FOAM FRACTIONATION OF ZINC

by

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* to my fiancée Olivia . . .

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ABSTRACT

The effect of pH, collector concentration, bulk zinc ion concentration, and effective hydrated radius of alkali metal ions were experimentally investigated in the foam fractionation of zinc ion by sodium dodecyl benzene sulphonate. All experiments were conducted on a single stage foam fractionating unit. Results were interpreted qualitatively by considering the existing equilibrium condition, and the various competing factors on the adsorption of zinc metal ion. The pH was observed to have an optimum range from 3.0 to 5.0. The decrease in bulk zinc ion concentration gave rise to an increase in distribution factor and a decrease in surface excess of zinc ion. At low zinc ion concentration, the surface excess and distribution factor of zinc ion increased with decreasing collector concentration. The order of increasing effectiveness in the removal of zinc ion by various forms of dodecyl benzene sulphonate is KDBS $<$ NaDBS $<$ LiDBS $<$ HDBS which is in the order of increasing effective hydrated ionic radius.

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NOMENCLATURE

B	bulk solution phase	
C	concentration of Zn^{++}	ppm or g - mol / 1
D	distribution factor of $Zn^{++} = \Gamma / C$	cm
F	foamate or foam on a gas free basic	
G	gas flow rate	ml / min
$\sum N$	total bubble emission frequency	min^{-1}
S	surface generating rate	cm^{2} / min
t	time	min
V_F	volumetric flow rate of foamate	cc / min
X_B	bulk Zn^{++} concentration	ppm or g - mol / cc
Y_F	zinc ion concentration in the foamate	ppm
γ	surface tension	dynes / cm
Γ	surface excess of Zn^{++}	g - mol / cm^{2}
DBS^{-}	dodecylbenzene sulfonate	

INTRODUCTION

Foam fractionation is the extraction of dissolved solutes, molecular or ionic, from a solution via adsorption at the bubble surfaces. The technique is essentially the dispersion of gas in the liquid by a bubble producer. The resulting foam is collected and condensed (or collapsed) into " foamate " (liquid product) which is relatively rich in adsorbed solutes, resulting in a partial separation of components.

Dissolved materials that are naturally surface active can be concentrated, frationated, or purified by the foam fractionation technique. Metal ions, generally not surface active, may also be separated and concentrated by foaming. This can be achieved by introducing to the solution a foaming agent capable of binding with the metal ions into surface active forms (complex, chelates, or compounds), or by simply attracting the metal ions to the anionic surface active agents electrostatically.

For this study, only solution parameters (pH, bulk zinc ion concentration, collector concentration, and effective hydrated radius of competing alkali metal ions) were investigated. The system chosen was zinc-sodium dodecylbenzene sulphonate in the presence of other competing ions such as hydronium, sodium, and other alkali metal ions.

LITERATURE SURVEY

Foam fractionation was originally employed as a technique to verify Gibb's adsorptive isotherm (1). Following this, it was used as a separation technique to separate and purify naturally active surfactants like enzymes, proteins, dyes, bacteria, fatty acids, detergents, and bile acids (2).

In 1957 Walling et al (3) reported the separation and concentration of metal ions by foam fractionation. According to their study on the relative adsorption of Ca^{++} and Na^{+} ions by N-palmitoyl methyl taurine, it was shown that the anionic surface layer has a strong preferential adsorption of Ca^{++} ion. The results were expressed in terms as $R = (b/a)_s / (b/a)$ where a and b are concentrations of Na^{+} and Ca^{++} ions respectively, and s refers to the ions held by the surface layer.

Schnepf et al (4) studied the foam separation for the removal of Sr^{++} ions in aqueous solution by Areskap 100 as collector using a circulatory foaming column. They obtained promising enrichment ratio as high as 40 below a 10^{-5} M concentration.

Factors such as gas flow rate, Areskap 100 concentration, and other alkali earth concentration, affecting enrichment ratio were studied. Increasing gas flow rate decreases the enrichment ratio of Sr^{++} due to liquid entrainment. Initially, the enrichment ratio of Sr^{++} increases with the foaming agent concentration. However, this was followed by a decrease in the enrichment ratio after reaching some higher foaming agent concentration. The authors explained this effect as follows. The enrichment ratio increases to its maximum value as foaming agent concentration increases to sufficiently complex all the Sr^{+2} ions in the solution. Further increase of the foaming agent concentration will cause a decrease in the enrichment ratio as a result of competition between the excess foaming agent and the Sr^{+2} - foaming agent complex for the gas-liquid interface. It was noted that metal ions of higher valency such as Fe^{+3}, Al^{+3}, Ba^{+2}, and Ca^{+2} have a much greater competitive effect on the Sr^{+2} ion as compared to univalent Na ion.

The separation of cobalt from nickel using Aresket 300 (monobutyl biphenyl sodium monosulphonate) and EDTA was done by Ghosh (5). Enrichment ratios of cobalt of up to about 2 were obtained.

Schonfeld et al (6) conducted additional works on foam separation of strontium, cerium, and samarium. Various surfactants were tested and many exhibited good possibilities for separation. DBTTA (dodecyl benzene diethylene triamine tetraacetic acid, tetrasodium salt) was found to have strong preference towards strontium and samarium even at high Na ion concentration.

Other studies made on the removal of radioactive material have been published. Schoen, Rubin, and Ghosh (7) reported on the removal of radium from dilute aqueous solution , and concluded that foam separation can be an effective means. However, further study is necessary to determine if the method is also effective when "synthetic or actual mill wastes " are used.

Rubin, E. and Gaden, E. L., Jr. (8) published an extensive discussion on foam fractionation in " New Chemical Engineering Separation Techniques ". Included is a compilation of various systems separable by foam fractionation. An ideal foam model was developed to explain the effect of collector concentration and bulk metal ion concentration on the distribution factor of collector and metal ions.

In 1965 attempts were made using foam fractionation to solve detergent problems on municipal waste streams (9). A pilot plant study in Los Angeles reported favourable results in the removal of alkyl benzene sulfonate (ABS) detergents from waste streams. The introduction of biodegradable detergents solved the pollution problem. As a result, there is no need of detergent removing process.

In the same year Banfield et al (10) used NaDBS as collector for the separation of Cs^{+2} , Sr^{+2} , and Ce^{+3} from dilute solution. The optimum surfactant concentration is about 10^{-4} M NaDBS for the removal of Sr^{+2} . The design of a foam column from the equilibrium data and the conventional operating line is shown. In addition, surface excess for the metal ions was noted to increase with the bulk metal ion concentration, and this leveled off at a higher metal ion concentration.

Controlled reflux was used as a means to improve the efficiency of foam fractionation of Sr^{+2} ions by NaDBS. Under Schonfeld, E. and Kibbey's experimental conditions (11) , the volume reduction factor was increased to 3700 from a value of approximately 30 for the nonrefluxing system. The Sr^{+2} decontamination factor, defined as the ratio of Sr^{+2} concentration in the feed to that in the effluent, was higher than 1,000. It was concluded that, in general, " the volume reduction was inversely proportional to the gas/liquid volume ratio but directly proportional to the percent of foam reflux: the Sr^{+2} decontamination factor, however, did not change very much within the throughput range studied ".

