To my wife Huguette

who made this thesis possible

ACKNOWLEDGMENT

The author is indebted to Dr. F. D. F. Talbot, the director of this thesis, for his encouragement and valuable guidance throughout the course of this work.

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ABSTRACT

The removal of copper from dilute aqueous solution by foam fractionation has been studied extensively in this work. The primary purpose of the study was to determine the optimum conditions for the removal of copper and to attempt to improve the efficiency of the process by the addition of an auxilliary complexing agent.

Distribution factors were therefore determined for copper as a function of pH, background salt concentration, auxilliary ligand concentration, surfactant concentration, and bulk concentration of copper. In general, the addition of the auxilliary ligand THPED* was found to increase the distribution factor significantly, except when the bulk concentration of either copper or surfactant was high.

A mechanism is presented to explain the foam fractionation process, based on the double layer concept and the neutralization of the zeta potential by the cations in the diffuse layer. It was found that for the simple system there was an exponential dependence of the surface excess of copper on the concentrations of all cationic species present in the bulk. An equation has been developed to quantitatively predict the surface excess knowing the pH, and the copper and sodium chloride concentrations.

* THPED is the convenient abbreviation for the substituted amine: N:N:N':N'-tetrakis-(2-hydroxypropyl)-ethylenediamine.

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NOMENCLATURE

a_i	activity of component i	g-mol/l
D	distribution factor = Γ/X	cm
D*	bulk phase diffusion coefficient	cm^2/sec
G	gas flow rate	cm^3/min
K	adsorption isotherm constants	
N	bubble emission frequency	min^{-1}
n	number of capillaries in the bubbler	
R	the gas constant	g-cal/g-mol°K
S	surface rate	cm^2/min
T	absolute temperature	°K
t	time	min or sec
V_f	volumetric flowrate of foam on a gas free basis	
X_i	bulk concentration of component i	ppm or $g\text{-mol}/cm^3$
Y_f	copper concentration in the foamate	

γ	surface tension	dynes/cm
Γ	surface excess	$g\text{-mol}/cm^2$
ζ	zeta potential	m.v.

Subscripts	s	surfactant
	c	copper
	B	bulk phase
	f	foamate
	F	feed

Abbreviations	NaLS	Sodium Lauryl Sulfate
	LS^-	Lauryl Sulfate Anion
	EN	Ethylenediamine

II. LITERATURE SURVEY

The earliest efforts to utilize foaming as a separation technique were by workers attempting to verify the Gibbs adsorption isotherm (1). Thus McBain and Davies (2) bubbled nitrogen through surfactant solutions and calculated the surface excess after analysing the collapsed foam.

In the following years many other researchers utilized foam separation methods for concentrating naturally surface active solutes in the foam phase. One of the first review articles on the subject appeared in 1947 (3). In it, examples are given of the foam fractionation of soaps, proteins, dyes, bacteria, bile acids, and enzymes.

The first reported separation of metallic ions by foam fractionation appeared in 1957 (4), and was quickly followed by the work of Schnepf et.al. (5) in which the effects of competing ions, reflux, and surfactant concentration were studied.

In 1965, a pilot plant size foam fractionation unit operating on a feed of 500,000 g.p.d. was succesful in reducing the concentration of alkyl benzene sulfonates in sewage to less than 1 ppm (6). The introduction of bio-degradable detergents has made the foam fractionation of sewage unnecessary however, with the result that a full size plant treating 12 m.g.p.d has been closed down (7).

I. INTRODUCTION

Foam Fractionation is based on the selective adsorption of solutes on the surface of bubbles as they rise through a liquid. The bubbles then form a foam which may be removed and collapsed. Because of the adsorption, the collapsed foam is richer in the surface active component than the liquid from which it is taken. A partial separation will therefore have been achieved.

Solutions of metal ions are not generally surface active however, and therefore the foaming of such a solution will not result in an enrichment. To accomplish this it is necessary to add a surface active agent to attract the ion in question, resulting in a surface excess of both the surfactant and the metal ion.

The purpose of this work was to determine the optimum conditions for removing traces of cupric ions from solution by means of foam fractionation and to attempt to improve the efficiency of separation by adding an auxilliary ligand to form a surface active copper complex. To this end, the surface excess and distribution factor of copper were determined, for varying conditions, using a foam fractionating unit operating in the simple mode ie: as a single theoretical stage unit.

The system investigated was aqueous copper nitrate with sodium lauryl sulfate as surfactant and THPED as the auxilliary complexing agent.

No further industrial sized foam fractionation units have been reported although several pilot plant sized units have been constructed to study the feasibility of removing radioactive materials from waste water (5,8,9). In the latter report, the effect of controlled reflux as a method of improving the efficiency of the foam fractionation process was discussed.

The chemistry of the foam fractionation of metals has not been extensively studied, but in general, most workers are of the opinion that the separation is achieved due to complex formation between the surfactant and the metal ion (8,10,11,12), while others have mentioned the possibility of electrostatic attraction between the surfactant and the metal ion (5,13). One of the most recent reports (14), compares the surfactant-cation equilibrium to that of a cation exchange resin, with the surface acting as a mobile ion exchange media of limited uptake.

The use of a neutral chelating agent to improve the efficiency of the foam fractionation process has not been previously considered although Aoki and Sasaki (15) used EDTA to complex ferric ions and then foamed the resulting negatively charged complex with a cationic surfactant. In addition, the complexation of inorganic species has been discussed at length by Sebba (16,17) as it applies to ion and precipitate flotation and to solvent sublation.

No literature dealing directly with the foam fractionation of copper has been found, although Rubin et.al.(18) used the ion and precipitate flotation techniques to separate copper hydroxide using sodium lauryl sulfate as collector. Rubin also reported that the separation of copper in the Cu/NaLS system was due primarily to charge effects, but no figures were quoted.

III. THEORY

1. Adsorption Isotherms

The adsorption of solutes which occurs at the gas-liquid interface is the basis for the separation achieved by such methods as foam fractionation (19).

Through rigorous thermodynamic considerations, Gibbs formulated the adsorption isotherm, eqn.(1), which relates the concentration of a surface active solute at an interface to the change in surface tension at the interface and to the activity of the surface active species in the bulk liquid (1).

$$d\gamma = -RT\Sigma \Gamma_i d\ln a_i \qquad (1)$$

Where Γ_i is the surface concentration or so called "surface excess" of component i, and γ is the surface tension of the solution. Eqn.(1) is of limited use however, because little is known regarding the activities of the various surfactants and because it is difficult to measure small changes in the surface tension accurately.

For very dilute solutions of a non-ionic surfactant the simplifying assumption that activity equals concentration can be made so that eqn.(1) can be written:

$$\Gamma_s = \frac{1}{RT} \times \frac{d\gamma}{d\ln X_s} \qquad (2)$$

In equation (2), the surfactant concentration is Γ_s at the surface and X_s in the bulk.

Fig. 1 shows the shape of the surface tension versus log concentration curve for a typical surfactant (20), and fig. 2 the surface excess versus concentration curve. It may be seen that at very low concentration, the term $d\gamma/d\ln X$ becomes almost constant and this corresponds to the linear portion of the surface excess versus concentration curve.

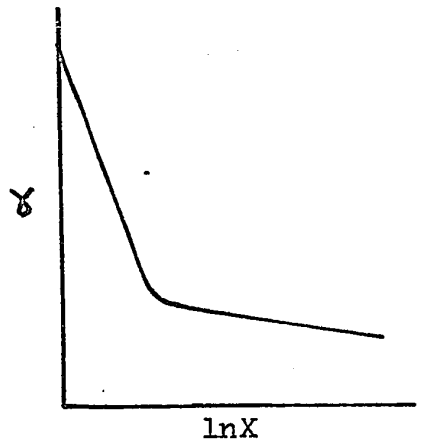

Figure 1: surface tension vs. log surfactant conc.

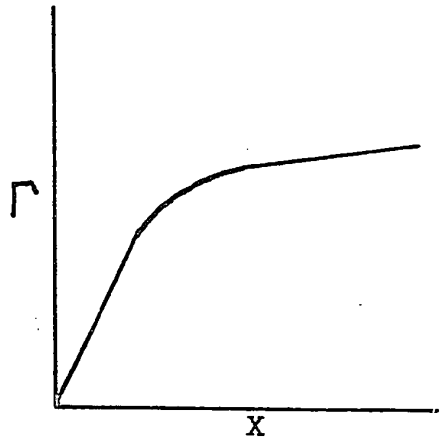

Figure 2: surface excess vs. surfactant conc.

According to simple adsorption theory (12), the linear portion of the Γ vs. X curve can be expressed by the equation:

$$\Gamma = K_1 X \qquad (3)$$

Lemlich has stated that the whole curve can be expressed by

a Langmuir type isotherm (12):

$$\Gamma = K_1 X/(1 + K_2 X) \qquad (4)$$

where K_1 and K_2 are constants for the given system. Thus K_1 is the slope of the linear portion of the Γ vs. X curve and K_1/K_2 is the surface excess at saturation. On the basis of molecular size and packing considerations, it has been determined that the surface excess is approximately 3×10^{-10} g-mol/cm^2 for a saturated monolayer of many different surfactants (21).

For the adsorption of surface active ions such as sodium lauryl sulfate however, the Langmuir equation no longer holds. Such equations are necessarily invalid because they contain no terms to account for the energy of the electrical double layer, which is constituted of the charged surface and the underlying counter ions (22).

The separation of non surface active species is not covered by equations (1) and (2) because $d\gamma/dX \approx 0$ and so their surface excess is zero. The foaming of such a solution will therefore yield no enrichment. It is possible however, to separate surface inactive ions by associating them with a surfactant of opposite charge, or to form a surface active complex or chelate. This aspect will be discussed more fully in section 3.

2. Surface Chemistry of Foam Fractionation

The actual situation at the air-liquid interface is considerably different than the idealized picture presented in the previous section. When a solute such as the lauryl sulfate anion comes into contact with the air-water surface it is held there by forces which oppose the removal of the polar $-OSO_3^-$ group from the water.

The approach of the lauryl sulfate anion is therefore governed by diffusion alone, while the desorption from the surface is controlled by quite a high energy barrier, see fig.3. The amount of lauryl sulfate in the surface therefore increases until the chemical potentials of the surface and the bulk are equal. This corresponds to a greater solute concentration in the surface than in the bulk.

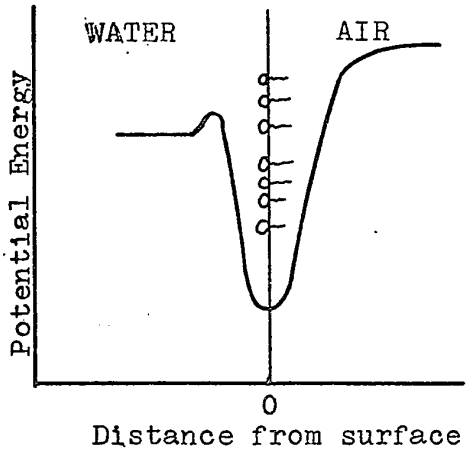

Figure 3: Potential Energy Diagram for a Surface Active Solute.

The presence of the packed monolayer of negatively charged $-OSO_3^-$ ions supports the existance of an electrical double layer at the surface of separation between the two phases. According to Stern (24) the double layer consists of a tightly bound layer which is a single molecule ($-OSO_3^-$ in this case) thick and across which there is a sharp drop in potential. The second part of the double layer extends some distance into the liquid and is a diffuse layer consisting of both solvent molecules and positively and negatively charged ions, although the electrostatic field at the surface will result in a preferential attraction of positive ions. The potential difference across the diffuse layer is known as the zeta potential after the symbol used in its representation.

It is generally assumed that the decrease in zeta potential leading to complex formation (and in the limit to coagulation and precipitation) is caused by the adsorption of ions of opposite charge to that of the surface layer. Since this is the case, electrically equivalent amounts of ions of different valence will be adsorbed. ie: singly, doubly, and triply charged ions will be adsorbed in the ratio of 3 to 1.5 to 1 .

Experiments have been performed (25) to relate the amounts adsorbed to the valence and the bulk concentration and in general if unit concentration of triply charged ions

will reduce the zeta potential by $\Delta \zeta$ m.v., then about ten times that concentration of doubly charged ions will be required to cause the same reduction while it will require a concentration of from 300 to 700 times as much singly charged ion to get the same effect.

The foregoing argument however, is based on the assumption that all ions are adsorbed equally but that of course is not strictly true: actually, large organic ions such as $Cu(THPED)^{2+}$ are adsorbed more readily than simple inorganic ions (26). It is this excess of positive ions in the diffuse layer which results in the enrichment of metal ions by foam fractionation.

Based on the previous double layer theory, the following idealized model is proposed in explanation of the results obtained in the foam fractionation of copper with sodium lauryl sulfate:

a) there is a complete monolayer of adsorbed lauryl sulfate anions at the surface and a diffuse layer of counter ions is associated with the adsorbed layer,

b) the excess positively charged ions within the double layer are composed of species of all cations present in the bulk, ie: Na^{+}, Cu^{2+}, and H_3O^{+}, although at the optimum pH there will be little H_3O^{+} present,

c) the relative amounts of each species of positive ions within the diffuse layer is determined primarily by the ability of each species to neutralize the negative charges of the anions adsorbed at the surface (ie: discharge the zeta potential),

d) the ability of an ionic species to discharge the zeta potential is an exponential function of the charge on the species and its effictive activity in the bulk.

That the reason for the separation achieved is not due simply to the formation of lauryl sulfate complexes may be seen from the following argument: if there is a large excess of surfactant, then presumably all of the metal ion would be complexed and in the form of $Cu(LS)^+$ or $Cu(LS)_2$. One could therefore assume that the surface excess of copper would be in proportion to the concentration ratio of the complexed to the uncomplexed form of the surfactant. This however, is not so, and in fact the concentration ratio of $Cu(LS)_2$ to NaLS in the surface is many times greater than their ratio in the bulk. For this reason the foregoing model based on the double layer theory has been postulated.

3. Single Theoretical Stage Foam Fractionation

In order to estimate the performance of a foam fractionating unit, it is necessary to know the surface excess as a function of such variables as pH, surfactant concentration, background electrolyte concentration, and the bulk concentration of the solute to be separated.

The easiest and most accurate method of determining the surface excess is to measure the performance of a single theoretical stage column operating in the so called "simple mode" (13) . The operating equations for such a column may be derived as follows: a mass balance is carried out on the collapsed foam assuming that the overall concentration is compounded from two independent sources (27) :

a) a surface concentration Γ which is dependent on the equilibrium between the surface and the bulk, and

b) an entrainment ratio which is dependent on the hydraulics of the system.

The mass balance may therefore be written:

$$V_f Y_f = S\Gamma + V_f X_B \qquad (5)$$

where V_f is the volumetric flow rate of foam on a gas free (collapsed) basis, Y_f is the collapsed foam composition, X_B is the bulk liquid composition and S is the surface rate.

For the case of a bubbler of n capillaries operating at a bubble emission frequency of N bubbles per minute per capillary, the surface rate is given by:

$$S = n\pi Nd^2 \qquad (6)$$

where d is the bubble diameter. Since the gas rate G is known, the bubble diameter can be calculated from:

$$d = \sqrt[3]{6G/n\pi N} \qquad (7)$$

The surface excess may therefore be determined by calculating d and S and rearranging eqn.(5) to yield:

$$\Gamma = \frac{V_f(Y_f - X_B)}{S} \qquad (8)$$

The foregoing equations apply equally to the metal ions and to the surfactant since they were derived by means of a mass balance which must necessarily be valid for all components in the foam.

Implicit in the derivation of eqn.(8) are the following assumptions:

a) The surface excess occurs totally on the surface, or stated differently, the diffuse layer volume is negligeable.

b) The bulk region of the foam has the same composition as the bulk liquid from which the foam originated. For this to be so, the adsorption must occur totally within the liquid phase of the column and this means that the bubbles must remain within the liquid phase long enough for the solute to diffuse to the surface and assume its' equilibrium concentration. (see Appendix D).

c) The bubbles are spherical and uniform in the liquid phase. This requirement arises because only the gas rate and bubble frequency are known for the surface rate calculations.

d) The bubbles do not break, or if they do, the rate of foam rise must exceed the drainage rate so that internal reflux of composition Yf does not enrich the interstitial liquid of composition X_B.

The previous assumptions in a somewhat different form were first proposed by Rubin and Gaden (20) as an ideal foam model.

One distinctive feature of foam fractionation is that, for the separation of metals, the process becomes more effective as the bulk concentration of the metal ion decreases, and in fact, foam fractionation can only enrich solutes present in low concentration. That this is so may be seen from an inspection of figure 4 which is a log-log plot of the distribution factor versus the bulk concentration of the metal ion, where the distribution factor is defined as $D = \Gamma/X_B$.

The distribution factor is constant from extremely low values of the bulk metal concentration to about 10^{-4} molar at which point it decreases and becomes almost zero by 10^{-2} molar metal ion concentration. (11) The distribution factor may therefore be considered a form of equilibrium constant between the surface and the bulk and for this reason it, rather than the surface excess, determines

the possible extent of separation.

