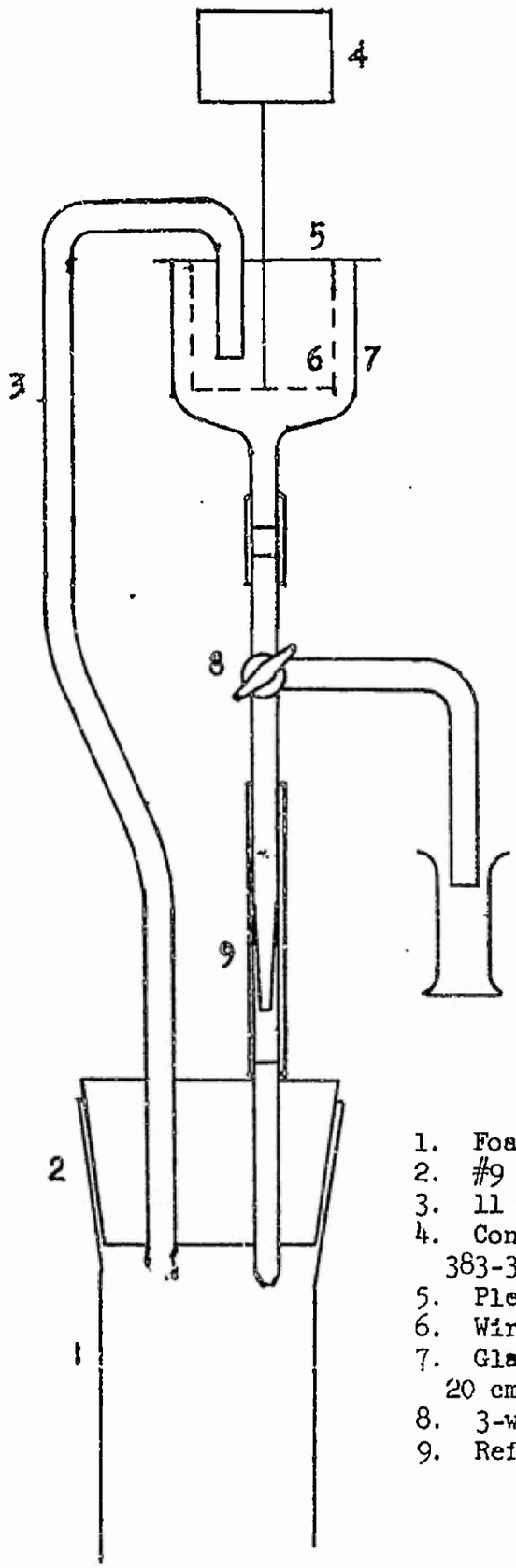


Figure 4 Recovery of methyl orange using Friedrichs condenser apparatus as a function of time of nitrogen flow through system.



1. Foam column
2. #9 Two-hole rubber stopper
3. 11 mm Pyrex glass tubing
4. Cone drive stirrer, La Pine 383-31
5. Plexiglass cover
6. Wire basket, 7 cm x 9 cm
7. Glass collector funnel, 20 cm x 13 cm, 130°, 2 mm stem
8. 3-way stopcock, 2 mm
9. Reflux dripper

Figure 5. Total reflux foam fractionation with mechanical breakage.