In the late 1960's, Rubin, E. and Jorne, J. (12) used theoretical models for the estimation of the relative distribution coefficient of two surface active solutes (α_{AB}) . The theoretical derivatives for the expressions of α_{AB} are obtained utilizing the Gibb's equation, the Langmuir isotherm, and the long - chain ions isotherm. Furthermore, a simple expression for α_{AB} was dervied based on the ideal foam model.

According to their experimental findings, they concluded that below the critical micelle concentration, theoretical estimation of α_{AB} based on the long - chain ion isotherm is in good agreement with the experimental value obtained with the solution containing two solutes. However, calculation based on the Langmuir isotherm may be used for α_{AB} estimation only at very low concentration.

In the same year Rubin, E. and Jorne, J. (13) proposed a modified model for metallic ions (non - surface active substance) based on Gouy - Chapman diffuse double layer concept, that the closest distance of approaching ions to the charged surface is determined by the size of the hydrated ions. The derived equations were used to estimate the distribution coefficient of the metal ions and the relative distribution coefficient between any two ions in the solution. Experimental data on the foaming of Sr^{++} and UO_2^{++} are in good agreement with the values obtaine from the proposed model.

Dick, W. L. and Talbot, F. D. (14) in 1971, investigated the use of an auxiliary ligand in the foam fractionation of Cu^{++}. The addition of the auxiliary ligand THPED (N, N, N - tetrakis (2 - hydroxypropyl) ethylenediamine, Quadrol) was shown to improve the distribution factor especially in the presence of excess NaCl and at a lower bulk Cu^{++} concentration.

The following year in the same laboratory, St Eloi, R. J. and Talbot, F. D. (15) conducted equilibrium and batch removal studies on the foam fractionation of zinc ion from dilute aqueous solution using NaDBS in the presence of excess NaCl. The mechanism for zinc fractionation was explained by the double layer concept. The removal of zinc cations was dependent upon the competing effect of the zinc and other ions of the solution for the collector.

Huang, R.C.K. and Talbot, F.D. (16) developed a mathematical equilibrium model of solution for pH lower than 4. A combination of this model and the modified Gouy-Chapman diffuse double layer theory was used to determine the distribution factor and the relative distribution factor of Cd^{+2} , Cu^{+2} , and Pb^{+2} ions foamed with NaDBS. Good agreement was obtained between experiment and theory. Their experimental results showed that the order of preferential ionic adsorption was in reverse order as the effective radius of the hydrated ions.

The removal of anionic (Nansa HS - 55) and nonionic (Alfenol (II)) detergents from aqueous solutions by foaming was done by Zwierzykowski et al (17) in Poland. Using a graphic method, they showed that in an identical separation, a greater number of separation stages are required for anionic detergent as compared to nonionic detergent.

In 1973, NaDBS was used in foam fractionation by Shirotsuka et al (18, 19). They derived expressions for the rate of adsorption of DBS ($d\Gamma / dt$), and the removal efficiency, E, of DBS from tap water. The adsorption of NaDBS followed the long-chain isotherm.

The same year in Russia (20), a study on the recovery of NaDBS from waste water by foam fractionation was reported.

A paper on the kinetics of foam fractionation of Co $^{++}$, Ni $^{++}$ and Cu $^{++}$ ions with potassium laurate as collector in aqueous and alcohol solutions was published in Russia (21). The rate of adsorption was observed to be faster with the alcohol laurate solution, however, the extent of separation is greater with the aqueous solution. The kinetic equation is analogous to that of first order kinetics.

An interesting application of foam fractionation was performed by Coste (22). He extended the foam technique to the liquid-liquid system (aqueous phase - oil phase). Petroleum emulsions are broken by removing vanadium, nickel, and apshaltenes (substances which stabilize emulsion) from the emulsion using the foaming technique. The substances removed are adsorbed at the oil - water interface of the foam.

A comprehensive review of the separation of materials by the foam separation technique was summarized by Rubin, E. and Gaden, E. L., Jr. (8) and by Somasundaran, P. (23, 24). The various modes of the foam fractionation column include foam fractionation in the simple mode with batchwise, and continuous flow operation, and in higher modes, with enriching, stripping, and the combination of both. General references concerning the technique have been published by Rubin, E. and Gaden, E. L., Jr. (8), Sebba (25), and Lemlich, R. (26).

THEORETICAL DISCUSSION

Foam fractionation has long been a subject of laboratory and pilot plant studies ; inconsistencies in its definition still exists. Various authors had compromised that foam fractionation be classified within the adsorptive bubble separation technique (27). This however did not give rise to a definite nomenclature as shown in P. Somasundaran's overview of foam separation method (23) and R. Lemlich's comprehensive review of adsorptive bubble separation technique (26).

Foam fractionation is defined in this paper as " the foaming off of dissolved solutes from a solution via adsorption at the bubble surface " (26 a). Its essential elements are 1) solute adsorption at the gas- liquid interface, and 2) removal and collection of interfacial solutes by foaming. Solute species are adsorbed at the bubble surfaces either because they are surface active in nature or because they are associated to a species that is surface active. Bubble surfaces or the gas - liquid interface can be effectively generated and collected by foaming.

Foam Fractionation of Metal Ions

Metal ions, generally non - surface active by their nature, may be foam fractionated by associating them with a foaming agent. The foaming agent used must have the following characteristics :

1) It must either be surface active or form a surface active complex with the metal ion.

2) It must have preferential attraction to the metal ion to be separated. Though in some cases, the attraction may be equal to that of other competing ions in the solution (4).

3) It must produce reasonable foam.

The mechanisms whereby a metal ion is separated by foaming

(4) are.

1) The metal ion may bond covalently with the foaming agent, forming a surface active complex, chelate, or other compound (Chemisorption).

2) The metal ion may be electrostatically attracted to the bubble surface by a negatively charge surface active agent (Physical Adsorption).

3) By both mechanisms.

When the electrostatic mechanism predominates, the sublate is soluble and the foaming metal ions are sensitive to the other components of the solution such as Na ion and other cations. In aqueous solution, unless the foaming agent (collector) is in the H^+ form, there will be at least two other different cations competing with the metal ion for the separation (26 b). Usually the collector used for foam fractionation of metal ions are in the Na^+ form. Thus aside from the metallic ions, at least Na^+ and H_3O^+ are also present in the solution. Proper choice of foaming agent and foaming conditions may allow the selective separation of metal ion from the other cations.