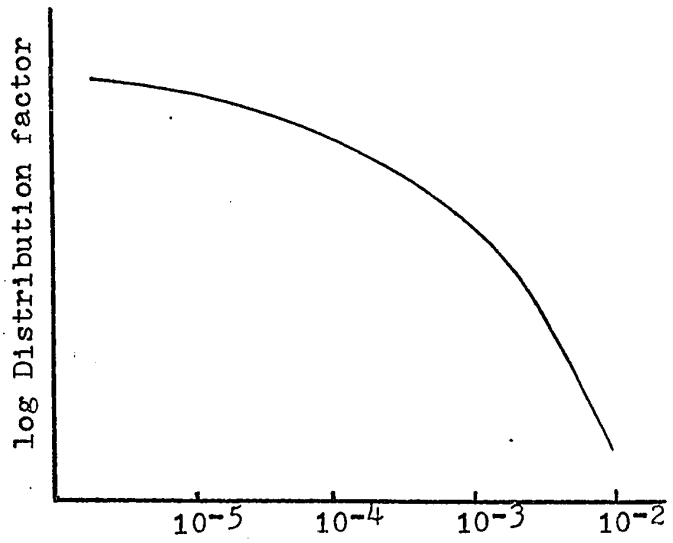

Figure 4: Distribution vs. Bulk Concentration of the Metal Ion

IV. EXPERIMENTAL

1. Apparatus

a) General:

In order to calculate the surface excess, a reliable single theoretical stage foam fractionating column was developed. A batch procedure was adopted rather than a continuous recirculating system (28) because it was considered unwise to risk micelle or precipitate formation in the recycled foamate.

A schematic diagram of the apparatus used is shown in figure 5, while the actual arrangement of the equipment may be seen from the photograph in figure 6.

b) Gas Delivery

Oil-free compressed air from cylinders was used throughout. The air pressure was first reduced to 9 psig and then humidified using a gas wash bottle followed by a saturator made of a fritted sparger contained in a flask of distilled water. The flow rate of the humidified air was then adjusted with a needle valve, measured with a calibrated flowmeter, and passed to the bubbler in the foam column.

c) Bubbler

In order to utilize a stroboscope in the determination

of bubble diameters, it is necessary to use a bubbler which is capable of supplying bubbles of a uniform size. This requirement was met using a bubbler consisting of five glass capillary tubes 0.240 inch long and 0.007 inch i.d. imbedded in a teflon chamber. The requirement for the teflon chamber became apparent after the first bubbler, made of lucite, partially dissolved while being cleaned in a chromic acid solution.

This bubbler design gave uniform, reproducible results and is recommended as a standard for any application where uniform bubble size and rates are required. A photograph of the bubbler in operation is shown in figure 7.

d) Column

The column used was constructed of an inverted three liter pyrex separatory funnel with the stopcock portion replaced by a foam delivery tube, and the bubbler inserted into the bottom. The liquid pool depth was approximately 33 cm. above the top of the bubbler. The foam/liquid interface height was controlled by means of a 300 ml. level control bulb and adjusting screw. The three liter separatory funnel was chosen so as to minimize bulk concentration changes during a run.

e) Foam Collection

After leaving the column, the foam was directed along a 15 cm. foam delivery tube of 0.9 cm. i.d. to a 1000 ml.

erlenmeyer flask. The foam delivery tube was adjusted so that it had a declination of about 10 degrees; drainage was therefore towards the flask.

f) Bubble Rate

The bubble diameter was determined by calculation after the bubble rate had been determined using a stroboscope. No problems were encountered with harmonics and the highest frequency showing distinct bubbles was utilized.

g) Analysis

Foamate analysis for copper was carried out colorimetrically using dihydroxyethyldithiocarbamic acid as reagent (29). The procedure used is detailed completely in Appendix A.

h) Water

Due to the sensitivity of the foam fractionation process to trace impurities (4), and because the laboratory still and distilled water reservoir were constructed of copper, it was necessary to utilize an ion exchange column as a final clean up step for the water used in the experiments. Thus distilled water was passed through a Barnstead mixed bed ion exchange column and stored in a glass vessel prior to use.

i) pH

All pH adjustments were carried out with 0.1 N NaOH and/or dilute HNO_3. All measurments were made with a Beckman Zeromatic SS-3 pH meter using a Beckman combination electrode cat. No. 39012 .