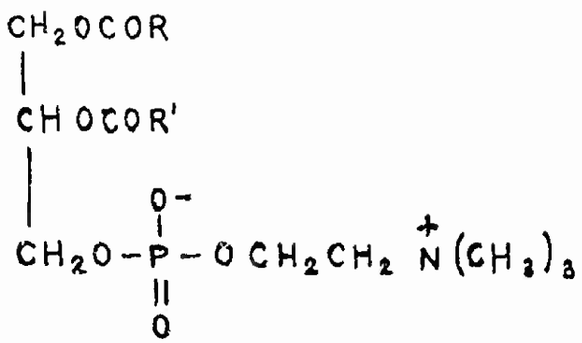
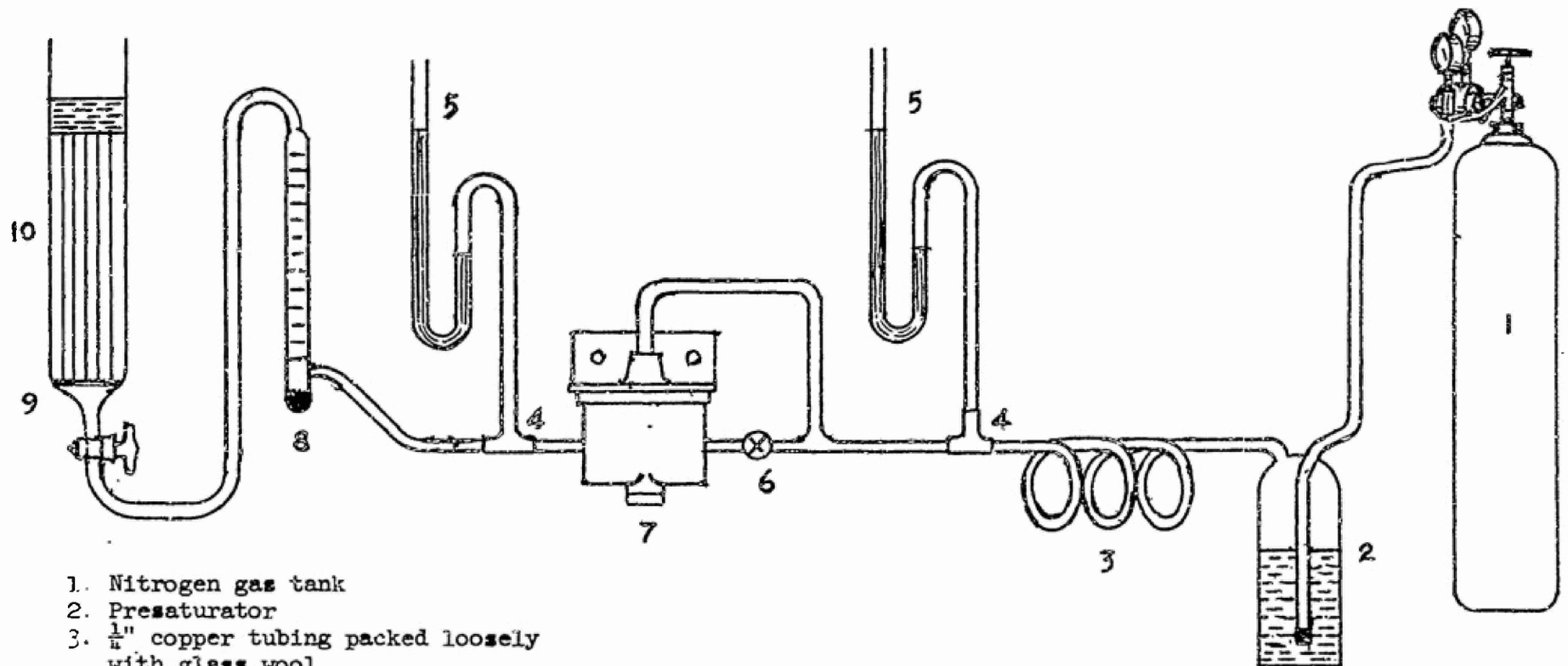


Figure 6. Structure of lecithin in aqueous media at neutral pH.

Figure 7. Apparatus for Solvent Sublation.



1. Nitrogen gas tank
2. Presaturator
3. $\frac{1}{4}$" copper tubing packed loosely with glass wool
4. $\frac{1}{4}$" glass tee
5. Open tube mercury manometer
6. $\frac{1}{4}$" Nupro needle vlave
7. Moore flow controller, Model 63BUL
8. 10 ml soap bubble flowmeter
9 Glass frit, 35 mm
10. Solvent sublation column