Basic Principle

The underlying principle of foam fractionation is the mechanism of adsorption at the gas - liquid interface. The separation is based on the differences in surface activity of the dissolved solutes, i. e., the tendency of the solutes to concentrate at the interfacial layer. Interfacial adsorption of the solute occurs when the interaction energy among the solvent molecules is greater than that between the solvent molecules and the solute (23). Hence it is less favourable for that solute to remain within the bulk solution than to stay at the gas - liquid interface. Substances that exhibit this property are termed surface active substances or surfactants. Generally, the surface active solute is polar at one end of the molecule and non - polar at the other end. One end of the molecule is relatively soluble in the particular solvent, whereas the other end is relatively insoluble.

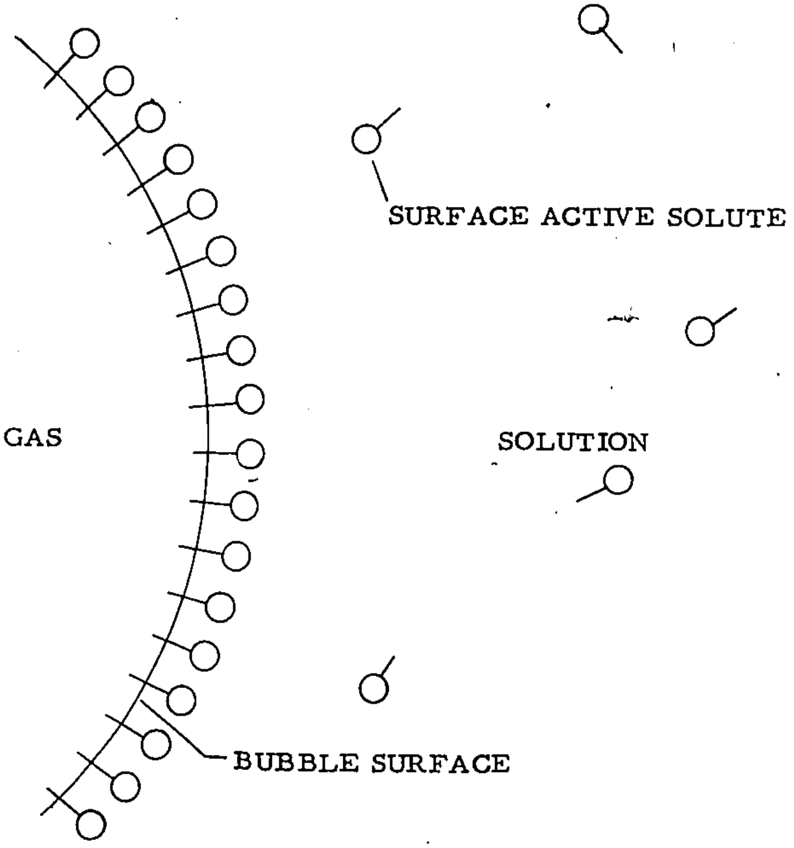

FIG. 1 - Cross Sectional Part of a Submerged Bubble

In aqueous solution, the surface active molecules will reorient its hydrophobic (organic and non-polar) end towards the gas - liquid interface in order to minimize contact with the solution with its hydrophilic (polar or ionic) end in the bulk liquid. As a result the surfactant molecules migrate and concentrate (or adsorb) at the interface surface. Increasing the size of the non- polar part of the surfactant molecules will enhance the hydrophobic nature of the surfactant and causes it to migrate more toward the interface. Consequently, there is an increase in surface adsorption. This effect on alkyl ammonium acetate of various chain lengths was demonstrated by P. Somasundaran in his experimental work (28).

Theoretical Models

Various models were proposed by several authors describing the surface adsorption of surface active substances and non - active surface substances.

I. Solutions containing one surface active solute

Gibbs adsorption isotherm relates the adsorption at the boundary between two phases in thermodynamic equilibrium at constant temperature to the change in surface tension (1). Its application to foam separation has been discussed in detail (8, 29, 30, 31). Based on the Gibbs convention of zero surface excess for the solvent, the equation for solutions containing one solute surfactant can be rearranged to

$$\Gamma_s = -\frac{1}{RT}\left(\frac{d\gamma}{d a_s}\right) = -\frac{1}{\beta RT}\left(\frac{d\gamma}{d \ln C_s}\right) \qquad (1)$$

The activity of the surfactant, a_s, can be replaced by the concentration C_s for an ideal solution. β is 1 for a solution containing non - ionic surfactant, or ionic surfactant in the presence of excess electrolytes. For a solution containing an ionic surfactant without excess electrolytes, the value is 2. The distribution factor, $(\frac{\Gamma}{C})_s$, an expression for the degree of separation is given by equation (2). From equation (2) , the distribution factor is shown to be dependent upon the slope of the surface tension versus concentration diagram.

$$\left(\frac{\Gamma}{C}\right)_s = -\frac{1}{\beta RT} \frac{d\gamma}{dC_s} \qquad (2)$$

The Langmuir Adsorption isotherm (32) was considered applicable for non - ionic surface active solutes, or for ionic surface - active solutes at very low concentrations when the potential of the electric double layer is very small. The distribution factor as expressed by this isotherm is

$$\left(\frac{\Gamma}{C}\right)_s = \frac{K_1}{K_2 C_s + 1} \qquad (3)$$

For " very low " surfactant concentration, the distribution factor of the surfactant approaches a constant value K_1.

An ideal foam model was proposed to explain the behaviour of foam fractionation. The model is based on the following assumptions (8 a) .

1) The foam consists of uniform spherical bubbles.

2) The foam is stable (no bubble breakage within the column) .

3) The liquid phase region in the foam has a " surface " region and a " bulk " region. The " surface " region is of constant thickness,

while the " bulk " region changes in thickness as drainage occurs.

4) The " bulk " region in the foam is of the same composition as the bulk liquid phase where the foam originated.

5) Adsorption at the surface is instantaneous.

For a system of one solvent and one solute, the derived equation is

$$\left(\frac{\Gamma}{X}\right)_s = \frac{fd}{6}\,(E-1) \qquad (4)$$

where

f = foam ratio , ml liquid / ml foam
d = bubble diameter
E = enrichment ratio

$$= \frac{\text{concentration of solutes in foamate}}{\text{concentration of solute s in bulk}}$$

$$= Y_s \,/\, X_s$$

An equation for the adsorption of long chain ionic surfactants is derived by considering the effect of the electrical double layer and the cohesive forces at the gas - liquid interface (32) . The distribution factor is given by

$$\left(\frac{\Gamma}{c}\right) = \frac{\left(\frac{B_1}{B_2}\right) \exp\left[\left(W - E\epsilon\psi_0\right)/KT\right]}{1 + \left(\frac{B_1}{B_2}\right) A_0 \exp\left[\left(W - E\epsilon\psi_0\right)/KT\right]} \qquad (5)$$

where

$$\frac{W}{KT} = \frac{521\,m}{RT} + \frac{1200\,m}{KTA^{\frac{1}{2}}} \qquad (6)$$

and

$$\psi_o = \frac{2\,KT}{G} \sinh^{-1}\left[\frac{\sigma}{C_s^{\frac{1}{2}}} \left(\frac{500}{DRT} \right)^{\frac{1}{2}} \right] \qquad (7)$$

W is the van der Waal's energy of desorption of one molecule of a long chain hydrocarbon, Z is the valency of that long chain ion. ψ_o is the surface potential, A_o is the limiting area available to each long chain ion at the surface and B_1 and B_2 are constants. m is the effective number of $-CH_2-$ group, and A is the area available at the surface to each ion.