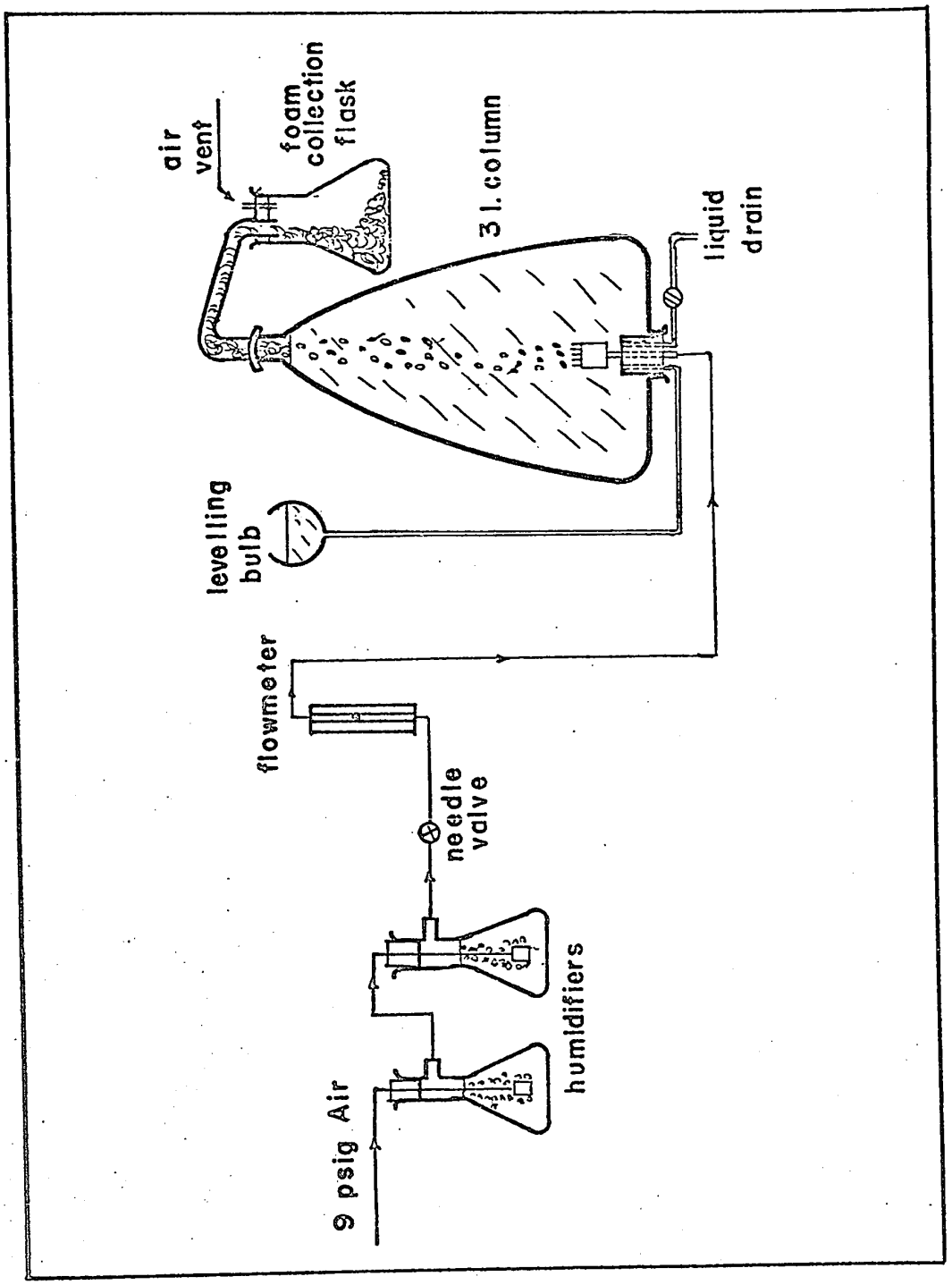

Figure 5: Schematic Diagram of the Single Stage Foam Fractionation Unit

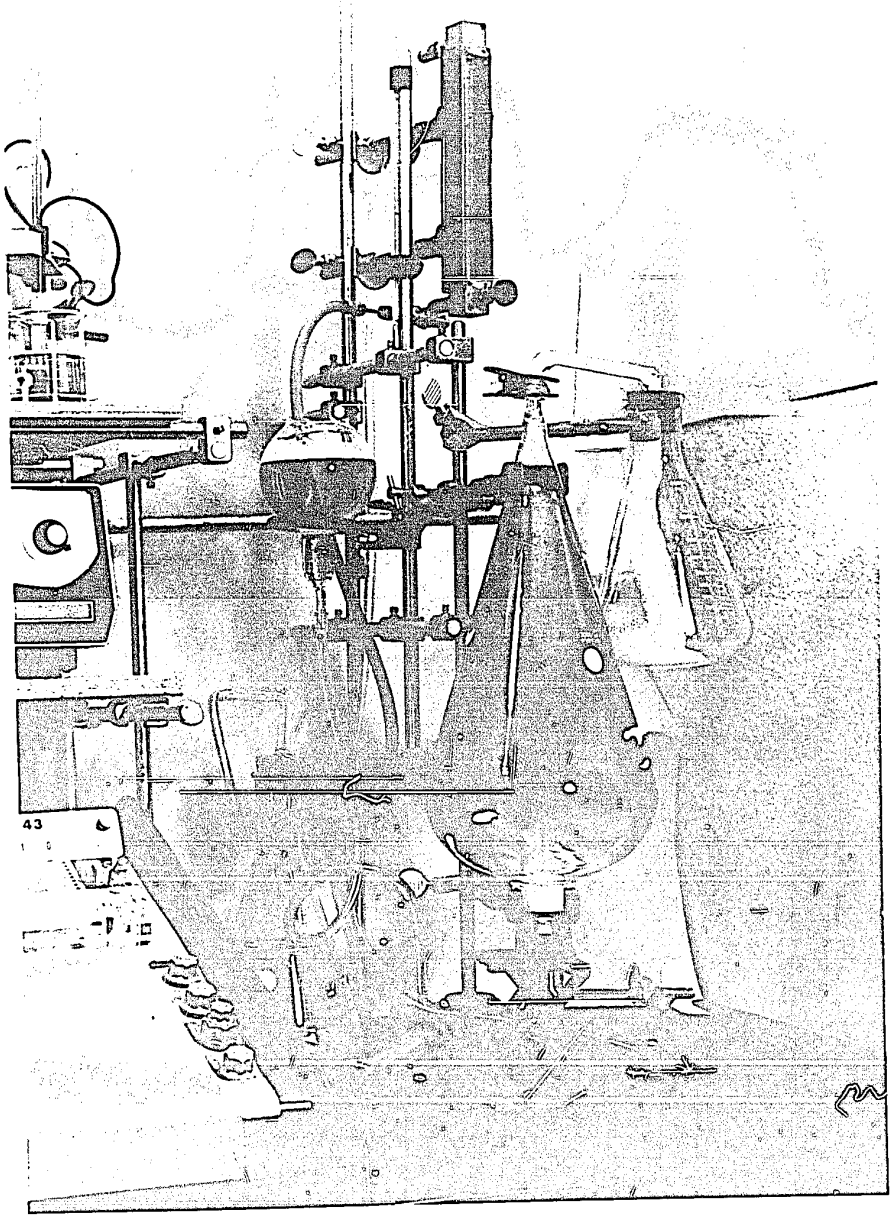

Figure 6: The Experimental Apparatus

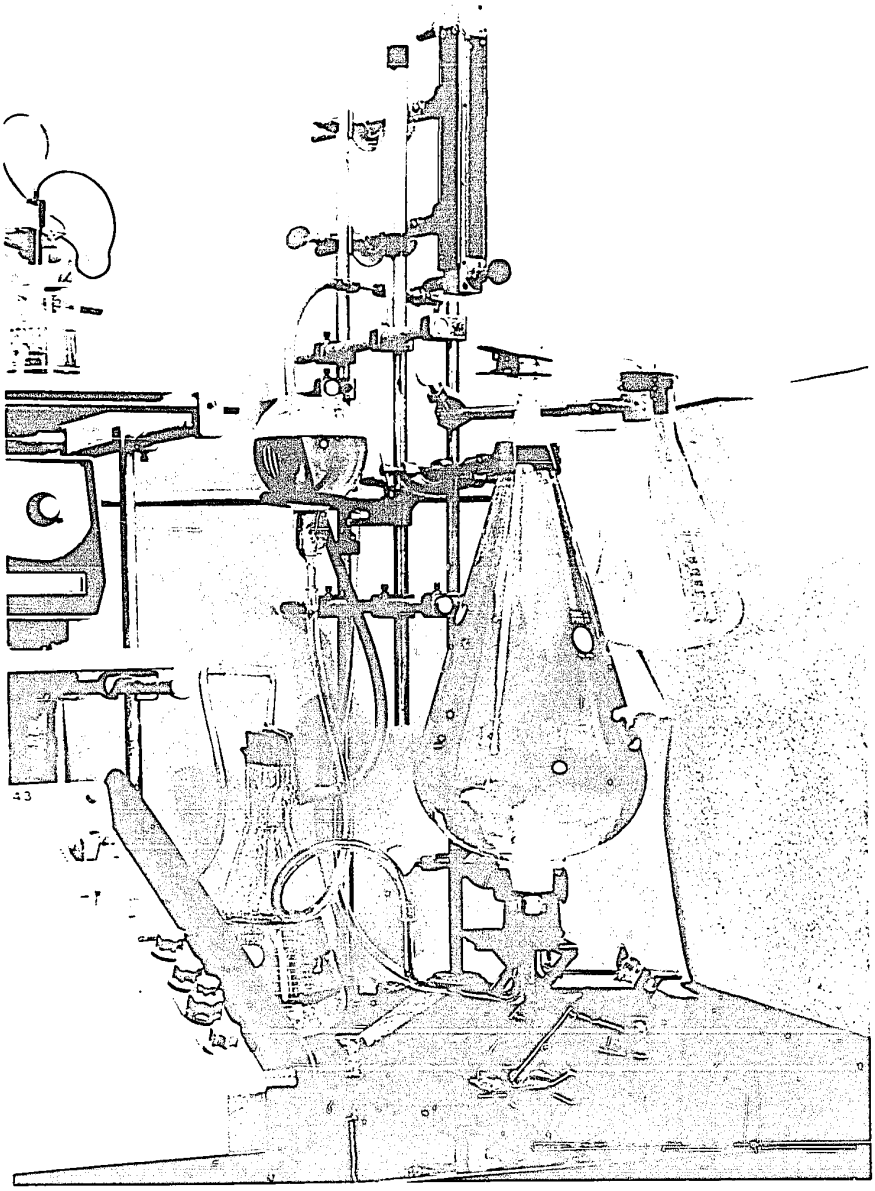

Figure 6: The Experimental Apparatus

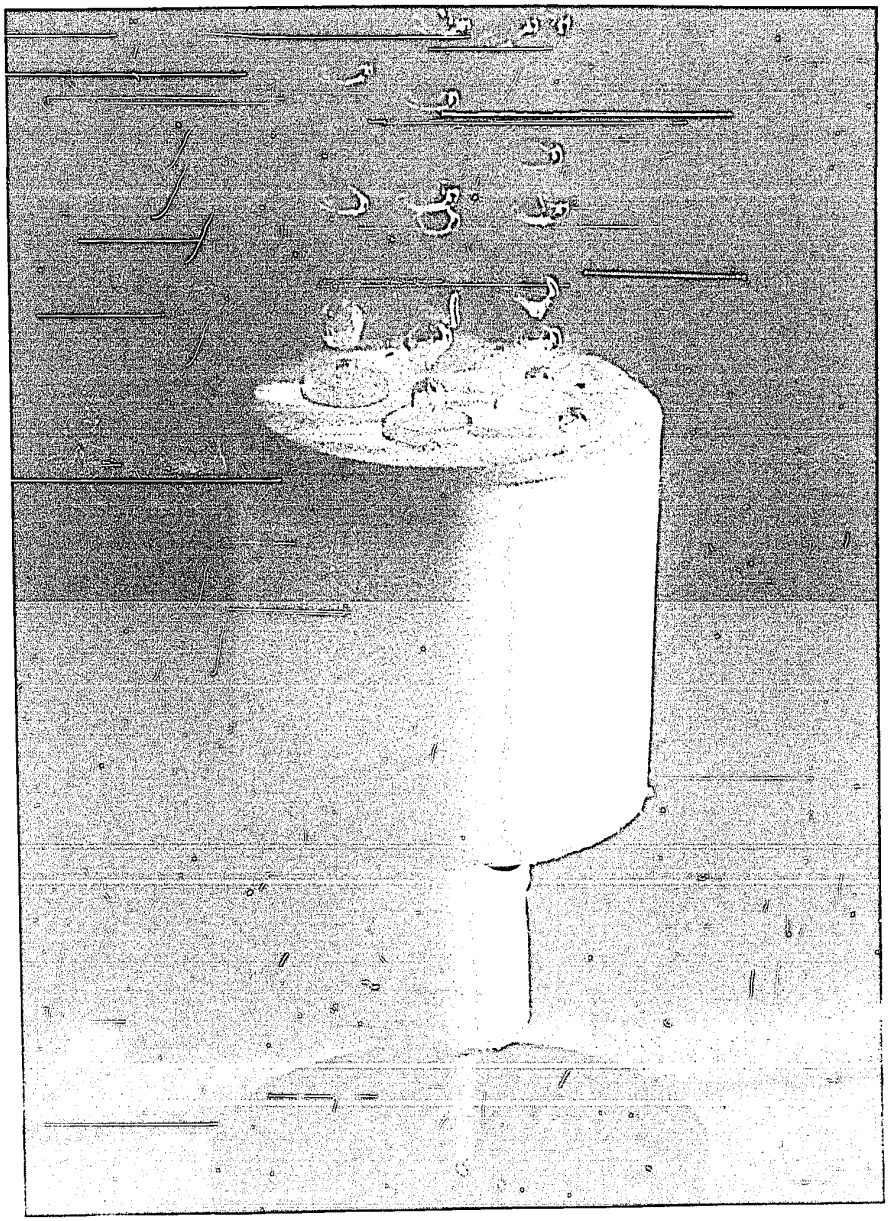

Figure 7: The bubbler in operation

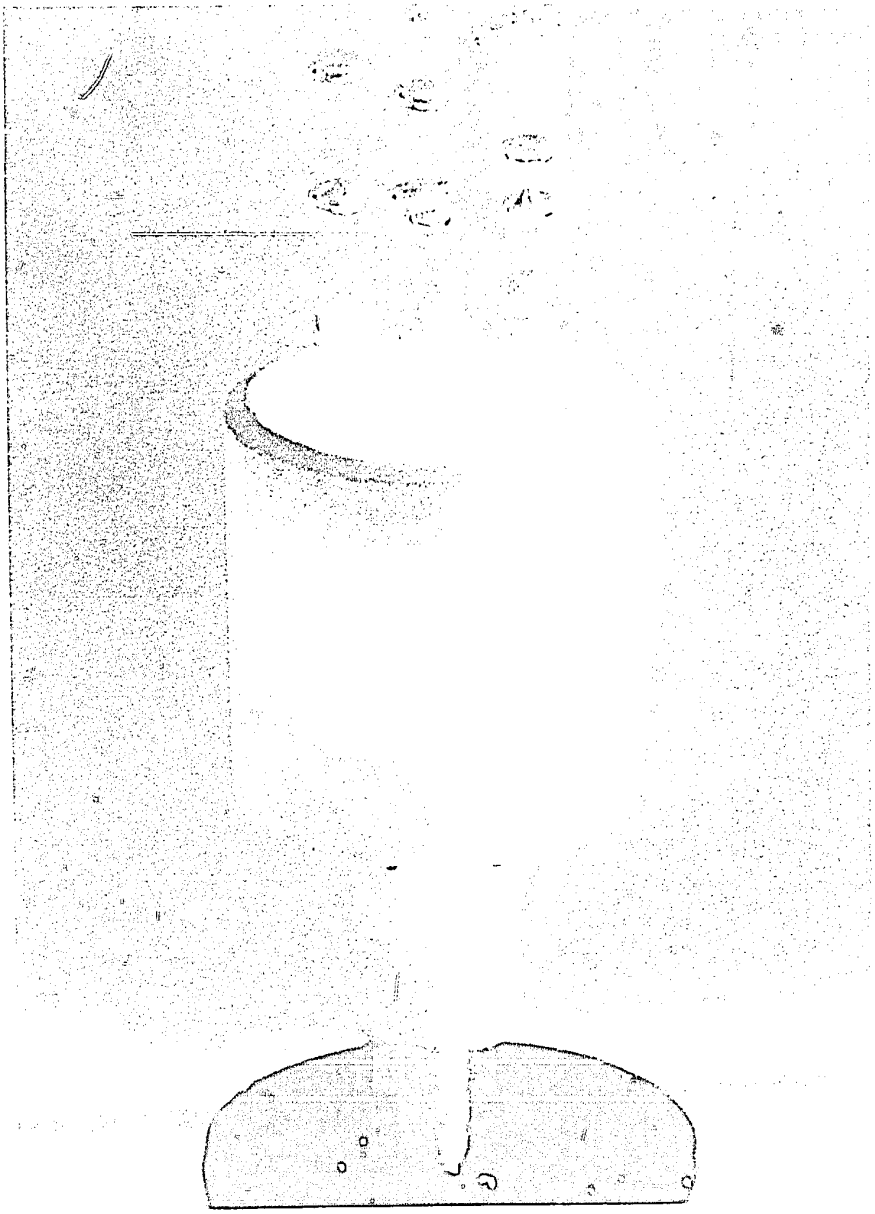

Figure 7: The bubbler in operation

2. Experimental Procedure

a) Feed Preparation

For each run, four liters of feed was prepared using distilled water which had been passed through the mixed bed ion exchanger. After addition of the required quantities of cupric standard, NaCl, THPED, and sodium lauryl sulfate, the pH was adjusted to the desired value using NaOH or HNO_3 .The chemicals used were as follows:

i) Copper Nitrate; 0.1000 mol/l ± 0.0005 mol/l , from Orion Research Inc.

ii) Sodium Lauryl Sulfate; Fisher Scientific Ltd., U.S.P. grade, lot no. 783703 .

iii) THPED ; from Wyandotte Chemical Corp., purity unknown.

iv) NaCl, NaOH, HNO_3 ; Research or Analytical grade.

b) Column Operation

Prior to charging the column, the foam reciever was weighed to 0.1 mg. The gas rate was adjusted to a value slightly above the desired rate and the column was filled through the levelling bulb. The gas rate was then adjusted to the exact value desired after the foam-liquid interface height had been set at the mark.

Once steady conditions had been reached, the foam reciever was swung into position and the stop watch started simultaneously. The gas rate was monitored constantly during the run, except when the bubble rate was being measured.

As soon as possible after the commencement of a run the bubble rate was determined using a stroboscope. For the easiest and quickest determination it was necessary to turn off the fluorescent room lights so that the bubbles were more distinct.

After sufficient foam had been collected for analysis (6 to 13 min.) the time was noted and the foam reciever was removed and stoppered to prevent evaporation. The foam plus reciever was then weighed to 0.1 mg. so as to obtain the exact weight of foam collected during the run. Since the solute concentrations were so low, a density of 1.0 was assumed so that the weight of foam collected would be numerically equal to the volume of foam collected.

Ambient temperature and pressure were recorded so that the flowmeter reading could be referred to the calibration curve which was set up using 25 °C and 760 mm Hg. as STP.

c) Post Run Procedure

On completion of the run the column was drained through a stopcock in the bottom and the solution discarded. The levelling bulb and column were then rinsed with copper free water and allowed to drain completely prior to the next run. A low gas rate was maintained through the bubbler at all times to prevent capillary wetting. The flask of foam was then allowed to sit so that the foam broke naturally, prior to analysis.

V. RESULTS AND INTERPRETATION

1. General

Approximately thirty preliminary runs were carried out in order to become familiar with the apparatus and to develop a consistent experimental technique. The only parameter varied during these runs was the pH, and while the data were subject to much scatter, they nevertheless indicated that a maximum occured in the distribution factor versus pH curve.

Between the 28th. May and the 4th. June, 1969, runs numbered 1 to 41 were performed. The experimental scatter was great however, and consistent results could not be obtained. The apparatus was therefore examined completely and it was found that a major air leak was occuring in the air delivery tube between the flowmeter and the bubbler. The air line was replaced with a new section of tygon tubing and the flowmeter recalibrated. No further problems with the apparatus were encountered for runs numbered 42 to 125.

Complete data for all runs are included as Appendix E.

2. Treatment of Experimental Data

Because the bulk concentration decreased slightly throughout a run, an iterative procedure was developed for determining the actual surface excess and distribution factor for copper based on the average bulk concentration during the

run. In brief, an approximate surface excess was calculated using $X_B = X_F$, the feed composition. Knowing the surface excess and surface rate, the amount of copper removed from the solution could be calculated, and by simple mass balance the bulk composition at the end of the run. Based on the average bulk composition, a new surface excess was calculated and so forth until succesive values of the average bulk composition differed by less than 0.001 ppm. The computer program used is included as Appendix D.

3. Errors

Equation (8) may be expanded and rearranged to yield:

$$D = \frac{\Gamma_c}{X_B} = \frac{V_f(Y_f - X_B)}{6GX_B} \times \sqrt[3]{6G/n\pi N} \qquad (9)$$

for which the error equation is:

$$\frac{\Delta D}{D} = \frac{\Delta X_B}{X_B} + \frac{\Delta \Gamma_c}{\Gamma_c}$$

$$= \frac{\Delta V_f}{V_f} + \frac{\Delta X_B}{X_B} + \frac{\Delta Y_f - \Delta X_B}{Y_f - X_B} + \frac{\Delta G}{G} + \left(\frac{\Delta G}{G} + \frac{\Delta N}{N}\right)\frac{1}{3} \qquad (10)$$

Equation (10) was included in the computer program and the error calculated for each run. In general the error limits ran between 4% and 7%, although where $Y_f - X_B$ was less than 3ppm considerably higher error was possible. The error for each run, calculated from equation (10), is included in Appendix E.

4. The Effect of pH on the Distribution Factor

The order in which the experimental runs were carried out was determined by the relative importance of the parameter being studied. The effects of varying pH on both the Cu/NaLS and the Cu/NaLS/THPED systems was therefore studied first. It was necessary, however, to fix the background salt concentration, the surfactant concentration, the copper concentration, and where used, the concentration of auxilliary ligand.

For the first runs, a background salt concentration of 0.01 g-mol/l NaCl was chosen so that minor changes in ionic strength due to the addition of acid or base for pH adjustment would least affect the system.

Based on visual observation of the foam fractionating column in operation using varying concentrations of NaLS, it was decided that 0.500 g/l would be satisfactory because no increase in foam stability was apparent when the NaLS concentration was increased further.

Throughout all of the experimental runs, except where copper concentration was a parameter, a feed concentration of 10.00 ppm copper was used. That concentration was chosen because it produced a foamate containing between 10 and 30 ppm copper and was therefore easily analyseable.

Because the stability constant of the Cu(THPED) chelate is so large (30), one stochiometric equivalent of THPED was

added for those runs in which the auxilliary ligand was required.

The results of the runs in which pH was a parameter are plotted in figure 8 and tabulated in tables 2 and 3 in Appendix E.

Figure 8 shows that as the pH increases from very low values, the distribution factor for the simple system (Cu/NaLS) increases and reaches a maximum at about pH 3.0 . The mechanism for this type of response is most likely as follows: at low pH values, the concentration of hydronium ion, H_3O^+, is such that it preferentially moves into the double layer to discharge the potential due to the lauryl sulfate anions. In addition, the nitrate ion concentration is such that much of the copper is complexed and in the form $Cu(NO_3)_2$. As the pH increases, the hydronium ion concentration decreases and the doubly charged cupric ions begin to play an increasingly important role in the discharge of the zeta potential. By pH 3.0, the hydronium ions have ceased to be a factor, and so the surface excess is made up only of cupric and sodium ions.

It is obvious from figure 8 that there is an exponential dependence of the distribution factor on the hydronium ion concentration, since the plot of D versus pH is a straight line over the range of pH values from 1 to 2.5 .

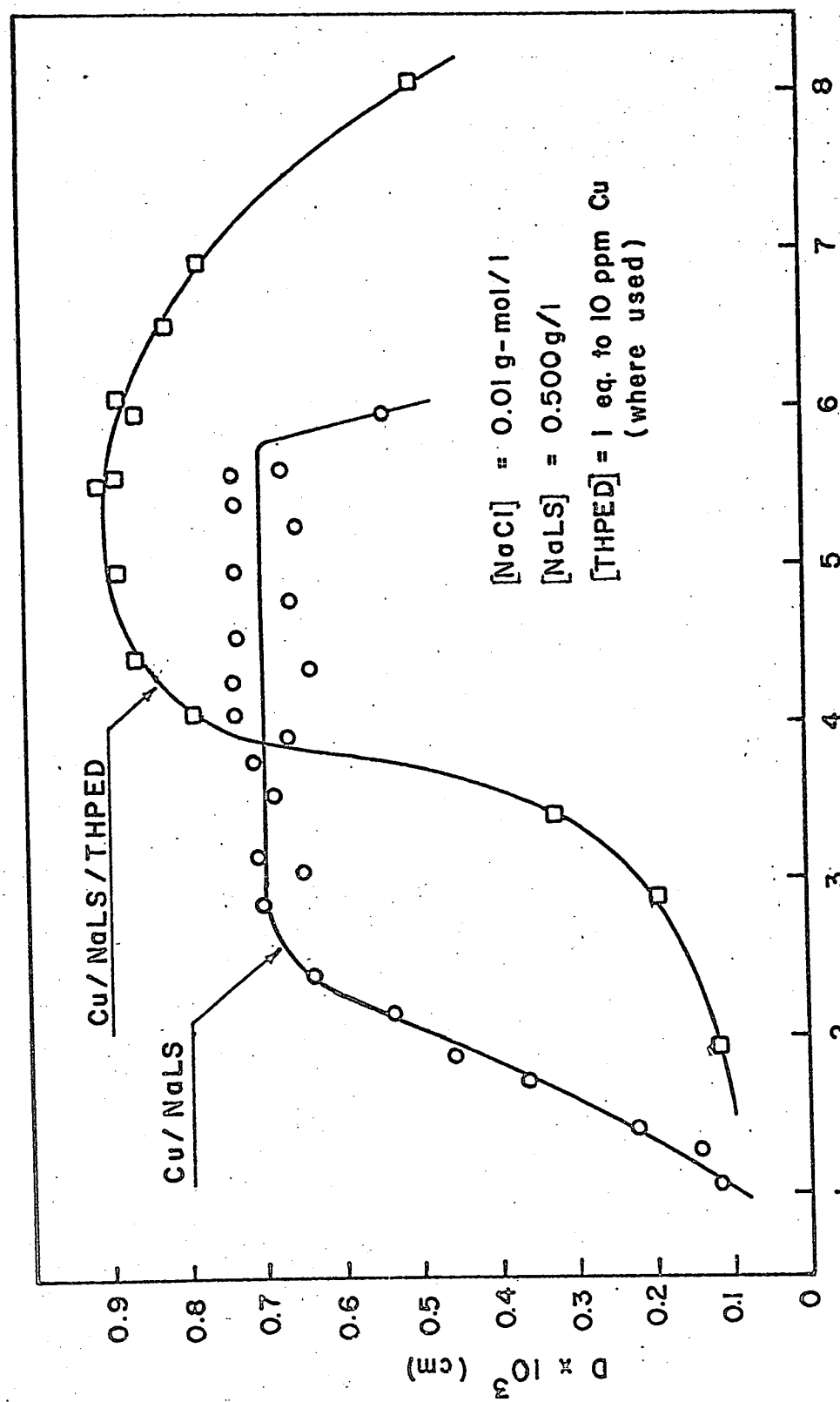

Figure 8: Distribution Factor versus pH for the Systems Cu/NaLS and Cu/NaLS/THPED

From pH 3.0 to pH 5.7, the distribution factor remains constant at a value of 0.7×10^{-3}cm. This region most likely corresponds to the discharge of the zeta potential by cupric and sodium ions only. At about pH 5.7 however, the distribution factor suddenly decreases and this is due to the formation of $Cu(OH)_2$ and the concomitant removal of Cu^{2+} from solution.

The addition of the powerful ligand THPED in stochiometric proportions to the amount of copper present causes the optimum pH range for foaming to be narrowed down to a value between pH 4.9 and pH 5.6. At the same time however, the distribution factor is increased by almost 30% to a value of 0.90×10^{-3} cm. The increase in the distribution factor is likely a result of the surface activity of the large metal-organic ion which is more readily adsorbed into the diffuse layer (26).

The same arguments can be used to explain the shape of the distribution factor versus pH curve for this system as were used for the Cu/NaLS system. At low pH values, both the lauryl sulfate anion and the THPED molecule are complexed with H_3O^+. As the pH rises however, the chelate formation between the cupric ion and the THPED is favored. That this is so may be seen from figure 9 which is a plot of the fraction of Cu^{2+} complexed vs. the pH with one stochiometric equivalent of THPED (to 10 ppm copper) present. The curve of figure 9 was calculated from cupric ion activities determined potentiometrically using a specific ion electrode. (see also App. B)

It is obvious that the increase in the fraction of cupric ion complexed is paralleled by an increase in the distribution factor (normalized). The dotted portion of the curve below pH 2.65 corresponds to complexation of the cupric ion by the nitrate anion added as HNO_3 for pH adjustment. As the pH rises further, complex formation of Cu(THPED) occurs decreasing the cupric activity and increasing the amount of Cu(THPED) available to the double layer.

On reaching pH 5.6 , the distribution factor begins to decrease, most likely due to the removal of Cu(THPED) from solution by the formation of $Cu(THPED)(LS)_2$. The formation of the latter compound is assumed because the lauryl sulfate anion is the salt of a strong acid while THPED is basic; in fact, a blue precipitate did form and settle out of solution on standing for 24 hours.