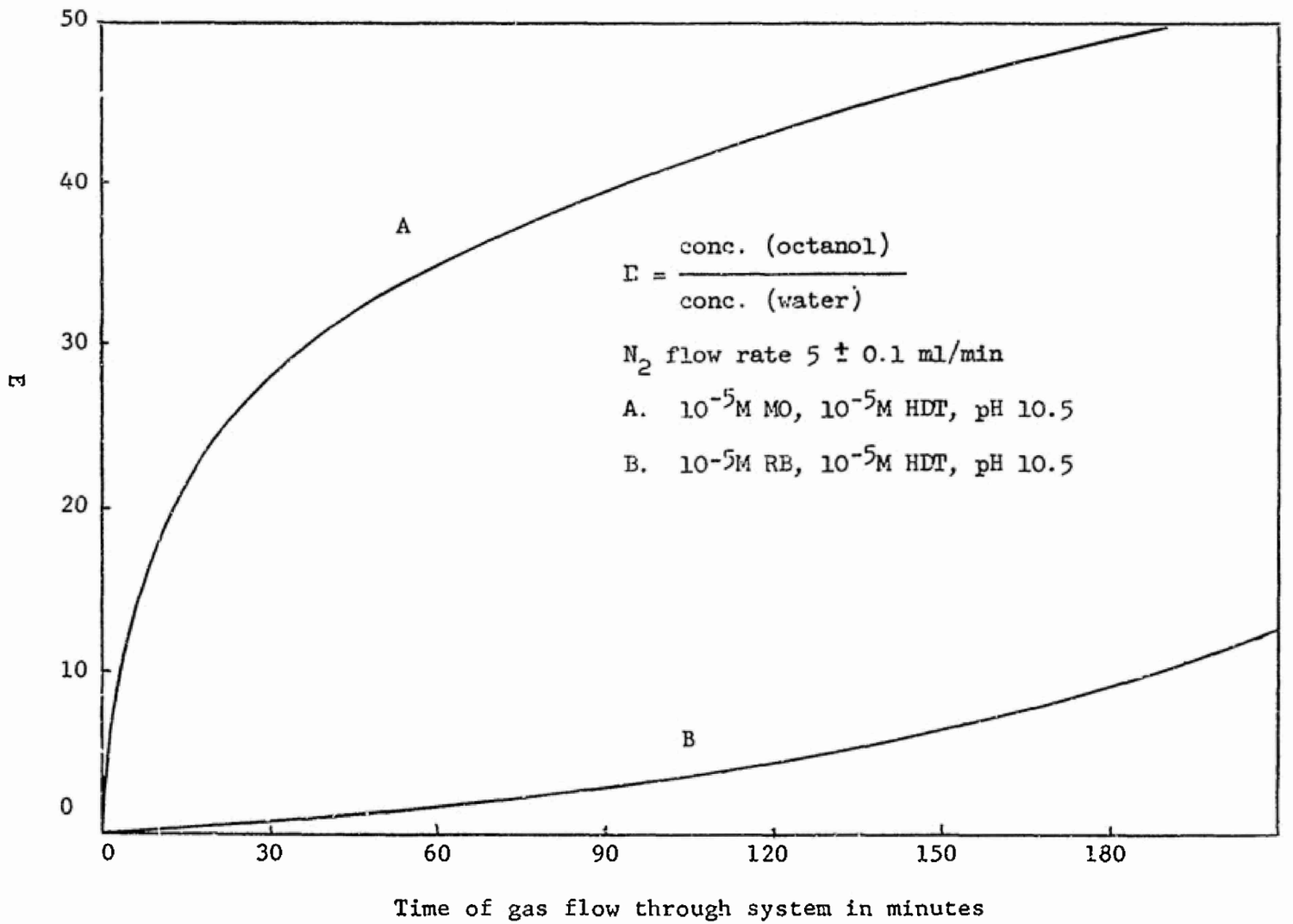
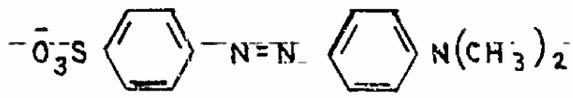
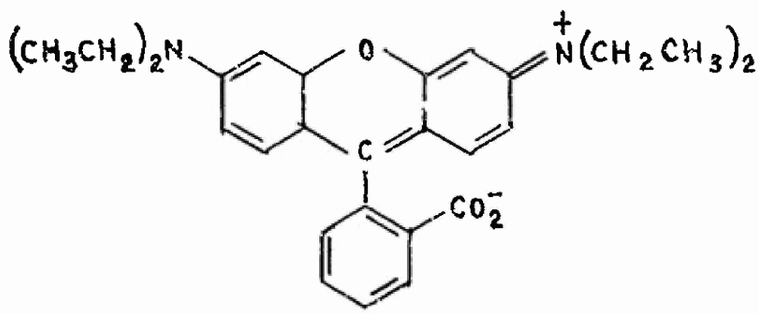


Figure 8. Extraction coefficient as a function of time.



Methyl orange



Rhodamine B

Figure 9. Structure of methyl orange and a resonance contributor of rhodamine B in basic media.

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Natick, Massachusetts

13. ABSTRACT

A simplified apparatus has been developed for the recovery and concentration of ionic species by foam fractionation. The process involves total reflux by thermal breakage of foam at the top of the column. Mechanical breakage can also be used when heat sensitive materials are used. The system has been applied to several dyes initially and then to the successful recovery of phospholipids and trace concentrations of salts of fatty acids.

Solvent sublation has also been investigated as a selective separation technique. Exploratory studies indicate that the extraction process is kinetically controlled and that time might therefore be an effective separation parameter.

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14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Distillation	10					
Foams	10					
Separation	8		8			
Recovery	8					
Concentrating	8					
Phospholipids	1,2					
Fatty acids	1,2					
Salts	1,2					
Dyes	1,2		1,2			
Water	1		1			
Ionic	0					
Solvent sublation			10			
2Ooctanol			1			

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