II. Solutions containing two or more surface active materials

Rubin and Jorne derived theoretically the expression for the distribution factor of one surfactant relative to another on the basis of Gibbs Adsorption isotherm, the Langmuir isotherm, the ideal foam model, and the long - chain ion isotherm. The various mathematical expressions for the relative distribution factor α_{AB} can be obtained from their paper (12). The theoretical estimation of α_{AB} based on the long chain ion isotherm is in good agreement with their experimental data. However, the expression based on the Langmuir isotherm may be used only for α_{AB} estimation at " very low " concentration.

III. Solutions containing non - surface active solute (metallic ions)

The foam fractionation of metal ions is closely related to that of the foaming agent. The ideal foam model was extended to non - surface active solutes specifically metallic ions. Two assumptions were made on the foaming of metallic ions (8 b):

1. The ideal foam model applied, and
2. Adsorption of the metallic ion is proportional to the adsorption of the pure foaming agent.

The distribution factor for the metal ion, $(\Gamma / C)_{Me}$, is defined as

$$(\Gamma / C)_{Me} = (E_{Me} - 1)(fd / 6) \tag{8}$$

where E_{Me} is the ratio of the concentration of free and associated metal ion in the foam to that in the bulk solution, thus

$$E_{Me} = (Y_{AMe} + Y_{Me}) / (X_{AMe} + X_{Me}) \tag{9}$$

where AMe refers to the metal ion - foaming agent complex and Me refers to the free metal ion. Since free metal ion is not adsorbed, therefore $Y_{Me} = X_{Me}$, and equation (9) is written as

$$E_{Me} = (Y_{AMe} + X_{Me}) / (X_{AMe} + Y_{Me}) \tag{10}$$

The modified model of the Gouy - Chapman diffuse double layer concept was derived to predict the distribution factor and the relative distribution coefficient between any two ions in the solution. The theory considers that the mechanism for the removal of metallic ions from the solution is of electrostatic attraction, and that the selectivity is dependent upon the charge and size of the hydrated ion.

The distribution coefficients of the ~~two~~ cationic species are :

$$\left(\frac{\Gamma}{n}\right)_A = \left(\frac{KT\epsilon}{8\pi e^2}\right)^{\frac{1}{2}} \int_{v_0''}^{1} \frac{(v_A - 1)\, dv}{v\left[\sum_i n_i (v_i^2 - 1)\right]^{\frac{1}{2}}} \tag{11}$$

$$\left(\frac{\Gamma}{n}\right)_B = \left(\frac{KT\epsilon}{8\pi e^2}\right)^{\frac{1}{2}} \left\{ \int_{v_0''}^{1} \frac{(v_B - 1)\,dv}{v\left[\sum_i n_i(v_i^2 - 1)\right]^{\frac{1}{2}}} + 2\left(\frac{1}{n_B}\right)^{\frac{1}{2}} \left[(v_0')^{\frac{1}{2}} - (v_0'')^{\frac{1}{2}}\right] \right\} \qquad (12)$$

where A is the larger ion (e. g. bivalent) and B is the smaller ion (e. g. univalent).

The selective adsorption coefficient between A and B ions is given by:

$$\alpha_{AB} = \frac{\left(\frac{\Gamma}{n}\right)_A}{\left(\frac{\Gamma}{n}\right)_B}$$

$$= \frac{\int_{v}^{1} \frac{(v_A - 1)\,dv}{v\left[\sum_i n_i(v_i^2 - 1)\right]^{\frac{1}{2}}}}{\int_{v_0''}^{1} \frac{(v_B^2 - 1)\,dv}{v\left[\sum_i n_i(v_i^2 - 1)\right]^{\frac{1}{2}}} + 2\left(\frac{1}{n_B}\right)^{\frac{1}{2}}\left[(v_0')^{\frac{1}{2}} - (v_0'')^{\frac{1}{2}}\right]} \qquad (13)$$

Detailed explanation of the the above equations are obtained from their paper (13).

Column Operation in the Simple Mode

Normally, the best apparatus for the study of foam - liquid equilibrium might be thought of as a closed system unit with the foamate recycled to the bulk solution column. However, recycle may not be the preferred technique because collector micelles which might form in the foamate may not dissociate fast enough when recycled upon dilution in the liquid pool (14). In this event, simple batch - type apparatus with a large liquid pool may be employed.

A batchwise foam fractionation operation in the simple mode is shown in Fig. 2 . The operation is approximately of one theoretical stage, provided the pool is thoroughly mixed, bubbler submergence is sufficient, and there is no coalescence in the rising foam (26 c).

For a bubbler of n capillaries generating bubbles at a frequency of N bubbles per minute per capillary, the surface generating rate is given by

$$S = n \pi N d^2$$

where d is the bubble diameter, which can be calculated by

$$d = (6 G / n \pi N)^{1/3}$$

where G is the gas flow rate. A simple material balance on the simple mode operating unit yield