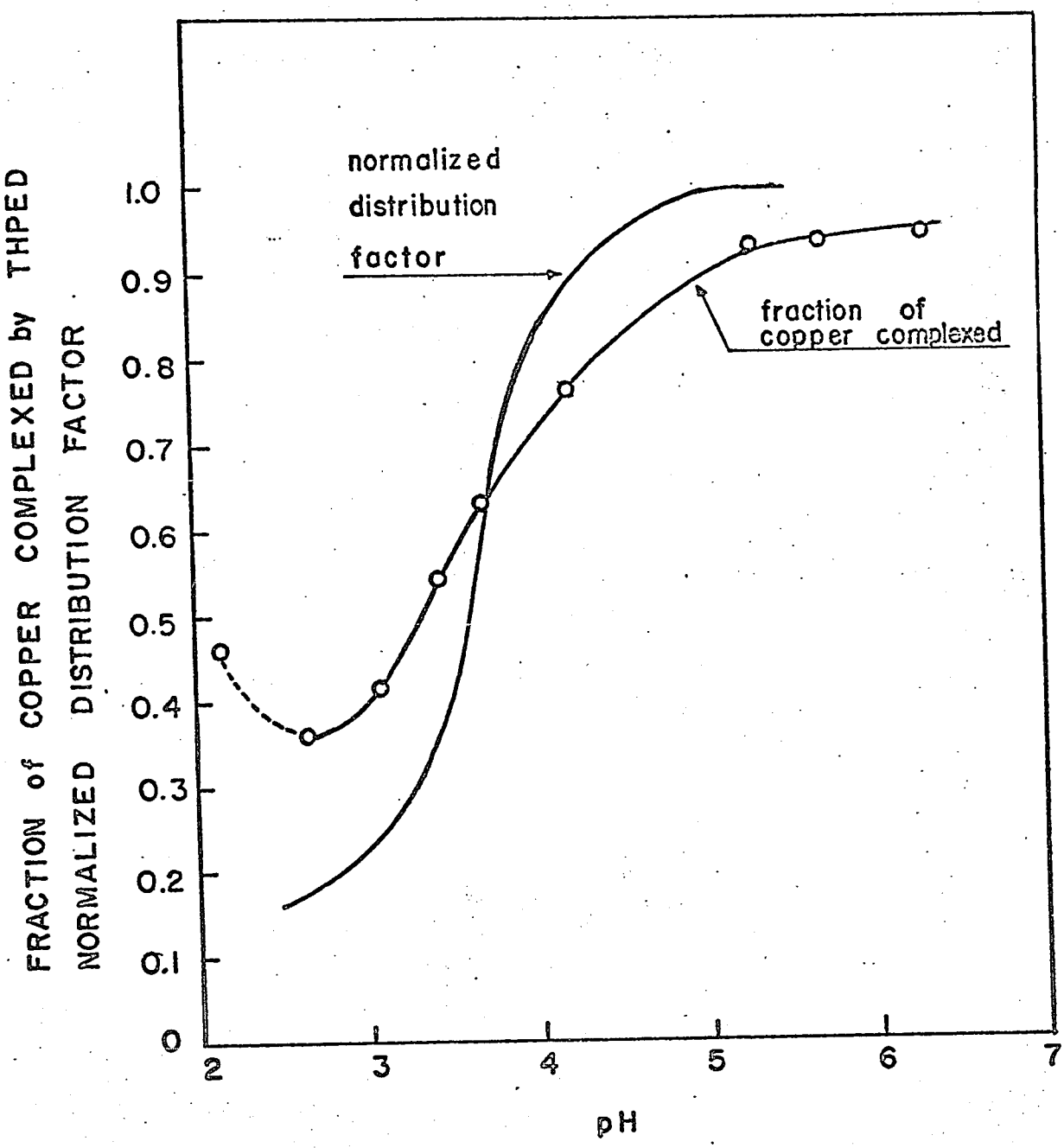

Figure 9: Total fraction of copper complexed and Normalized distribution factor vs. pH

5. The Effect of Auxilliary Ligand Concentration

Because of the promising results obtained by adding the auxilliary ligand, the next set of runs were performed with varying THPED concentrations. These runs were all carried out at the optimum pH of 5.5 ± 0.1 , using a feed concentration of 10.00 ppm copper and 0.010 mol/l sodium chloride. The results of these runs are plotted in figure 10 and tabulated in table 4, Appendix E.

From figure 10 it may be seen that the distribution factor increases rapidly from 0.7×10^{-3} cm. to 0.9×10^{-3} cm. as the THPED concentration is increased from zero to 1/2 equivalent. It then remains essentially constant until six equivalents of THPED have been added at which point it begins to decrease. Because the pH is optimum for the complexation of copper with THPED, the effect of even slight amounts of added ligand is great, and so the distribution factor reaches its maximum value very quickly.

As more THPED is added, it will increase the amount of copper complexed only slightly and the effect is therefore too small to be noticed. Eventually however, a point is reached where the THPED interferes by its very concentration as it begins to compete with the lauryl sulfate anions for positions at the surface. Because it has no charge, it will contribute little to the surface excess of copper since it is

present in such excess that relatively few THPED molecules are complexed with copper.

It is to be expected that similar results could be obtained with any large uncharged organic molecule which had a large cupric complex formation constant, and which did not react with the surfactant, sodium lauryl sulfate. Conversely, if the auxilliary ligand - copper complex were negatively charged (such as the Cu-EDTA* complex), no enrichment should occur since the ligand would effectively sequester the cupric ions.

* EDTA is the convenient abbreviation for ethylenediamine-tetraacetic acid.

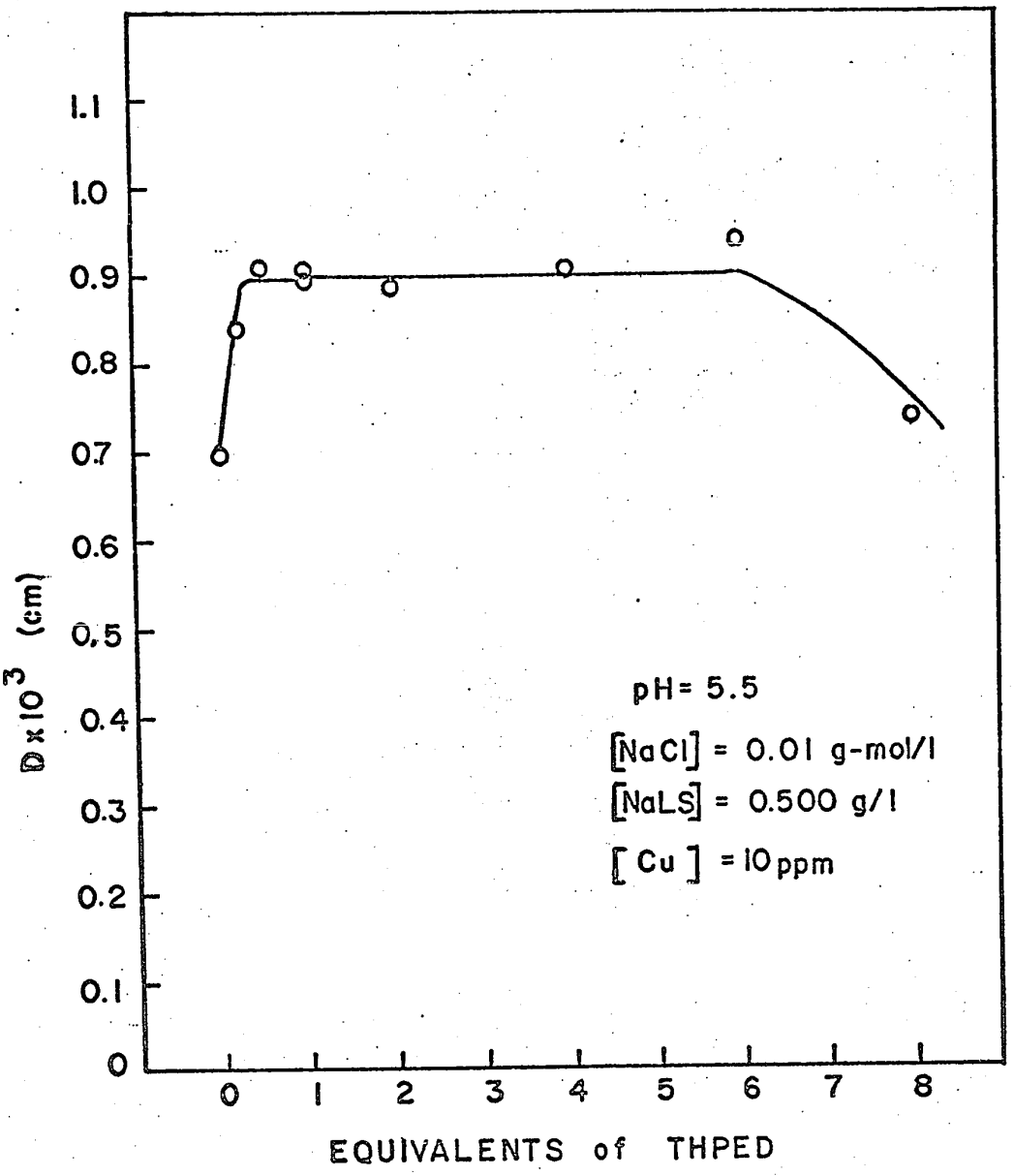

Figure 10: The Effect of THPED Concentration on the Distribution Factor.

6. The Effect of Electrolyte Concentration

The effect of the background electrolyte concentration was studied next, for both the simple system, and with added THPED. Copper concentration was held constant at 10 ppm, NaLS at 0.500 g/l, and where used, 1 stochiometric equivalent of THPED. For all runs without THPED, the pH was held at 5.0, and with THPED, pH was 5.5 . These results are plotted in figure 11, and tabulated in tables 5 and 6 of Appendix E.

For the simple Cu/NaLS system the effects of even slight amounts of NaCl are drastic: the distribution factor decreases rapidly from a maximum of 1.04×10^{-3} cm. to a value of 0.042×10^{-3} cm. as the concentration of NaCl is raised from zero to 0.1 g-mol/l. Further increase in the NaCl concentration results in the decrease of the distribution factor to zero. This is typical of the response of a simple cation/surfactant system to added electrolyte, and is essentially the same as the results found by Schonfeld et.al. for NaCl and many other electrolytes (11).

For the system with added THPED however, the opposite effect is noted as the NaCl concentration is raised from zero to 0.01 g-mol/l. In this range the distribution factor increases from 0.83×10^{-3} cm. to 0.9×10^{-3} cm. . The reason for this behavior is not completely understood but Schonfeld (5) has suggested that a surface active chelate can be "salted out" by the addition of a background electrolyte.

From 0.01 g-mol/l up, the distribution factor decreases rapidly at first, and then more slowly until the limiting value of zero is reached asymptotically.

The advantages of utilizing THPED are readily apparent when figure 12 is studied. There, the ratio of the distribution factors with and without THPED are plotted as a function of the NaCl concentration.

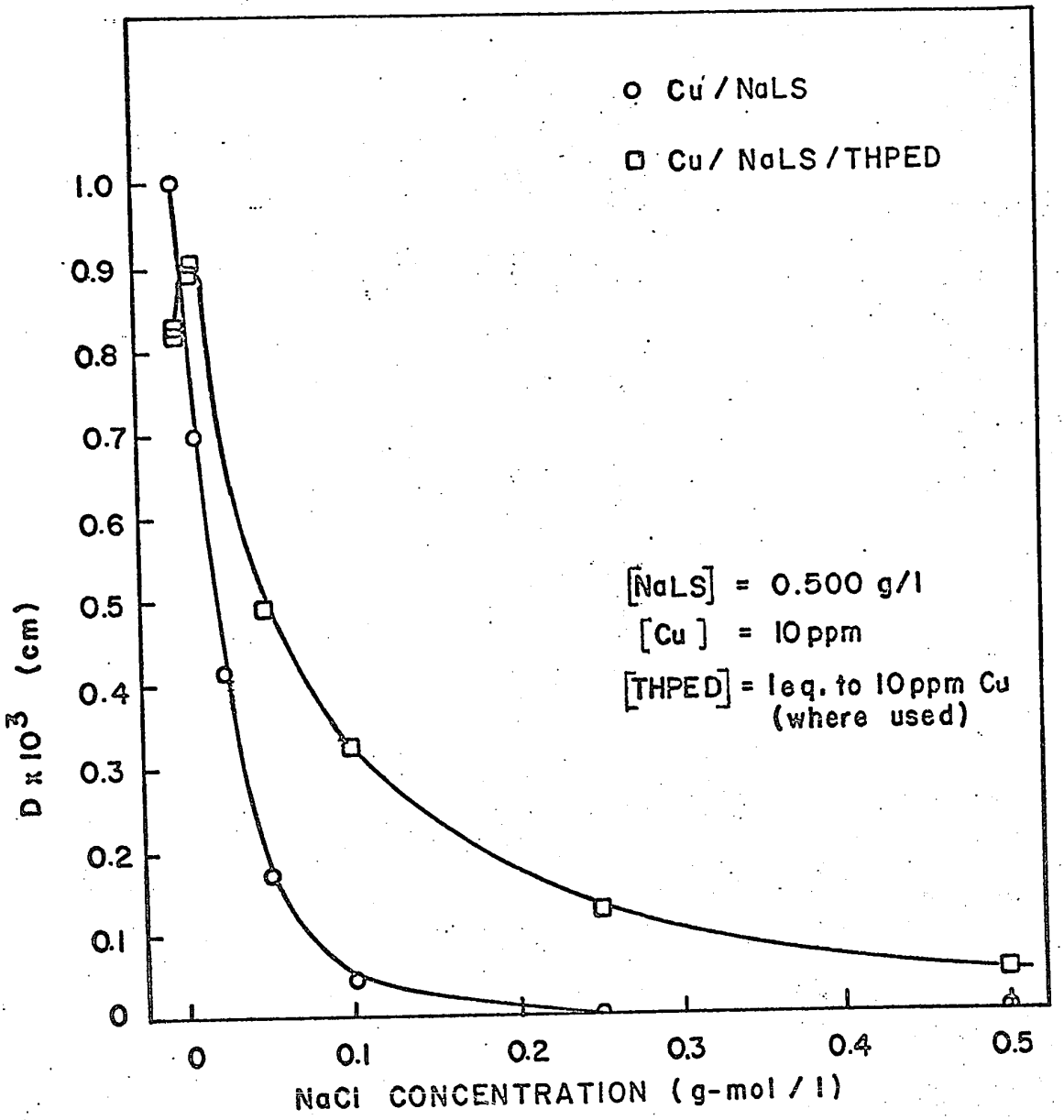

Figure 11: Distribution Factor vs. NaCl Concentration

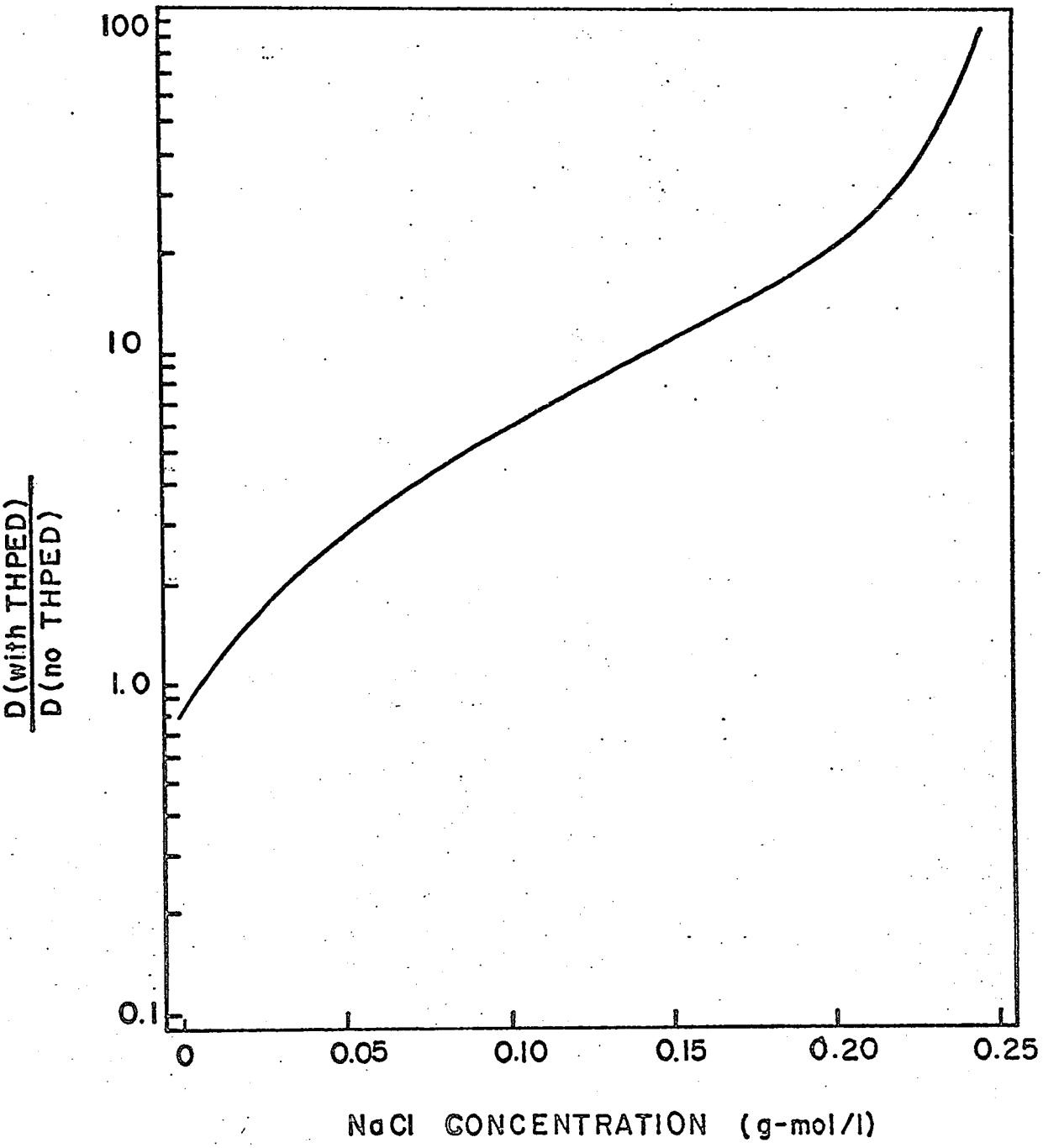

Figure 12: Ratio of Distribution Factors with and without THPED as a Function of the Concentration of sodium chloride

7. The Effect of Surfactant Concentration

For the next series of runs the concentration of NaLS was varied while holding all other parameters constant. As before, the simple system was run at pH 5.0 while those runs with added THPED were carried out at pH 5.5 . These results are plotted in figure 13 and tabulated in tables 7 and 8 in Appendix E.

It is apparent that the optimum concentration of NaLS for the simple system is 0.500 g/l. Below that figure, the distribution factor decreases and this is due to the fact that the bubble surface is not completely packed with NaLS, ie: a monolayer has not formed, therefore the maximum adsorption of colligand cannot occur.

As the sodium lauryl sulfate concentration increases above 0.5 g/l however, no additional surfactant is adsorbed on the surface and the additional surfactant remains in the bulk and competes with that in the surface for the available cupric ion, thus lowering the distribution factor.

The addition of THPED however, shifts the optimum NaLS concentration to 0.25 g/l. Above 0.25 g/l the distribution factor decreases at a much faster rate than that of the simple system, and in fact the two curves cross at 1.1g/l NaLS. Higher concentrations of NaLS than 1.1 g/l therefore result in THPED lowering the distribution factor to a value below that of the simple system. This effect may be due to the formation of $Cu(THPED)(LS)_2$ as noted previously.

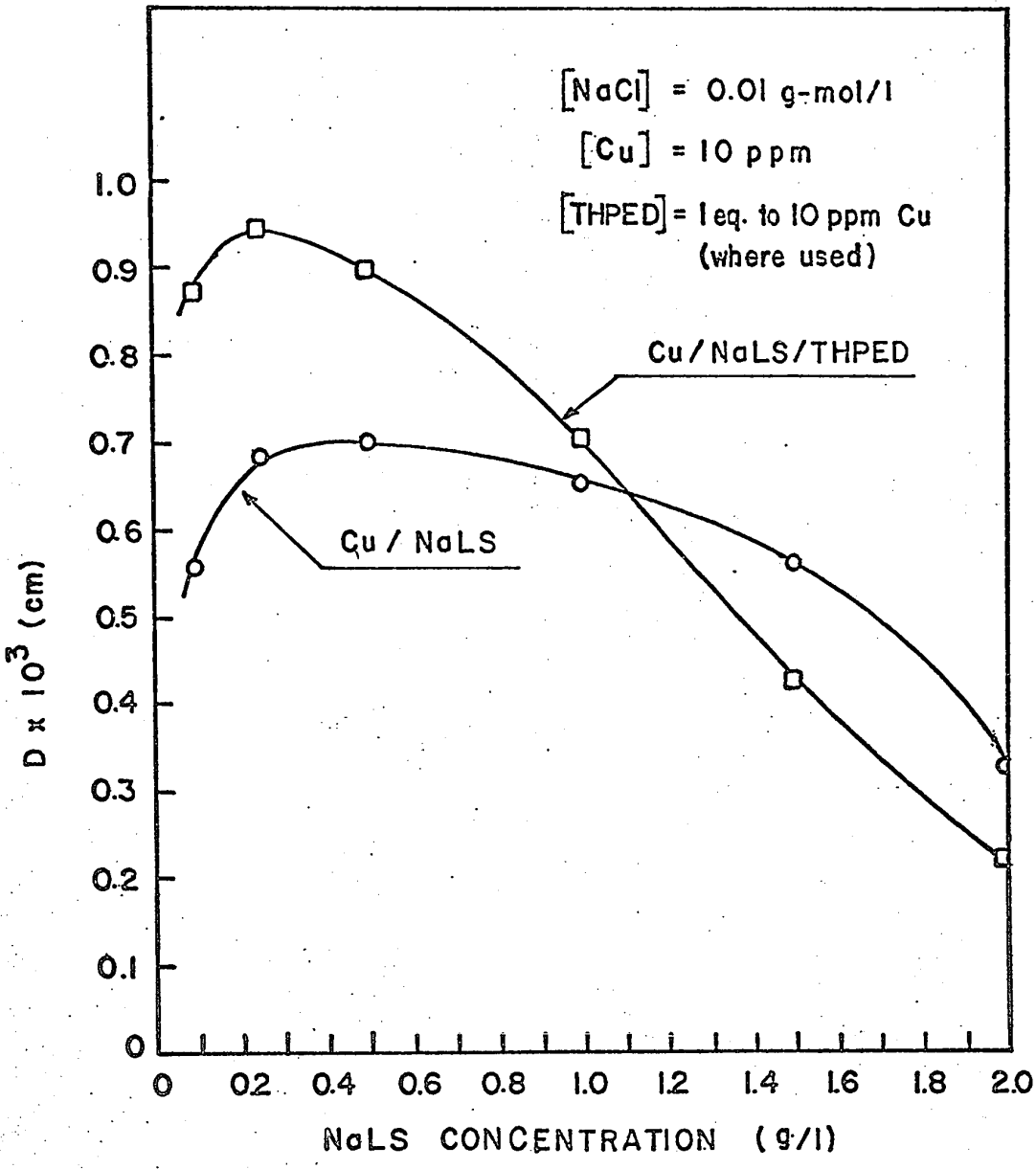

Figure 13: Distribution Factor vs. NaLS Concentration

8. The Effect of Bulk Copper Concentration

The final variable studied was the effect of the bulk concentration of copper on the surface excess and the distribution factor. For this series of runs the surfactant concentration was held at 0.500 g/l, the salt background at 0.010 g-mol/l, and where used, the THPED was added as one stochiometric equivalent to the amount of copper in the run. These results are plotted in figure 14 and listed in tables 9 and 10 in Appendix E.

It is seen that the distribution factor increases rapidly as the bulk copper concentration decreases from about 10 ppm. For the system with added THPED however, the rate of increase is considerably faster than for the simple system. Conversely, the distribution factors for both systems approach zero assymptotically as the bulk concentration of copper becomes very large.

The reason for the foregoing behavior is more readily apparent when figure 15, the graph of surface excess versus bulk concentration, is studied. The distribution factor, which is the slope of the Γ_C vs. X_B curve, is seen to be a maximum in the low concentration region where the curve is linear and the slope a maximum.

It is difficult to predict from figure 14, what the maximum distribution factor will be for each system. Similarly, figure 15 cannot be used to predict the maximum possible slope. From figure 16 however, which is a plot of

the distribution factor versus the bulk copper concentration on log-log coordinates, it is seen that the distribution factors are levelling out and approaching a maximum value of about 8 and 4 respectively for the systems with and without added THPED.

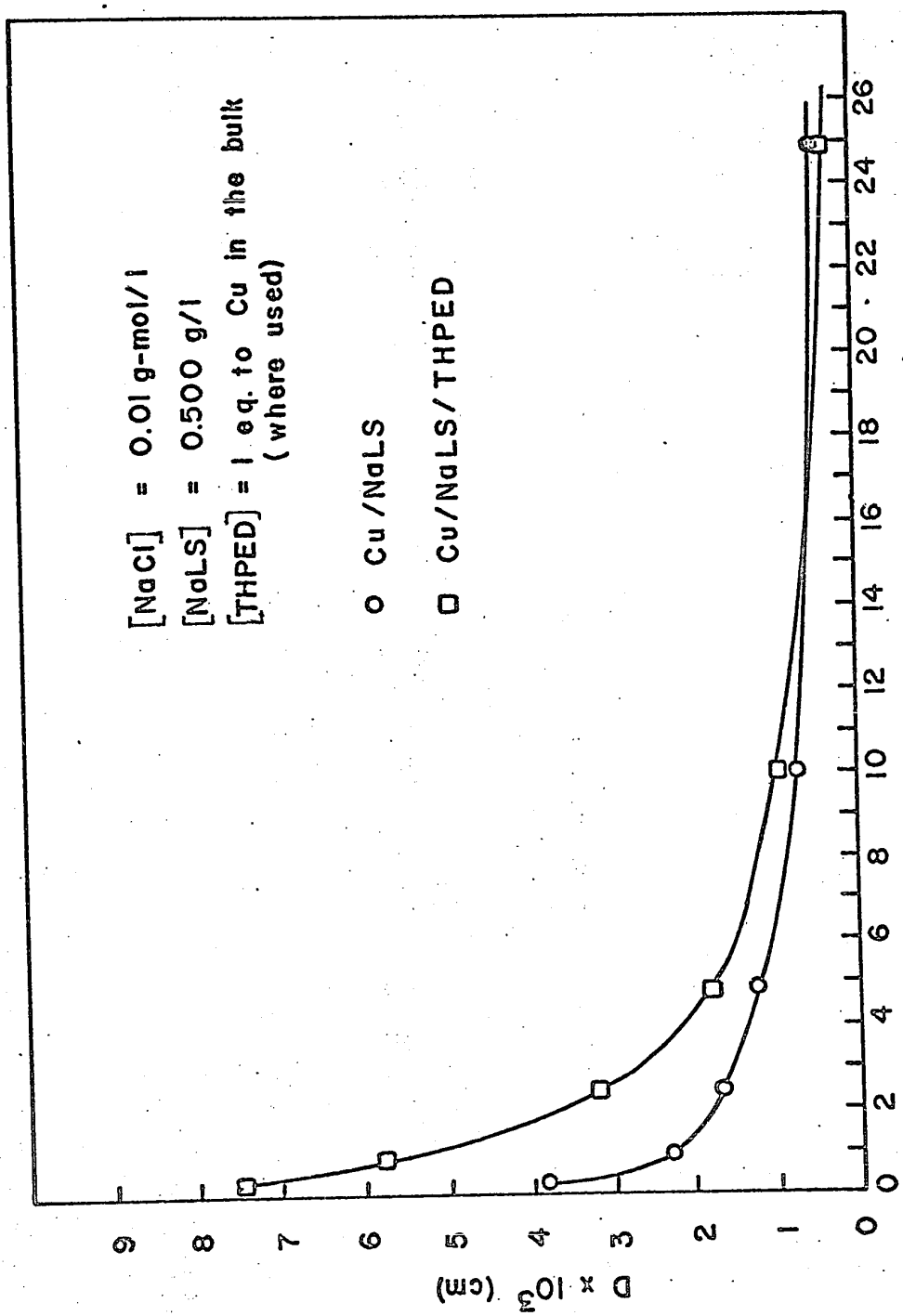

Figure 14: Distribution Factor versus Bulk Copper Concentration

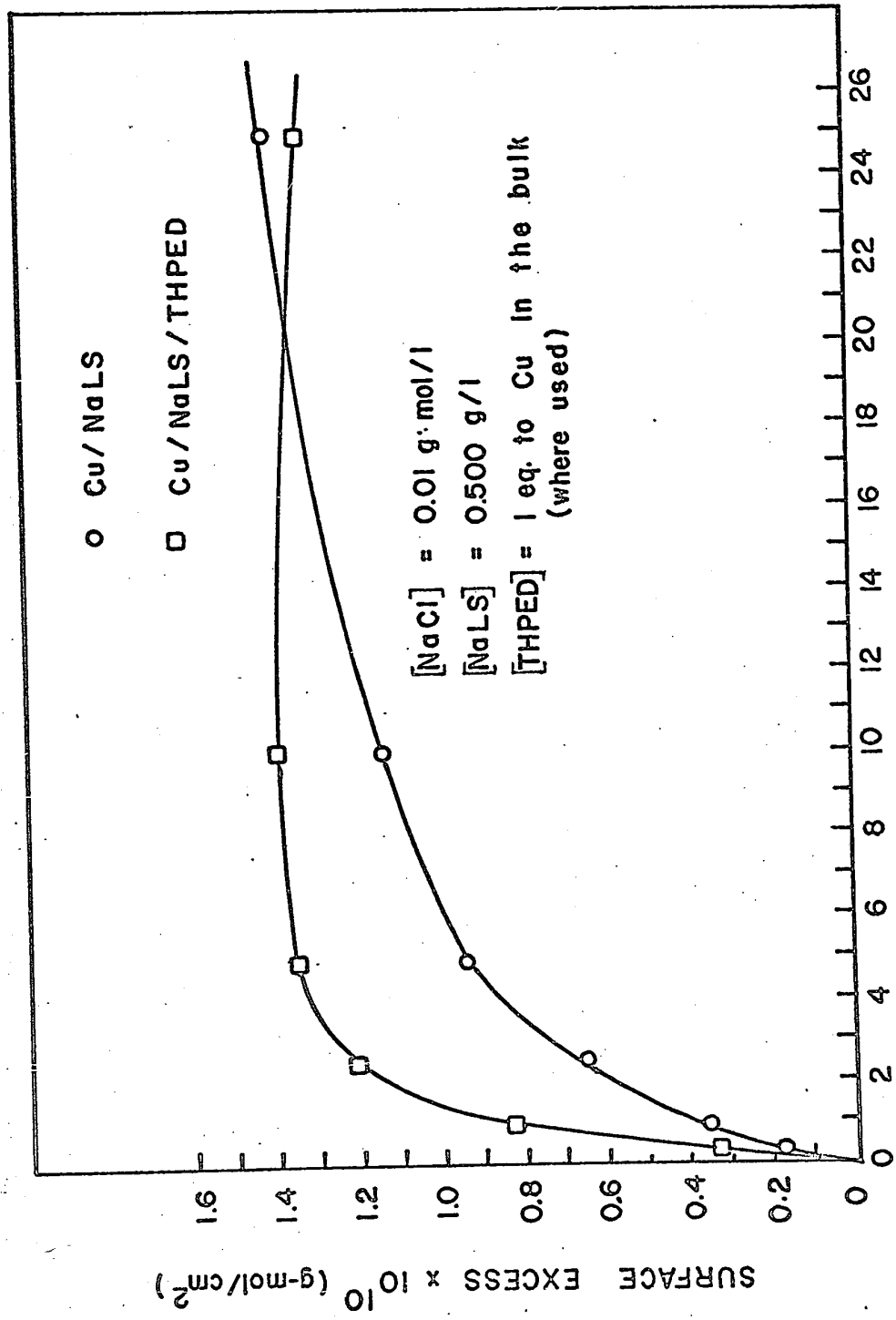

Figure 15: Surface Excess versus Bulk Copper Concentration

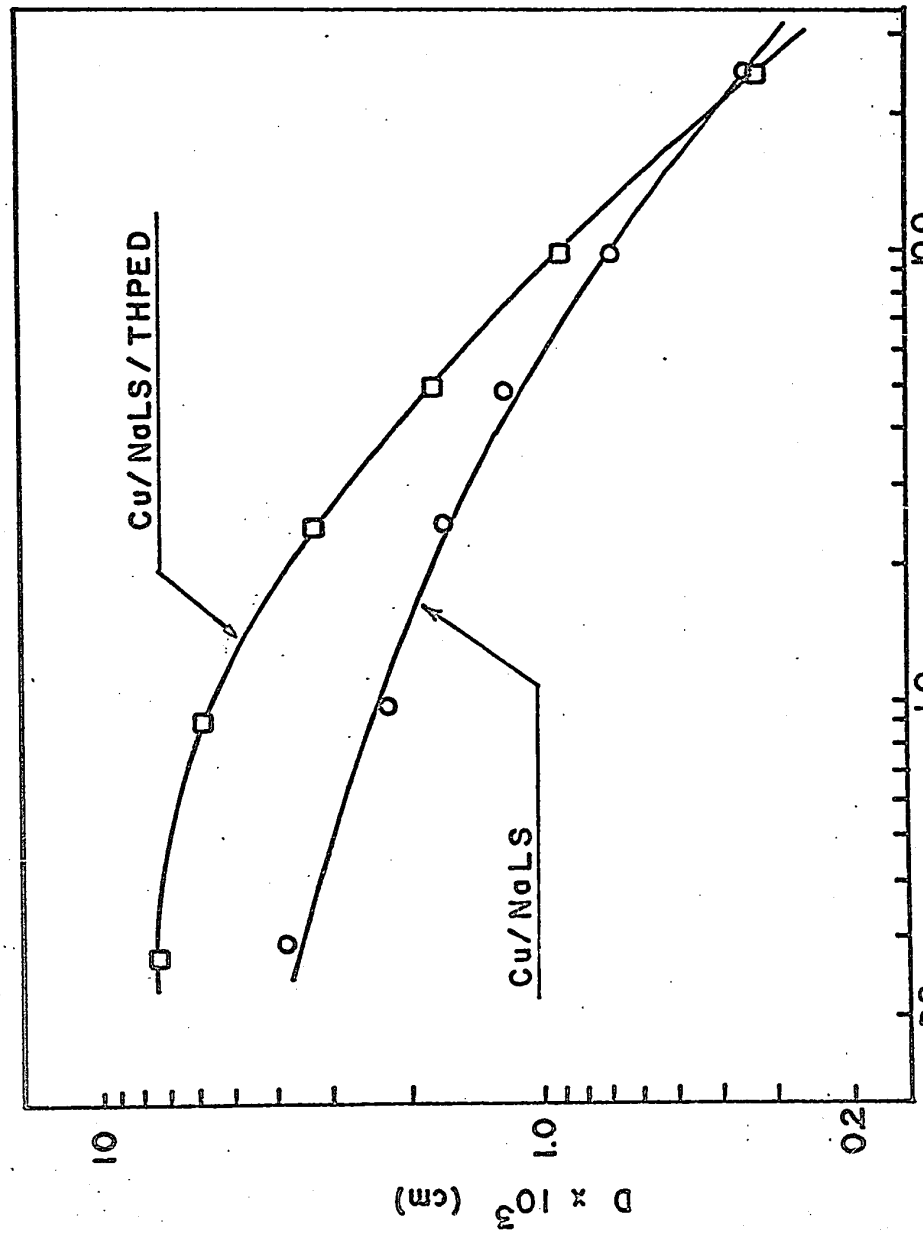

Figure 16: Distribution Factor vs. Bulk Copper Concentration

9. The Effect of Added Ethylenediamine

Because of the improvement in the separation of copper by the addition of THPED, it was decided to add the unsubstituted amine, ethylenediamine, to the Cu/NaLS system. One equivalent (to 10 ppm Cu) was therefore added to the feed solution containing 0.500 g/l NaLS, 0.0100 g-mol/l NaCl, and 10.00 ppm copper. The pH was then varied within the range from 3 to 10.

The solutions were found to be extremely sensitive to pH: below pH 5.0 , a white precipitate formed immediately, while above pH 6.8 a deep purple precipitate formed as soon as the ethylenediamine was added to the feed. Within the range of pH values from 5.0 to 6.8 there was no immediate precipitation, however a deep blue precipitate formed within 30 minutes in all cases.

Notwithstanding the foregoing, the surface excess, and therefore the distribution factor, was higher than that obtained using THPED as the auxilliary ligand. The results were quite scattered, and a heavy precipitate was present in the foamate from each run . It is concluded therefore that a precipitate flotation process (16) and not true foam fractionation caused these results. The data obtained are plotted in figure 17 and tabulated in table 11 in Appendix E. The D vs. pH curves for the Cu/NaLS and Cu/NaLS/THPED systems are plotted for comparison .