$$\Gamma = V_f (Y_f - X_B) / S$$

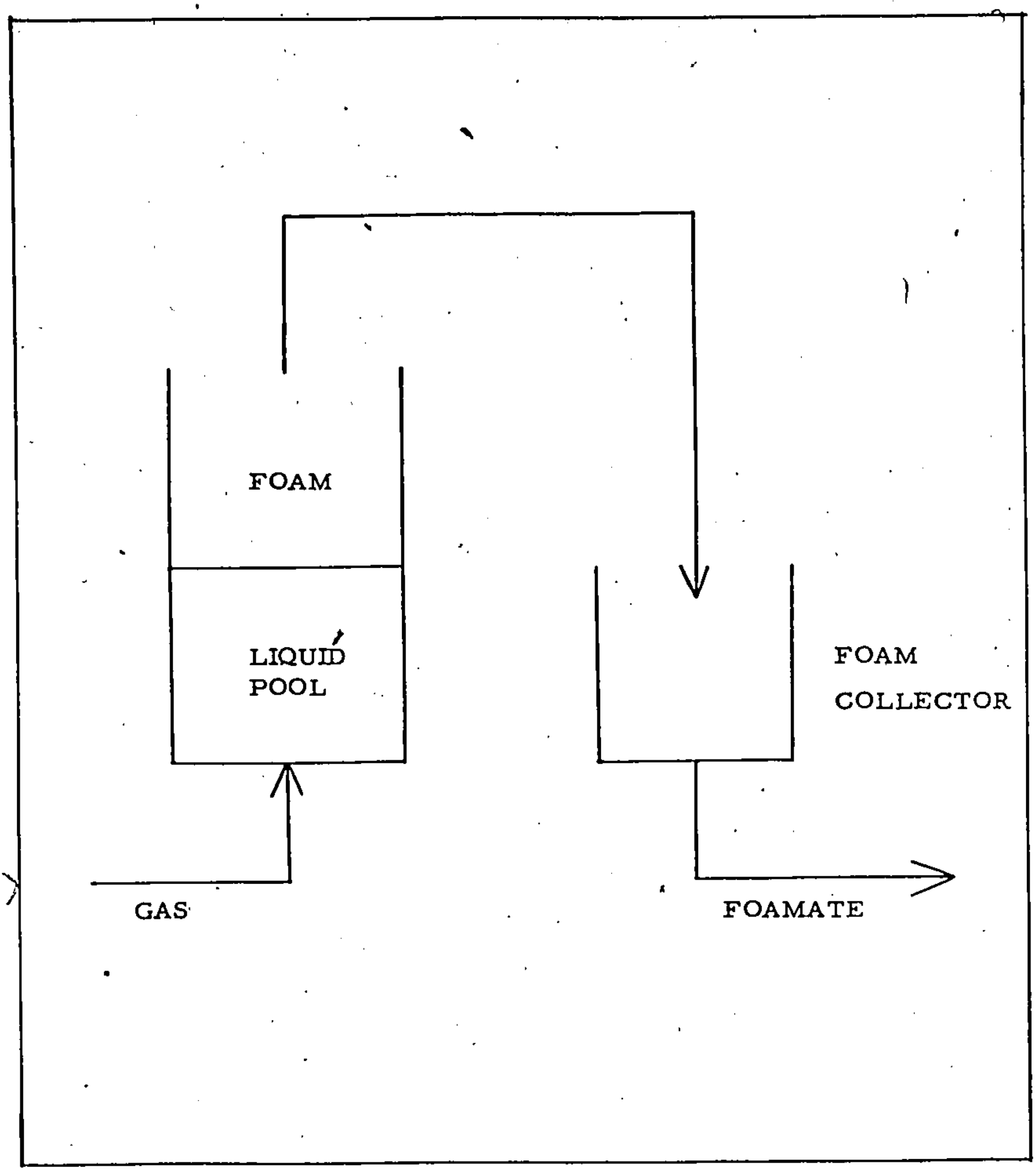

FIG. 2 - Foam Fractionation in the Simple Mode

where V_f is the foam generating rate, Y_f is the foamate concentration and X_B is the bulk concentration. The derived equation applies equally to collector and colligend.

EXPERIMENTAL METHODS AND MATERIALS

Experimental Apparatus

Foaming apparatus developed by W. L. Dick and F. D. Talbot (14) was modified and used for this study. The modification made are the following . 1) In addition to the upstream pressure valve, another needle valve was connected to control the downstream pressure. The flowmeter was calibrated and operated at the same upstream and downstream pressures. 2) A round teflon disk with five holes was inserted the teflon chamber of the bubbler to produce more uniform size bubbles. 3) The foam fractionating column was painted with light blue colour as background to aid visually the stroboscopic bubble counting. A schematic flow diagram of the apparatus used is shown in Fig. (3).

For all runs, oil - free compressed air coming from a cylinder was maintained at 6 psig. The air was then humidified by two humidifiers, each consisting of a sparger within a flask of distilled water. The flow rate of the humidified air was adjusted with the calibrated flowmeter. Downstream pressure of the flowmeter, recorded by the manometer, was maintained at 3 psig via the needle valve.

The humidified air then passed to the bubbler in the foam column. The bubbler consisted of five glass capillaries of 0. 24 inch long and 0.007 inch i. d. imbedded in a teflon chamber. Within the teflon chamber is a piece of round teflon disk with five holes placed perpendicular to the air flow. This is to uniformly distribute the air even within the chamber, thus producing bubbles of uniform size.