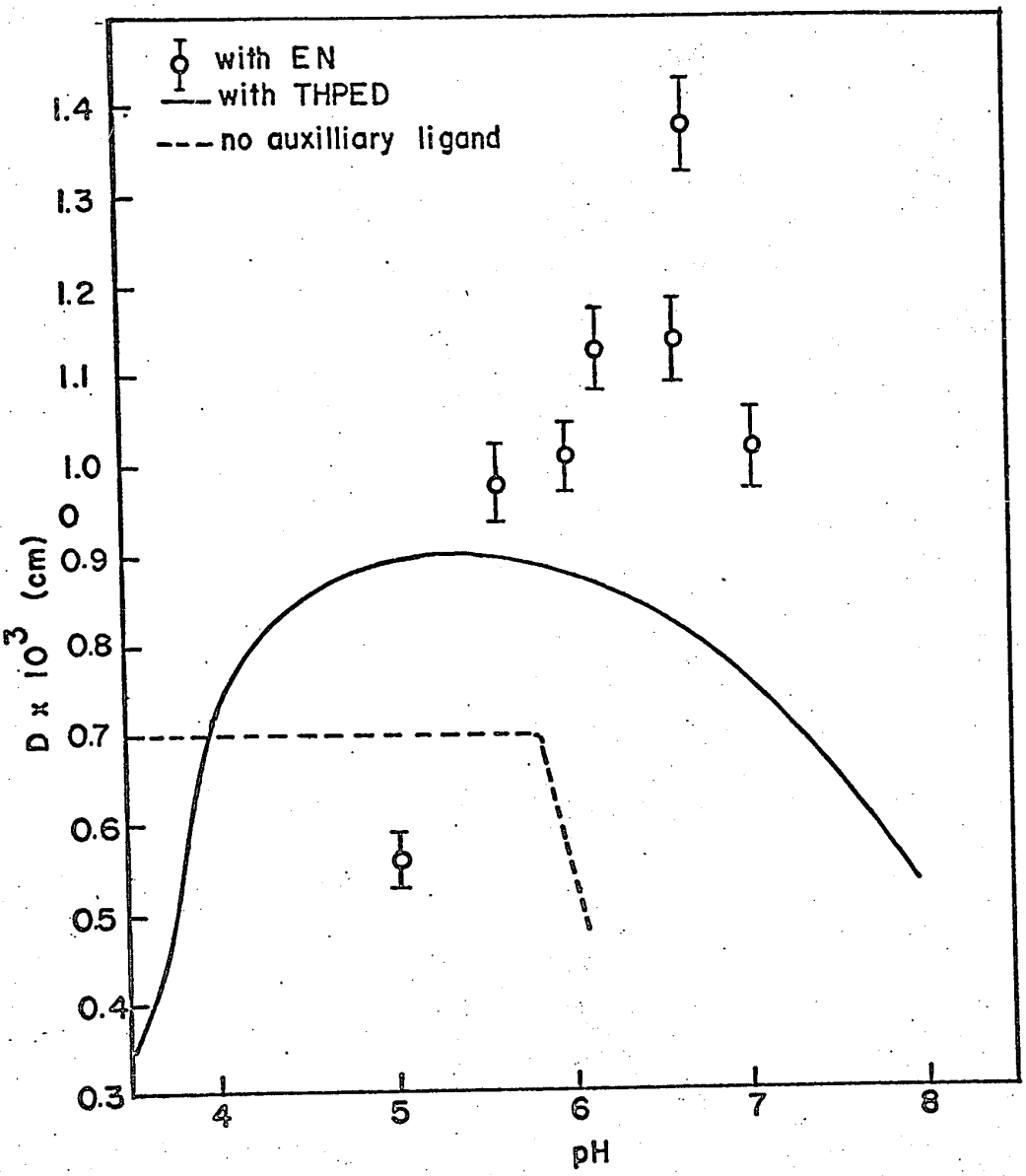

Figure 17: Distribution Factor versus pH with added Ethylenediamine.

VI DISCUSSION

It is obvious from the experimental results that there is an exponential dependence of the surface excess upon the concentrations of the H_3O^+, Na^+, and Cu^{2+} ions in the bulk. An attempt was therefore made to develop an equation describing the simple system and which would account for the pH, NaCl concentration, and the bulk concentration of copper.

The adsorption of cupric ions is described by equation (9) where $K_1 = 0.004$ cm. and $K_2 = 1.75 \times 10^7$ cm.^{3}/g-mol:

$$\Gamma_c = K_1 X_B / (1 + K_2 X_B) \qquad (9)$$

The use of the Langmuir form of equation has no particular significance other than that a two constant exponential equation fits the data more accurately than a one constant equation such as eqn.(10) which describes the effect of added sodium chloride on the system:

$$\Gamma_c = \Gamma_{cmax} (10^{-K_3[NaCl]}) \qquad (10)$$

In the above equation, $K_3 = 15.75$ l/g-mol and Γ_{cmax} is the value of Γ_c at a given copper concentration when there is no added NaCl in the system, ie: $\Gamma_{cmax} = \Gamma_c$ of eqn.(9) . Equations (9) and (10) may therefore be combined to give the surface excess of copper as a function of both the added sodium chloride and the bulk copper concentration, eqn. (11) ;

$$\Gamma_c = (K_1 X_B/(1 + K_2 X_B))10^{-K_3[NaCl]} \qquad (11)$$

The influence of the pH on the distribution factor can be accounted for by multiplying eqn.(11) by the term $10^{-K_4[H_3O^+]}$ and this correction will be valid provided the precipitation of copper hydroxide has not begun; ie: the pH of the system is less than about 5.75. The value of K_4 is 14.5 l/g-mol. The system equation is therefore:

$$\Gamma_c = (K_1 X_B/(1 + K_2 X_B))10^{-K_3[NaCl]-K_4[H_3O^+]} \qquad (12)$$

Equation (12) has been used to calculate values of the surface excess as a function of NaCl concentration, bulk copper concentration, and the pH. The calculated curves and the experimental values are plotted in figures 18, 19, and 20. In each case, the calculated and experimental values agree within the limits of the experimental error.

The addition of THPED to the system appears to be advantageous except under the following circumstances:

a) in the absence of electrolyte,

b) if the solution pH is less than 4,

c) the surfactant concentration is greater than 1.0 g/l, and

d) the bulk copper concentration is greater than 20 ppm.

In particular, THPED enhances the separation by a considerable degree when the bulk concentration approaches zero or if there is much electrolyte present.

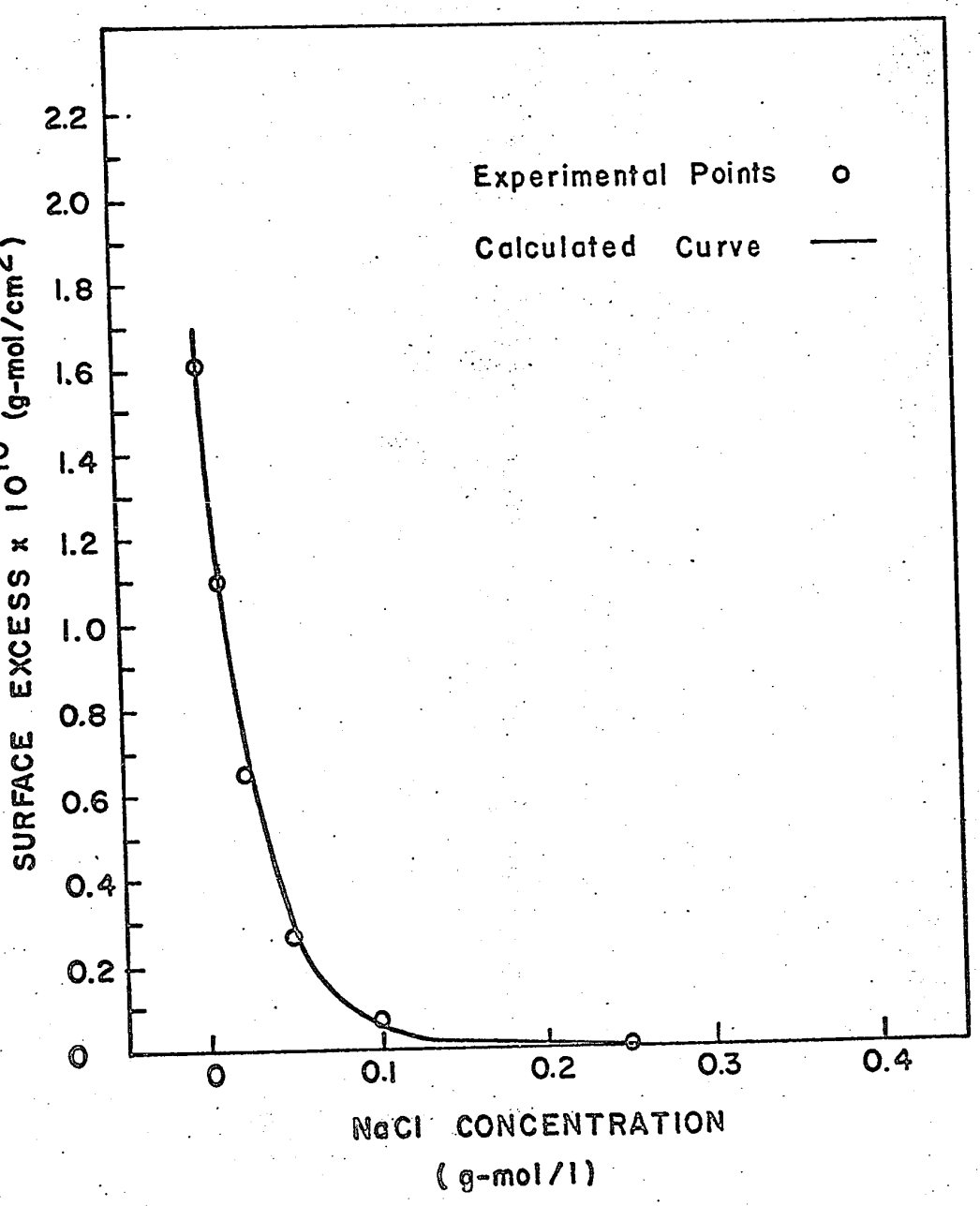

Figure 18: Surface Excess vs. Concentration of NaCl
Calculated and Experimental Values

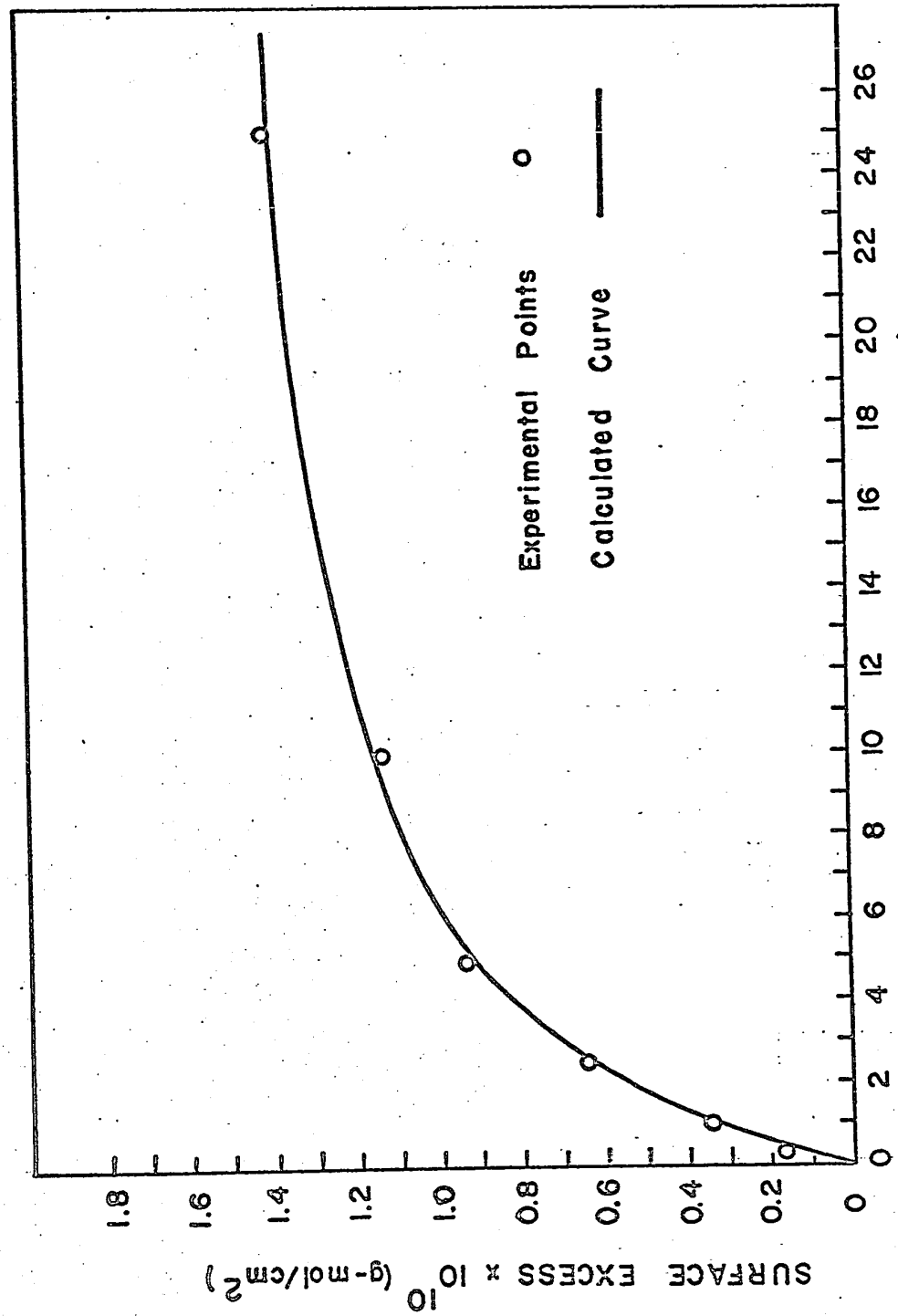

Figure 19: Surface Excess versus Bulk Concentration of Copper
Calculated and Experimental Values

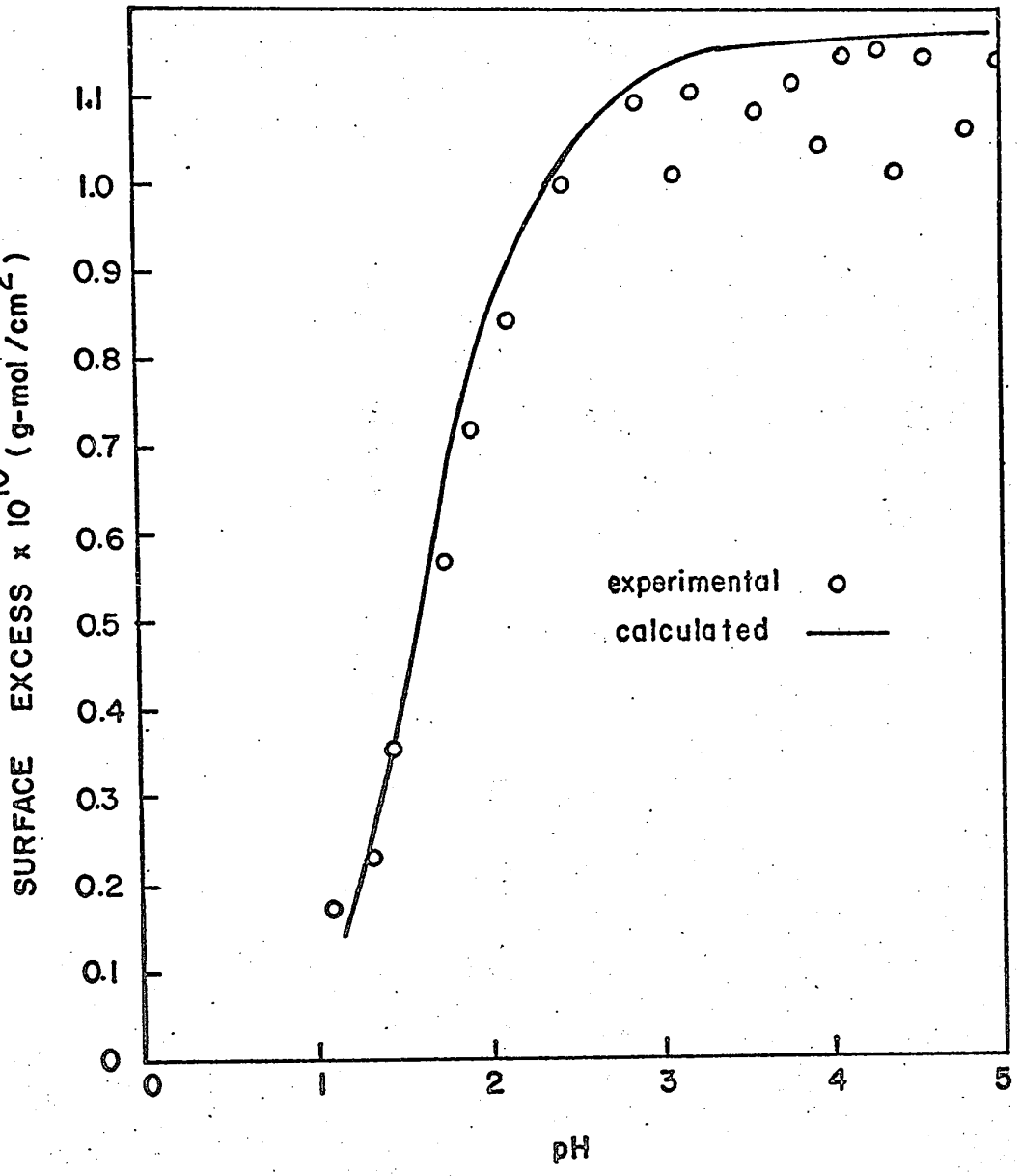

Figure 20: Surface Excess versus pH , Calculated and Experimental Values

VII CONCLUSIONS

Based on the studies carried out using a single stage foam fractionating unit it was concluded that:

a) the optimum conditions for the foam fractionation of aqueous solutions of cupric ions with sodium lauryl sulfate are as follows:

   i) pH range between 3.0 and 5.7 ,

   ii) NaLS concentration of 0.5 g/l ,

   iii) the efficiency increases with decreasing electrolyte concentration,

   iv) the efficiency increases with decreasing bulk copper concentration,

b) the simple Cu/NaLS system is quantitatively described, within the limits of the experimental data obtained, by equation (12) provided that the surfactant concentration is such that a complete monolayer is formed, but not so high that it competes with the surface for the available copper,

c) the basis for the foam fractionation of metals is the attraction of the charged surface layer of surfactant molecules for the cations in the diffuse layer, and the concentration of cations within the diffuse layer is greater than in the bulk,

d) the attraction of the surface layer for a given species of cation can be increased by complexing the cation with

a large organic molecule such as THPED. Thus the addition of THPED will increase the distribution factor above that of the simple system provided that:

i) the pH is between 3.9 and 7.3,

ii) the electrolyte concentration is at least 0.01 g-mol/l,

iii) the surfactant concentration is less than 1 g/l,

iv) the bulk copper concentration is less than 20 ppm.