The foam column was constructed from an inverted 3 - liter

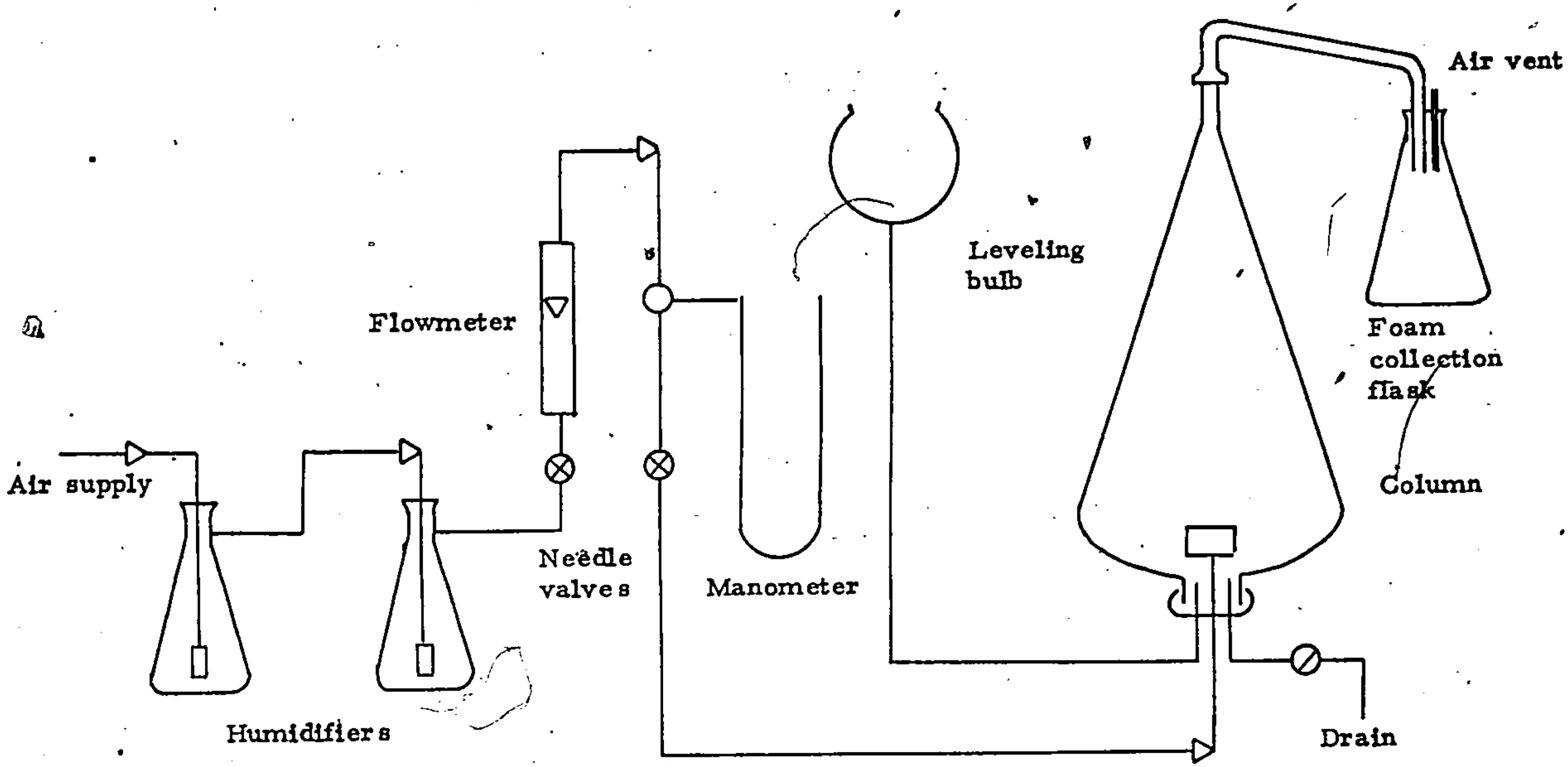

FIG. 3 - Schematic Diagram of the Single Stage Foam Fractionating Unit

separatory funnel with the stopcock portion replaced by a foam delivery tube and the bubbler inserted into its bottom. A liquid depth of approximately 33 cm. above the bubbler was maintained by a 300 ml. level control bulb. Foam was collected in a one liter Erlenmeyer flask with the foam delivery tube inclined toward it. The overall foam height in the column, including the vertical portion of the delivery tube, was about 6 cm.

Experimental Procedure

Four liters of feed solution was prepared for each run . All solutions were prepared from deionized distilled water and their pH was adjusted to the desired value using NaOH and HNO_3 .

Air was introduced into the foam column and the feed solution was charged through the leveling bulb. The air flow rate and the liquid height were set to the desired values. Once steady state conditions were reached, the weighed foam receiver was put in position and the timer started. During the foam collection period the bubble rate was measured by means of a stroboscope. When the receiver was filled, it was then removed, and the time recorded. The receiver was weighed and stoppered. The collected foam was allowed to break naturally over a period of about a week before its analysis. On the completion of each run, the column was drained and then rinsed with distilled water. Gas flow rate was maintained throughout the operation and in washing so as to prevent capillary wetting.

Analytical Techniques

The concentrations of zinc and sodium ions were determined using the atomic absorption spectrophotometer , UNICAM SP 90 . Operating conditions , calibration data , and calibration curves for the analyses of the zinc and sodium ions are presented in Appendixes C and D respectively .

The determintation of NaDBS concentration was done using the standard method of test for alkyl benzene sulphonate in industrial water and industrial waste water , ASTM Designation D233 - 68 (33). This extraction step is essential because the direct measurement of the absorbance of the solution at the UV wavelength range can be interfered by the presence of metal ions and the pH of the solution (37) . Briefly , the method consists of serial chloroform extractions . The combined chloroform extract is then washed with an acid solution which hydrolyzes the interfering complex and separates them from the chloroform to the aqueous phase . The remaining blue colour from the DBS - complex in the chloroform is measured at a wavelength of 652 mu using a Bausch and Lomb Precision Spectrophotometer . Calibration data and calibration curve are presented in Appendix E .

The critical micelle concentration of the NaDBS was determined by surface tension measurements using a #2370 Deluxe Surface Tension Accessory with the Cahn Electrobalance Model RG . All measurements were taken after 10 minutes at room temperature . Resulting data and surface tension - concentration diagram are given in Appendix F .

Experimental Equipments and Chemical Reagents

Experimental Equipment

1) Atomic absorption spectrophotometer , UNICAM SP90, Unicam Instruments Ltd., England

2) Precision spectrophotometer, Bausch & Lomb, Cat. No. 33-26-50

3) Digital pH / mv meter, model 801, Orion Research Inc.

4) Strobotac electronic stroboscope, type 1538-A, General Radio Company

5) #2370 Delux Surface Tension Accessory with the Cahn Electrobalance Model RG, Cahn Instruments

6) Chart Recorder, Texas Instruments Incorporated

Chemical Used in the Foaming of Zn^{++}

1) Certified Atomic Absorption Standard, Zinc Reference Solution, 1000 ppm, Fisher Scientific Company, Lot No. 751670

2) Certified Atomic Absorption Standard, Sodium Reference Solution, 1000 ppm, Fisher Scientific Company, Lot No. 746664

3) Sodium Dodecylbenzene Sulfonate, K and K Laboratories, Inc., Lot No. 60959

4) Lithium Nitrate, Fisher Certified Reagent, Fisher Scientific Company, Lot No. 710325

5) Potassium Nitrate, Analytical Reagent, BDH Chemicals Ltd., England, Lot No. 51580

6) HNO_3 and NaOH , Analytical Grade

7) HN-Ultrapure (mixed bed) ion exchanger, Barnstead Hose Nipple Cartridge, Barnstead Company, Lot No. 9-034-3

8) Cation Removal ion exchanger, Barnstead Hose Nipple Cartridge, Barnstead Company, Lot No. 9-034-10

EXPERIMENTAL RESULTS AND DISCUSSION

Effect of pH on the Surface Excess of Zn^{++}

Experimental runs (nos. 1 - 17) were done to study the effect of pH on the foaming of Zn^{++} . The concentration of NaDBS was 0.5 g / 1 and that of Zn^{++} was 10 ppm . The pH of the solution was adjusted by the addition of standard NaOH solution and standard HNO_3 solution .

Experimental results are tabulated in Table III, Appendix A, and plotted in Fig. 4 . Fig. 4 shows that there is a maximum for the Zn^{++} surface excess curve at pH ranging from 3.0 to 5.0 . There is a drop beyond these two pH's , and at pH of 8.0 , the Zn^{++} is precipitated as $Zn(OH)_2$.

The shape of the curve can be explained as follows . The adjustment of the pH at the two extremes , i.e. , beyond the optimum range (which in our curve lie at pH lower than 3.0 and higher than 5.0) will increase the ionic strength of the solution . This increase in the ionic strength is caused either by the addition of HNO_3 for lower pH or by the addition of NaOH for higher pH . At low pH the presence of large amounts of H_3O^+ will exhibit two effects : 1) it will compete with the Zn^{++} for the collector , and 2) the H_3O^+ will render the DBS^- to be less accessible by shifting the equilibrium more towards the HDBS which is less ionized than NaDBS (15 a) .

Similarly at higher pH , the additional Na^+ from NaOH will compete with the Zn^{++} , and the excess OH^- precipitate the Zn^{++} as $Zn(OH)_2$. This precipitation occurs at pH greater than 8.0 . These effects give rise to the drop at the high and low pH as shown

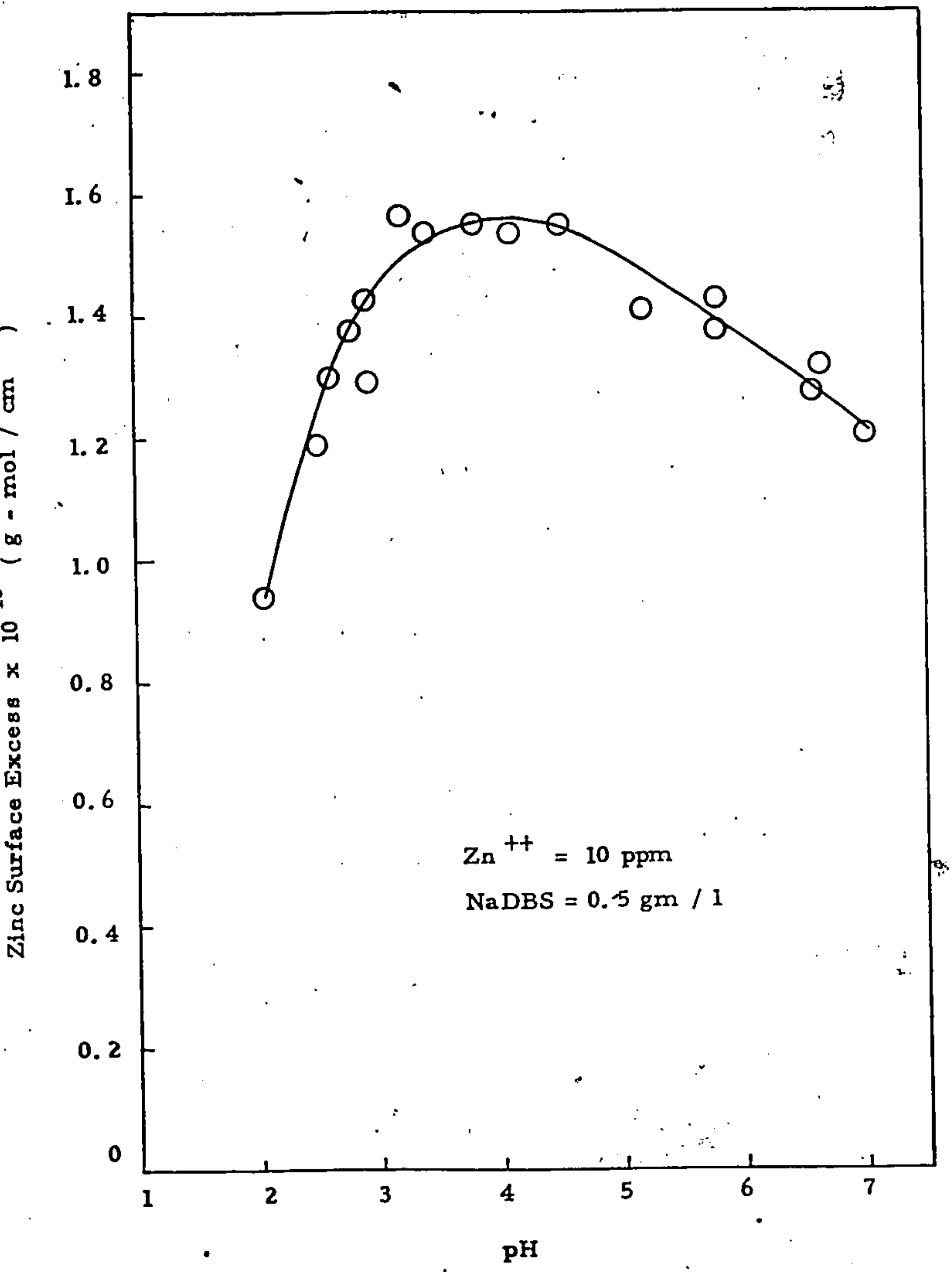

FIG. 4 - Zinc Surface Excess versus pH

in Fig. 4. Similar shape of curve was also obtained on the foam fractionation of Cu^{++} by NaLS (14).

Foam fractionation of Zn^{++} by NaDBS in the presence of 0.01 g-mole / 1 of NaCl was done by St. Eloi and F. D. Talbot (15). The curve of the Zn^{++} surface excess has a maximum at the pH range of 2.5 to 5.5, but with a lower surface excess (1.2×10^{-10} g-mole / cm^2) as compared to 1.4×10^{-10} g-mole / cm^2 as shown in Fig. 4. This difference is attributed to the presence of NaCl in their system which increases the ionic strength of the solution and simultaneously, the amount of competing Na$^+$ and thereby lower the curve of Zn^{++} surface excess.

Effect of Bulk Zn^{++} Concentration on Surface Excess and Distribution Factor of Zn^{++} .

The effect of metal ion concentration on surface excess and distribution factor of Zn^{++} is shown in Fig. 5 and Fig. 6 respectively for various surfactant concentration . The collector concentration was varied from 0.1 g / 1 to 0.5 g / 1 . Experimental data are tabulated in Table IV , Appendix A .

The adsorption of the metal ion to the bubble surface can be explained briefly as follows . The collector , being surface active , was adsorbed to the bubble surface . For an ionic collector such as sodium dodecylbenzene sulphonate , the adsorbed collectors on the surface (termed " surface " collectors) will constitute negative charges on the surface . To maintain electrical neutrality , the surface must be associated with an equal charge of cations via electrostatic attraction . In this study where the collector is not of H^+ form, there will be , in addition to the metallic Zn^{++}-, at least two cations that will compete with the metal ion for the " surface " collector . The two cations are Na^+ (from NaDBS and pH adjustment) and H_3O^+ (from H_2O and pH adjustment) .

At low bulk Zn^{++} concentration as the amount of Zn^{++} is increased , it will become more competitive with the other cations in the solution for the collecton . Likewise , it will lessen the competing effect of " free " and " surface " collector for Zn^{++} because more Zn^{++} are available for them . This effect is shown in Fig. 5 with the Zn^{++} surface excess increases as the bulk Zn^{++} concentration increases . As the bubble surfaces become saturated with the Zn^{++} , further increase in bulk Zn^{++} concentration will have no additional adsorption effect . This phenomenon is illustrated