VIII RECOMMENDATIONS FOR FUTURE WORK

The ability of the auxilliary ligand THPED to improve the distribution factor of the Cu/NaLS system opens up new vistas for foam fractionation. It should be possible to selectively separate a desired metal ion from a multicomponent solution by choosing an auxilliary ligand which will selectively complex the desired metal into a more surface active form. Conversly, the addition of ligands which will effectively sequester interfereing ions, thus removing them from the bulk-surface equilibrium, could be an important means of separation for multicomponent systems. Both of the foregoing suggestions should be completely investigated.

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APPENDIX A

QUANTITATIVE ANALYSIS OF COPPER

Quantitative Analysis of Copper

All preliminary runs, including runs numbered 1 to 32 were analysed using a Unicam Model SP90a Atomic Absorption Spectrophotometer. Unfortunately, physical interferances caused by the presence of the surfactant in the foamate limited the accuracy of the method to ± 1 ppm. Many methods were devised in an attempt to overcome these problems but none was consistantly better than ± 1 ppm.

It was therefore decided to use the SP90a as a colorimeter, and to this end a bracket was constructed to hold a 50 mm light path absorption cell in the light path of the instrument. The method of Geiger and Muller, as reported by Sandell (29) was used to prepare the sample for absorption measurments. By adding a few drops of an alcoholic solution of dihydroxyethyldithiocarbamic acid to a dilute buffered cupric solution, a yellow-brown soluble copper(II) complex salt is formed which is strongly absorbent in the region of 4300 to 4400 A°. The procedure used is as follows:

a) 2.00 ml. of foamate and 50 ml. of copper free water are pipetted into a 100 ml volumetric flask.

b) 5.0 ml. of 0.5 M $NaHCO_3$ solution is added to the flask.(pH is then buffered to between 7 and 8)

c) 0.2 ml. of the reagent (see below) is then added to the flask and distilled water is added to the mark.

d) a 50 mm light path absorption cell is filled with the above solution and the absorbance measured at 4370 A°.

The reagent solution is easily prepared by treating 10 g. of diethanolamine in 85 ml. of methanol with 1.0 g. of carbon disulfide and diluting to 100 ml with methanol. Fresh reagent was prepared immediately prior to the analysis as it was found that after a few days the reagent would form a white precipitate when added to the foamate solution.

In the computer program, Appendix D, a best fit procedure was used to linearize the absorbance versus concentration of cupric standards within the range of 10 to 30 ppm copper. Sample concentration was then obtained by substituting the absorbance into the equation for the line. In general, scatter was very slight and Beers Law appeared to hold well for copper concentrations between 10 and 30 ppm for direct readings, and between 0 and 10 ppm for x2 scale expansion on the SP90a.

The results obtained by this method were consistent and duplicate determinations never differed by more than 0.25 ppm.

APPENDIX B

CUPRIC ION ACTIVITY MEASUREMENTS

Cupric Ion Activity Measurements

Cupric ion activities were determined at varying pH by using the recently developed (31) cupric ion electrode. The particular electrode used was an Orion model 94-29-00 solid state cupric electrode , and an Orion model 90-01 single junction reference electrode. All potentials were measured using an Orion model 601 pH/m.v. meter.

A calibration curve was prepared using cupric concentration/activity standards prepared from Orion 0.1000 g-mol/l $Cu(NO_3)_2$ solution. These data are plotted in figure 21 and tabulated in table 1(a).

A typical feed sample was then prepared using 0.500 g/l NaLS, 0.0100 g-mol/l NaCl, 10.00 ppm copper, and 1 eq. (to 10 ppm copper) THPED. The cupric ion activity of 250 ml. samples was then measured at different pH's from 1.75 to 6.70 . Since the original copper concentration was known and since the free copper concentration is equal to the activity, the concentration of copper bound up in all complexes (with THPED, Cl^-, NO_3^-, and OH^-) could be determined.

No thermostat was used and no attempt was made to determine the contribution of any individual ionic species to the complexation. The results of these studies are plotted in figure 9 (page 31) and tabulated in table 1(b).

TABLE 1(a)

Cupric Ion Electrode Calibration

Copper concentration (g-mol/l)	Copper activity (g-mol/l)	Electrode potential (m.v.)
10^{-5}	10^{-5}	+94.4
10^{-4}	9.2×10^{-5}	+122.2
10^{-3}	7.9×10^{-4}	+151.0

TABLE 1(b)

Cupric Ion Activity versus pH

pH	Electrode potential (m.v.)	Cupric activity x 10^5 (g-mol/l)	Concentration of copper complexed x 10^5 (g-mol/l)	fraction of copper complexed
1.75	118.7	6.7	8.95	0.569
2.15	121.5	8.5	7.25	0.461
2.65	123.5	10.0	5.75	0.365
3.08	122.1	9.2	6.55	0.416
3.42	119.2	7.2	8.55	0.543
3.68	116.5	5.8	9.95	0.632
4.20	109.6	3.7	12.05	0.765
5.28	97.5	1.07	14.67	0.932
5.73	94.8	1.02	14.73	0.936
6.30	91.7	0.84	14.9	0.947
6.70	89.2	0.69	15.06	0.957

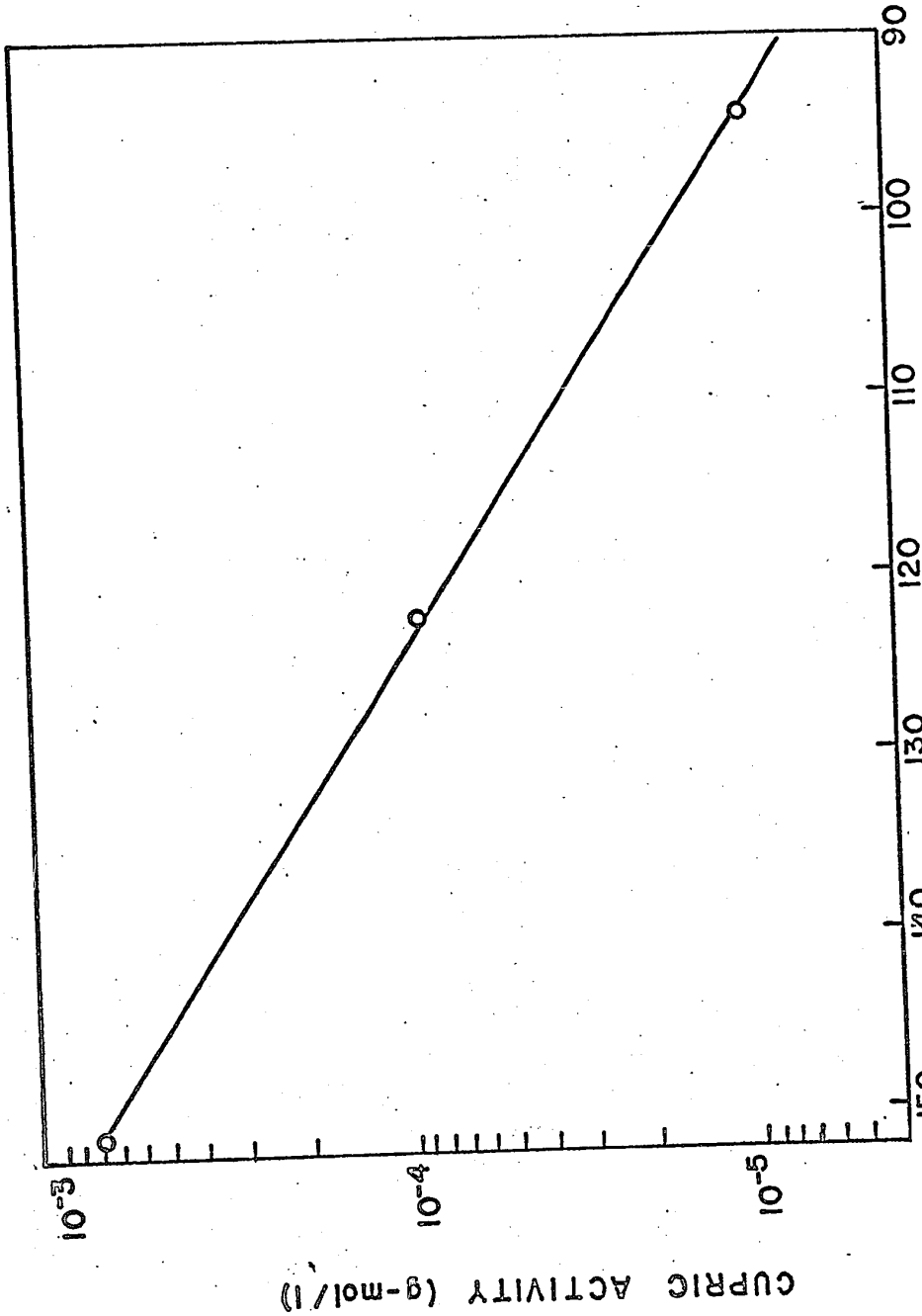

Figure 21: Cupric Ion Electrode Calibration Curve

APPENDIX C

LAURYL SULFATE DIFFUSION

Lauryl Sulfate Diffusion

Equations for the diffusion of a surfactant starting from a zero surface concentration were derived by Ward and Tordai (32). The rate of diffusion to the surface for no back diffusion is:

$$\frac{d\Gamma}{dt} = \left(\sqrt{D^*/\pi}\right)\left(X/\sqrt{t}\right) \qquad (13)$$

where D* is the bulk phase diffusion coefficient in cm^2/sec, t is the time in seconds, and and X have their usual meaning. Assuming constant D* and X, and integrating eqn.(13) between the limits of $\Gamma = 0$ to Γ, and t=0 to t, and rearranging gives:

$$t = (\pi/4D^*)(\Gamma/X)^2 \qquad (14)$$

The diffusivity of the lauryl sulfate anion was determined using Wilkes' method as presented in Treybal (33). Using a molal volume of 318.5 $cm^3/g\text{-mol}$ at the normal B.P., the value of the diffusion coefficient was found to be $D^* = 4.6 \times 10^{-6}$ cm^2/sec. For the majority of experimental runs, the bulk concentration was 0.500 g/l of NaLS, and this corresponds to $X = 1.73 \times 10^{-6}$ $g\text{-mol}/cm^3$. The value of the surface excess has recently been reported (34) as $= 4.8 \times 10^{-10}$ $g\text{-mol}/cm^2$. Substituting the foregoing values into eqn.(14) it is found that the time required to form a complete monolayer of surfactant is 0.013 sec. Since the residence time of the bubbles within the bulk is approximately 0.5 sec., there is

ample time to complete the monolayer of surfactant.

In the case of run no. 103, where X_S = 0.100 g/l , equation (14) predicts a time of 0.33 sec for complete diffusion to occur, and this too is within the bubble residence time of 0.5 sec.

Ward and Tordai also developed a diffusion equation allowing for the back diffusion of surfactant. The same workers however, also found that the back diffusion of surfactant was negligable and that eqn.(14) gave adequate results.

APPENDIX D

COMPUTER PROGRAM

Computer Program

The following nomenclature has been used in the program:

ABSORB	the absorbance of a copper standard
STDCON	the concentration of the standard of ABSORB
NDATA	an integer counter for the number of points in the calibration curve
BESFIT	subroutine for a line of best fit
YINT	the y intercept of the line of best fit
SLOPE	the slope of the line of best fit
P , T	pressure and temperature
BUBRAT	bubble emission frequency
GASRAT	the gas flow rate at STP
G	the gas flow rate at the experimental conditions
XSUBB	the bulk phase copper concentration
FEEDXB	the feed concentration of copper
YABS	the absorbance of the sample
TIME	time of run in minutes
FOAMWT	the weight of foam collected in time TIME
PH	pH of the feed
VSUBF	volumetric flowrate of foam on a collapsed basis
BUBDIA	bubble diameter
GAMMAC	the surface excess of copper
SURFRT	the surface rate in cm^2/min
CUREM	the amount of copper removed in the foam during a run
CUNEW	the amount of copper left in the bulk after the removal of CUREM

ENDXB	the final bulk concentration at the end of a run
AVGXB	the average bulk concentration during a run
D	the distribution factor
ERROR	the maximum possible error in D in %.
DIFFXB	the error criteria for the iteration loop

```
C     THE FIRST PART OF THE PROGRAM CALCULATES THE BEST STRAIGHT LINE
C     BETWEEN ABSORBANCE AND STANDARDS CONCENTRATION FOR THE SYSTEM
C     COPPER-DIHYDROXYETHYLDITHIOCARBAMIC ACID.
C
0001        REAL NEWXB
0002        INTEGER RUN,NDATA
0003        DIMENSION ABSORB(10), STDCON(10)
0004      3 READ(1,12)NDATA
0005        DO 7 I=1,NDATA
0006      7 READ(1,11) STDCON(I), ABSORB(I)
0007        SLOPE=0.0
0008        YINT=0.0
0009      9 CALL BESFIT(STDCON,ABSORB,NDATA,1,YINT,SLOPE)
C
C     THIS NEXT PART OF THE PROGRAM CALCULATES THE SURFACE-EXCESS
C     AND THE DISTRIBUTION FACTOR .
C
0010        WRITE(3,30)
0011        WRITE(3,31)
0012        WRITE(3,32)
0013      1 READ(1,10) RUN,P,T,BUBRAT,GASRAT,XSUBB,YABS,TIME,FOAMWT,PH
0014        IF(RUN)2,3,4
0015      4 G=GASRAT*760.0/P*T/298.0
0016        FEEDXB=XSUBB
0017        VSUBF=FOAMWT/TIME
0018        YSUBF=(YABS-YINT)/SLOPE
0019        BUBDIA=(G*0.38197/BUBRAT)**0.33333
0020        SURFRT=15.70795*BUBRAT*BUBDIA*BUBDIA
0021      5 GAMMAC=VSUBF*(YSUBF-XSUBB)*1.573811E-8/SURFRT
0022        CUREM=GAMMAC*SURFRT*(TIME+10.0)
0023        CUNEW = (XSUBB*5.508335E-5 - CUREM)/3.50
0024        ENDXB=CUNEW/1.573811E-5
0025        AVGXB=(FEEDXB+ENDXB)/2.0
0026        DIFFXB=ABS(XSUBB-AVGXB)
0027        IF(DIFFXB.LE.0.001)GO TO 6
0028        XSUBB=AVGXB
0029        GO TO 5
```

```
0030            6 D=GAMMAC/(XSUBB*1.573811E-8)
                C
                C     THE NEXT EQUATION CALCULATES THE ERROR IN THE DISTRIBUTION FACTOR.
                C
0031              ERROR=100.0*(0.005/VSUBF + 0.005/XSUBB + 0.255/(YSUBF-XSUBB) +
                 1 0.9/GASRAT + (0.9/GASRAT + 100.0/BUBRAT)/3.0)

0032              WRITE(3,20)RUN,XSUBB,YSUBF,BUBDIA,SURFRT,GAMMAC,D,PH, ERROR
0033              GO TO 1
0034            10 FORMAT(I3,2F5.1,F5.0,2F4.1,F6.4,F5.2,F7.4,F5.2)
0035            11 FORMAT(2E10.4)
0036            12 FORMAT(I3)
0037            20 FORMAT(1X,I3,8X,F6.3,11X,F6.3,9X,F6.5,7X,F7.2,6X,E10.3,7X,E10.3,
                  15X,F5.2,5X,F5.2,/)
0038            30 FORMAT(1X,/,'                    BULK                FOAMATE          BUBBLE
                  1     SURFACE      SURFACE              DISTRIBUTION                  DIST.FAC
                  2T. ')
0039            31 FORMAT(1X,' RUN    CONCENTRATION    CONCENTRATION    DIAMETER
                  1AREA RATE    EXCESS                FACTOR           PH          ERROR',/)
0040            32 FORMAT(1X,/,'                      (PPM)            (PPM)       (CM)
                  1  (SQ.CM/MIN)  (G.MOL/SQ.CM)        (1/CM.)                     (PERCEN
                  2T) ',///)
0041              2 CONTINUE
0042              END
```

```
FORTRAN IV G LEVEL 1, MOD 3          BESFIT          DATE = 69248          13/30/44

0001            SUBROUTINE BESFIT(X,Y,NDATA,NSIX,YINT,SLOPE)
                C     SUBROUTINE FOR A LINEAR LINE OF BEST FIT Y=A*X+B USING THE LEAST
                C     SQUARES METHOD. LIMIT OF 100 DATA POINTS.
                C
                C     THIS SUBROUTINE WAS WRITTEN BY HARRY LAUDIE.
                C
0002            DIMENSION X(100),Y(100)
0003            A=0.0
0004            B=0.0
0005            C=0.0
0006            D=0.0
0007            DO 100 I=1,NDATA
0008            A=A+X(I)
0009            B=B+Y(I)
0010            C=C+X(I)*X(I)
0011        100 D=D+X(I)*Y(I)
0012            IF(NSIX) 102,102,103
                C     IF NSIX=0 ORIGIN IS INCLUDED
                C     IF NSIX=1 ORIGIN IS NOT INCLUDED
0013        102 E=NDATA+1
0014            GO TO 101
0015        103 E=NDATA
0016        101 AA=(E*D-A*B)
0017            BB=(C*B-A*D)
0018            CC=(E*C-A*A)
0019            SLOPE=AA/CC
0020            YINT=BB/CC
0021            WRITE(3,104) SLOPE,YINT
0022        104 FORMAT(1H1,/,'  THE LINE OF BEST FIT IS: Y=',F14.7,'*X +',F14.7,/
                1///)
0023            RETURN
0024            END
```

APPENDIX E

TABLES OF EXPERIMENTAL AND CALCULATED DATA

TABLE 2

Surface Excess and Distribution Factor vs. pH

Run NO.	pH	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
42	1.09	0.172	0.109	0.019
43	1.44	0.352	0.224	0.024
44	1.75	0.568	0.363	0.030
45	2.19	0.841	0.538	0.036
46	2.45	0.996	0.638	0.039
47	2.88	1.09	0.701	0.042
48	3.20	1.10	0.706	0.043
49	3.58	1.08	0.694	0.042
50	3.95	1.04	0.667	0.041
51	4.39	1.01	0.644	0.040
52	4.82	1.06	0.681	0.041
53	5.28	1.02	0.657	0.040
54	5.64	1.07	0.686	0.040
55	6.00	0.853	0.545	0.050
56	4.10	1.14	0.733	0.042
57	1.92	0.718	0.459	0.032
58	3.10	1.01	0.650	0.039
59	3.80	1.11	0.711	0.041
60	1.32	0.230	0.146	0.020
61	4.58	1.14	0.731	0.042
62	5.43	1.14	0.730	0.041
74	5.00	1.14	0.732	0.039
75	4.30	1.15	0.736	0.038
76	5.60	1.14	0.734	0.040

Feed Composition: [NaLS] = 0.500 g/l

[Cu] = 10.00 ppm

[NaCl] = 0.100 g-mol/l

No THPED

TABLE 3

Surface Excess and Distribution Factor vs.pH with added THPED

Run No.	pH	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	$\pm$ D x 10^3 (cm)
63	4.09	1.23	0.789	0.040
64	5.00	1.37	0.883	0.044
65	6.00	1.33	0.856	0.042
66	6.95	1.21	0.777	0.042
67	8.08	0.781	0.499	0.033
68	6.08	1.37	0.880	0.046
69	5.58	1.39	0.892	0.046
70	6.55	1.27	0.816	0.039
71	2.92	0.307	0.196	0.022
72	4.47	1.35	0.867	0.040
73	1.95	0.180	0.115	0.021
79	5.55	1.41	0.907	0.041
83	3.45	0.505	0.322	0.025

Feed Composition: [NaLS] = 0.500 g/l

[Cu] = 10.00 ppm

[NaCl] = 0.0100 g-mol/l

[THPED] = 1.0 stochiometric equiv. to 10 ppm copper.

TABLE 4

Effect of THPED on the Distribution Factor and Surface Excess

Run No.	[THPED] (equiv)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
69	1.00	1.39	0.892	0.046
76	0.00	1.14	0.734	0.040
77	0.20	1.32	0.845	0.040
78	0.50	1.42	0.912	0.041
79	1.00	1.41	0.907	0.041
80	2.00	1.38	0.886	0.039
81	4.00	1.42	0.913	0.040
82	8.00	1.16	0.742	0.035
113	6.00	1.46	0.941	0.041

Feed Composition: [NaLS] = 0.500 g/l

[Cu] = 10.00 ppm

[NaCl] = 0.0100 g-mol/l

pH = 5.5 ± 0.1

TABLE 5

Surface Excess and Distribution Factor vs. NaCl Concentration

Run No.	[NaCl] (g-mol/l)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
84	0.000	1.61	1.040	0.050
**	0.010	----	0.700	-----
94	0.025	0.650	0.415	0.029
85	0.050	0.266	0.170	0.020
86	0.100	0.068	0.043	0.019
87	0.250	0.000	0.000	0.000
88	0.500	0.000	0.000	0.000

** this value of D taken from figure 7

Feed Composition: [NaLS] = 0.500 g/l

[Cu] = 10.00 ppm

No THPED

pH 5.0 0.1

TABLE 6

Surface Excess and Distribution Factor vs. NaCl Concentration with added THPED

Run No.	[NaCl] (g-mol/l)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
96	0.000	1.29	0.825	0.038
89	0.000	1.30	0.833	0.038
69	0.010	1.39	0.892	0.046
79	0.010	1.41	0.907	0.041
95	0.025	1.19	0.763	0.036
90	0.050	0.766	0.490	0.029
91	0.100	0.515	0.328	0.024
92	0.250	0.198	0.126	0.019
93	0.500	0.073	0.046	0.016

Feed Composition: [NaLS] = 0.500 g/l

[Cu] = 10.00 ppm

[THPED] = 1.0 equiv. to 10 ppm copper

pH = 5.5 ± 0.1

TABLE 7

Surface Excess and Distribution Factor vs. Surfactant Concentration

Run No.	[NaLS] (g/l)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
98	0.100	0.869	0.555	0.054
99	0.250	1.06	0.683	0.055
**	0.500	----	0.700	-----
100	1.000	1.03	0.658	0.035
101	2.000	0.512	0.327	0.026
102	1.500	0.877	0.562	0.032

** taken from figure no. 8

Feed Composition:

[NaCl] = 0.0100 g-mol/l

[Cu] = 10.00 ppm

No THPED

pH = 5.0 ± 0.1

TABLE 8

Surface Excess and Distribution Factor Surfactant Concentration with added THPED

Run No.	[NaLS] (g/l)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
103	0.100	1.36	0.871	0.063
104	0.250	1.47	0.943	0.043
***	0.500	----	0.900	-----
105	1.000	1.09	0.702	0.035
106	1.500	0.668	0.426	0.028
107	2.000	0.343	0.218	0.023

*** taken from figure 8

Feed Composition: [NaCl] = 0.0100 g-mol/l

[Cu] = 10.00 ppm

[THPED] = 1.0 equiv. to 10 ppm Cu

pH = 5.5 ± 0.1

TABLE 9

Distribution Factor and Surface Excess vs. Bulk Copper Concentration

Run No.	X_B (ppm)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	$\pm$ D x 10^3 (cm)
125	0.286	0.171	3.80	1.04
120	0.967	0.347	2.28	0.31
118	2.480	0.652	1.67	0.14
116	4.911	0.941	1.22	0.08
***	10.0	1.102	0.70	----
114	24.876	1.400	0.357	0.017

*** from figure 8

Feed Composition: [NaCl] = 0.0100 g-mol/l

[NaLS] = 0.500 g/l

No THPED

pH = 5.0 $\pm$ 0.1

TABLE 10

Distribution Factor and Surface Excess versus Bulk Copper Concentration, with added THPED

Run No.	X_B (ppm)	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	$D \times 10^3$ (cm)	$\pm D \times 10^3$ (cm)
124	0.271	0.316	7.42	1.20
121	0.920	0.834	5.76	0.40
119	2.426	1.210	3.18	0.17
117	4.877	1.350	1.77	0.08
***	10.0	1.390	0.90	-----
115	24.887	1.320	0.337	0.016

*** from figure 8

Feed Composition: [NaCl] = 0.0100 g-mol/l

[Cu] = 10.00 ppm

[THPED] = 1.0 equiv. to 10ppm Cu

pH = 5.5 ± 0.1

TABLE 11

Surface Excess and Distribution Factor vs. pH with added EN

Run No.	pH	$\Gamma_c \times 10^{10}$ (g-mol/cm^2)	D x 10^3 (cm)	± D x 10^3 (cm)
108	5.98	1.57	1.01	0.040
109	7.03	1.60	1.03	0.043
110	5.01	0.874	0.560	0.032
111	6.60	1.76	1.14	0.046
112	5.58	1.52	0.976	0.042
122	6.15	1.76	1.13	0.046
123	6.65	2.13	1.38	0.052

Feed Composition:

[NaCl] = 0.0100 g-mol/l

[Cu] = 10.00 ppm

[NaLS] = 0.500 g/l

[EN] = 1.0 stochiometric equiv. to 10 ppm copper

TABLE 12

Experimental and Calculated Data For Each Run

Run No	P (mmHg)	T (°C)	X_B (ppm)	Y_f (ppm)	pH	S (cm^2/min)	foam wt. (gram)	G (cc/min) (STP)	N (min^{-1})	t (min)
42	765.0	25.5	9.987	11.74	1.09	1969.4	15.9273	64.0	3330	13.00
43	764.8	26.0	9.972	13.33	1.44	2002.7	17.3495	64.0	3488	13.00
44	764.4	26.0	9.954	15.08	1.75	1989.1	18.2222	64.0	3414	13.00
45	764.2	26.0	9.932	17.37	2.19	1981.3	18.4952	64.0	3372	13.00
46	764.0	26.5	9.919	18.84	2.45	1981.1	18.2599	64.0	3358	13.00
47	763.8	26.6	9.912	19.56	2.88	1968.0	18.4268	64.0	3288	13.00
48	764.8	26.0	9.912	19.12	3.20	1940.3	19.1609	64.0	3172	13.00
49	764.4	26.0	9.913	19.12	3.58	1944.6	18.8910	64.0	3190	13.00
50	764.4	26.8	9.916	18.90	3.95	1964.2	18.8146	64.0	3314	13.00
51	764.0	27.0	9.919	18.47	4.39	1961.0	19.0603	64.0	3246	13.00
52	763.7	27.8	9.915	20.00	4.82	1953.0	18.4071	64.0	3187	13.00
53	763.3	28.0	9.918	19.01	5.28	1956.4	18.2076	64.0	3196	13.00
54	763.0	28.4	9.912	20.00	5.67	2000.2	17.5207	64.0	3404	13.00
55	752.2	29.0	9.933	14.36	6.00	1901.7	30.2862	64.0	2832	13.00
56	752.0	29.0	9.908	20.51	4.10	1958.2	17.4467	64.0	3090	13.00
57	751.7	29.0	9.941	17.00	1.92	2039.0	17.1345	64.0	3486	13.00
58	759.5	29.5	9.919	19.56	3.10	1940.2	16.8587	64.0	3056	13.00
59	759.5	30.0	9.910	20.10	3.80	1974.5	17.7492	64.0	3210	13.00
60	759.3	30.2	9.982	12.40	1.32	2052.7	16.0965	64.0	3600	13.00
61	758.9	31.0	9.907	20.28	4.58	1979.0	17.9746	64.0	3206	13.00
62	758.8	31.3	9.906	20.97	5.43	2017.3	17.1470	64.0	3388	13.00
63	757.8	33.3	9.897	25.14	4.09	2031.1	13.5241	64.0	3404	13.00
64	757.6	33.8	9.885	25.14	5.00	2034.9	15.1367	64.0	3410	13.00
65	757.4	34.0	9.889	27.38	6.00	2032.1	12.7752	64.0	3390	13.00
66	757.2	34.2	9.903	23.74	6.95	1947.0	14.0730	64.0	2976	13.00
67	757.0	34.4	9.935	17.74	8.08	2016.4	16.6686	64.0	3300	13.00
68	760.1	32.0	9.897	27.27	6.08	1832.3	11.9352	64.0	2536	13.00
69	759.7	33.0	9.893	26.54	5.58	1878.1	12.9356	64.0	2710	13.00

Run No	P (mmHg)	T (°C)	X_B (ppm)	Y_f (ppm)	pH	S (cm^2/min)	foam wt. (gram)	G (cc/min) (STP)	N (min^{-1})	t (min)
70	759.3	33.2	9.887	22.62	6.55	2479.6	15.7231	84.0	3612	10.00
71	761.8	29.6	9.973	12.92	2.92	2616.2	17.2980	84.0	4344	10.00
72	761.6	30.0	9.880	22.33	4.47	2620.4	16.2248	84.0	4380	9.00
73	761.3	30.0	9.985	11.64	1.95	2615.1	15.3434	84.0	4350	8.50
74	761.1	30.2	9.896	18.83	5.00	2621.5	20.2052	84.0	4374	9.50
75	760.9	31.0	9.903	19.16	4.30	2632.3	16.5882	84.0	4402	8.00
76	759.9	28.0	9.906	18.49	5.60	1559.6	17.3410	84.0	4118	8.00
77	759.9	29.0	9.895	21.56	5.50	2564.0	13.7810	84.0	4112	7.50
78	759.9	29.5	9.881	22.84	5.55	2606.2	14.5084	84.0	4304	8.00
79	759.9	29.8	9.884	23.11	5.55	2601.4	13.6665	84.0	4272	7.75
80	759.3	30.4	9.877	23.23	5.55	2618.0	15.4434	84.0	4330	9.00
81	758.7	31.0	9.891	24.01	5.54	2632.5	10.6049	84.0	4378	6.30
82	758.6	31.0	9.913	21.34	5.50	2624.7	10.0881	84.0	4338	6.00
83	752.3	29.0	9.963	14.75	3.45	2618.8	10.2033	84.0	4294	5.80
84	752.8	29.0	9.861	22.00	4.95	2662.8	17.9725	84.0	4520	8.00
85	753.0	29.0	9.980	12.46	5.05	2631.7	12.5909	84.0	4366	7.00
86	752.7	29.0	9.996	10.61	5.10	2634.0	15.5655	84.0	4374	8.50
87	751.6	30.0	10.00	10.00	5.03	2645.6	11.7335	84.0	4390	6.75
88	751.6	29.6	10.00	10.00	5.05	2621.5	14.3823	84.0	4254	9.00
89	754.2	30.2	9.897	22.84	5.45	2609.9	11.6307	84.0	4238	7.00
90	754.5	30.5	9.941	17.65	5.48	2623.2	11.2702	84.0	4298	6.80
91	754.4	31.0	9.960	15.25	5.45	2616.1	11.3253	84.0	4248	7.00
92	754.0	31.0	9.983	12.01	5.55	2607.1	14.5433	84.0	4200	9.00
93	754.0	31.5	9.996	10.78	5.50	2596.4	7.6470	84.0	4162	5.00
94	755.6	32.0	9.950	15.65	5.05	2601.2	12.7090	84.0	4162	6.75
95	755.8	32.7	9.906	21.93	5.50	2592.6	11.4076	84.0	4104	7.00
96	755.8	32.7	9.897	23.09	5.50	2499.9	12.3832	78.4	4224	8.00
97	755.2	32.9	9.901	22.30	5.45	2621.4	11.7349	84.0	4230	7.00
98	758.3	31.4	9.939	13.76	5.05	2176.7	25.1428	84.0	2466	8.00
99	758.3	31.6	9.905	14.56	5.00	2387.0	38.1851	78.4	3728	11.00

Run No	P (mmHg)	T (°C)	X_B (ppm)	Y_f (ppm)	pH	S (cm^2/min)	foam wt. (gram)	G (cc/min) (STP)	N (min^{-1})	t (min)
100	753.5	31.0	9.914	19.04	5.00	2690.8	14.1440	87.5	4250	7.35
101	752.8	31.0	9.960	14.68	5.07	2723.8	12.0142	87.5	4400	6.40
102	752.0	31.2	9.924	17.81	5.03	2710.3	15.3219	87.5	4320	8.00
103	751.0	31.6	9.915	16.06	5.50	2181.2	18.4007	87.5	2240	5.50
104	751.0	31.0	9.880	22.55	5.48	2618.4	14.4417	87.5	3890	7.50
105	751.0	30.8	9.908	19.95	5.50	2680.7	13.9193	87.5	4180	7.50
106	750.8	30.5	9.946	16.06	5.53	2704.8	13.1394	87.5	4300	7.00
107	750.5	30.5	9.973	13.09	5.45	2716.0	13.3065	87.5	4350	7.00
108	747.9	30.0	9.859	26.99	5.98	2617.6	13.7382	87.5	3880	9.00
109	747.6	30.0	9.872	26.13	7.03	2625.0	11.4741	87.5	3910	7.00
110	747.6	30.1	9.927	18.24	5.01	2630.1	13.7939	87.5	3930	7.85
111	746.2	30.5	9.854	27.54	6.60	2637.9	12.4320	87.5	3940	7.45
112	746.2	31.0	9.880	24.65	5.58	2676.1	11.5363	87.5	4100	6.60
113	746.4	31.0	9.882	24.02	5.40	2662.5	12.2528	87.5	4040	7.00
114	760.0	27.5	24.88	35.60	5.05	2628.4	18.8108	87.5	4124	8.65
115	759.9	27.0	24.89	37.10	5.45	2630.8	14.4624	87.5	4148	8.00
116	759.9	27.0	4.911	11.60	5.00	2634.6	23.5515	87.5	4166	10.00
117	759.4	26.8	4.877	16.15	5.50	2636.2	18.1212	87.5	4174	9.00
118	759.2	27.0	2.480	7.13	5.00	2634.1	23.4722	87.5	4156	10.00
119	759.1	26.9	2.426	12.20	5.53	2652.1	20.9292	87.5	4272	10.00
120	759.0	28.0	0.967	3.42	4.95	2645.0	23.7569	87.5	4178	10.00
121	758.9	27.0	0.920	7.13	5.55	2662.4	22.7226	87.5	4288	10.00
122	758.8	26.9	9.843	26.00	6.15	2625.5	16.1287	87.5	4114	8.90
123	758.8	27.0	9.830	29.05	6.65	2673.3	12.2550	87.5	4340	6.50
124	760.0	25.0	0.271	2.42	5.40	2610.8	24.4397	87.5	4110	10.00
125	760.0	25.0	0.286	1.39	5.00	2646.3	20.2140	87.5	4280	7.75