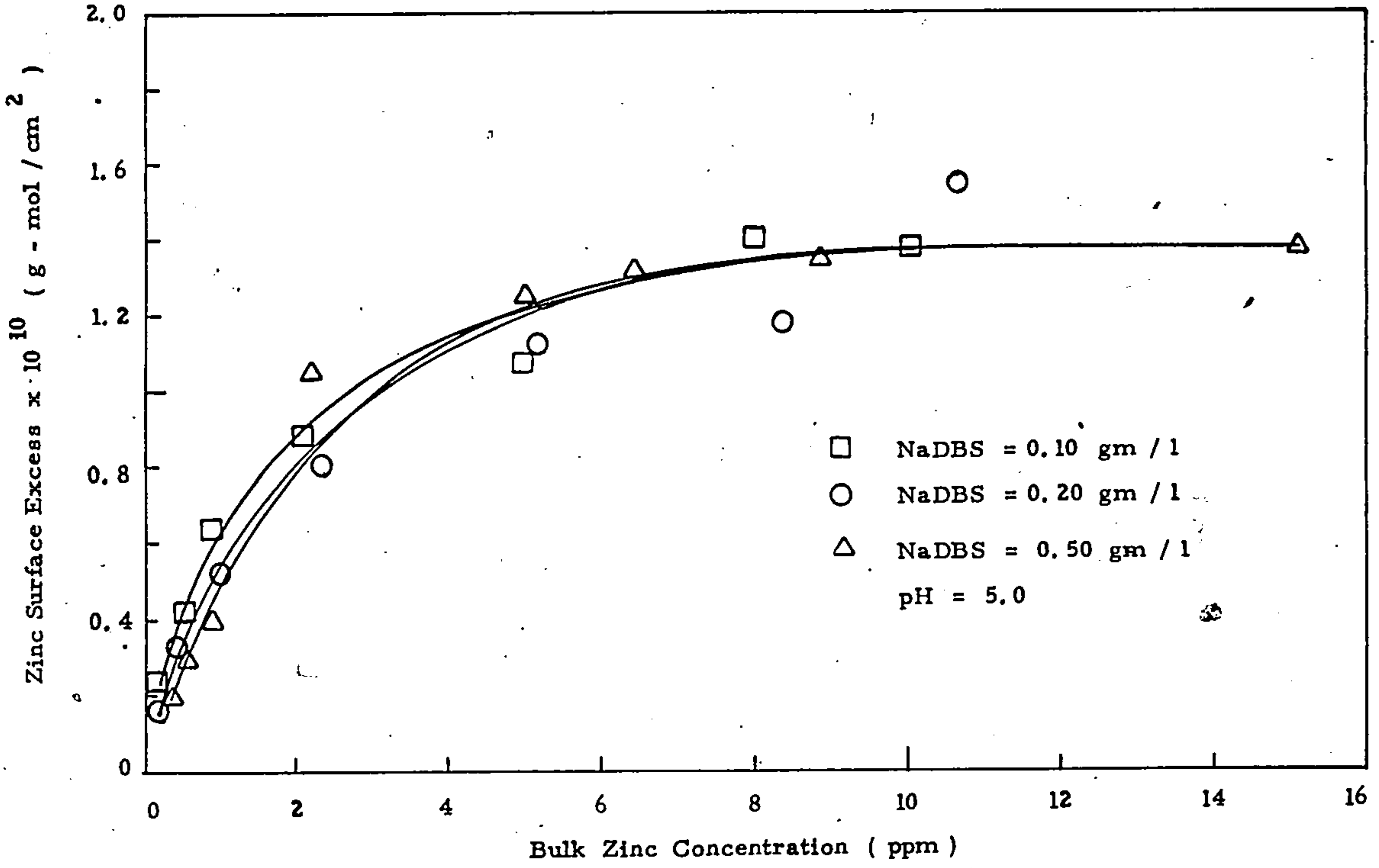

FIG. 5 - Zinc Surface Excess versus Bulk Zn^{++} Concentration

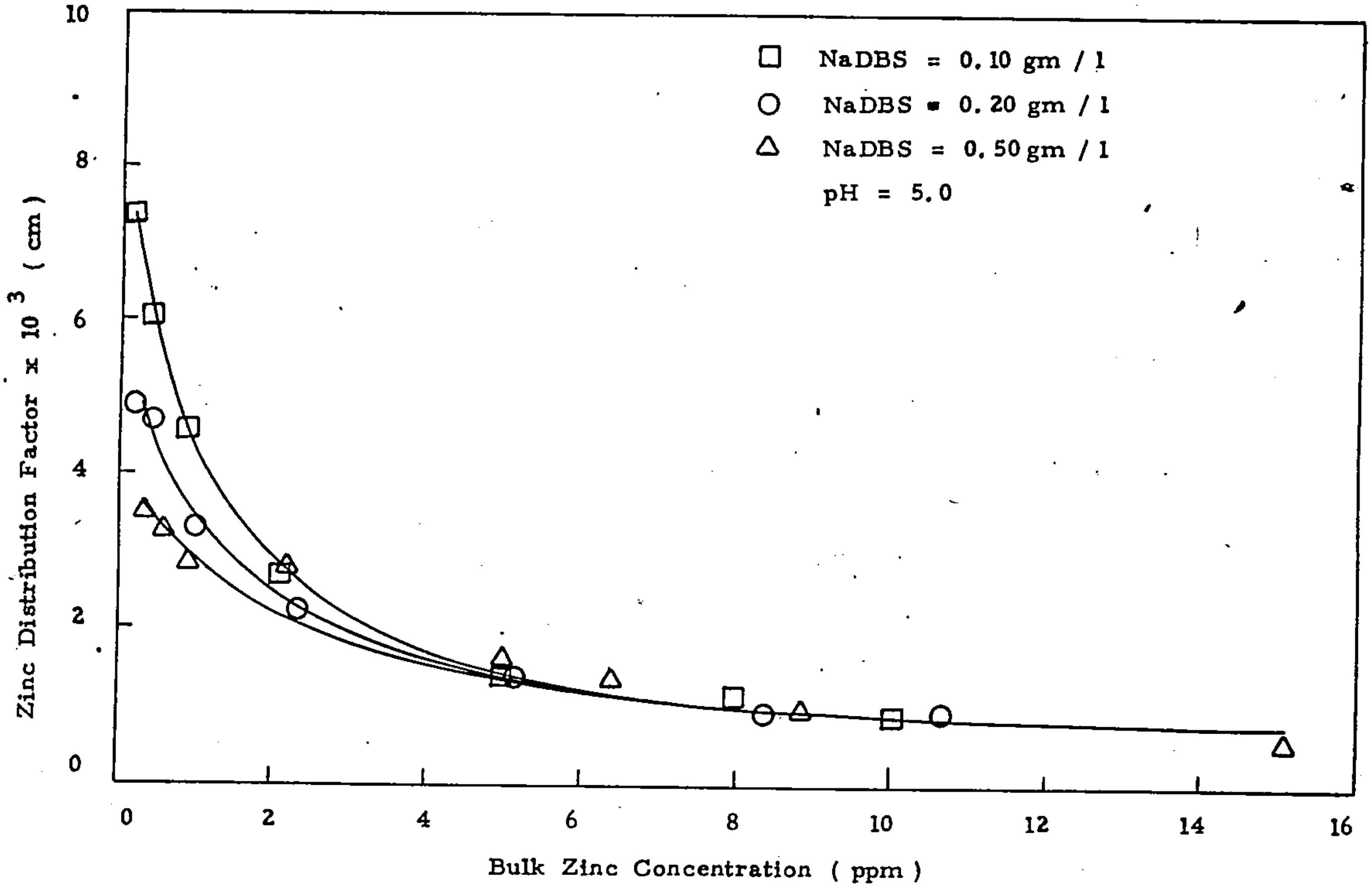

FIG. 6 - Zinc Distribution Factor versus Bulk Zn^{++} Concentration

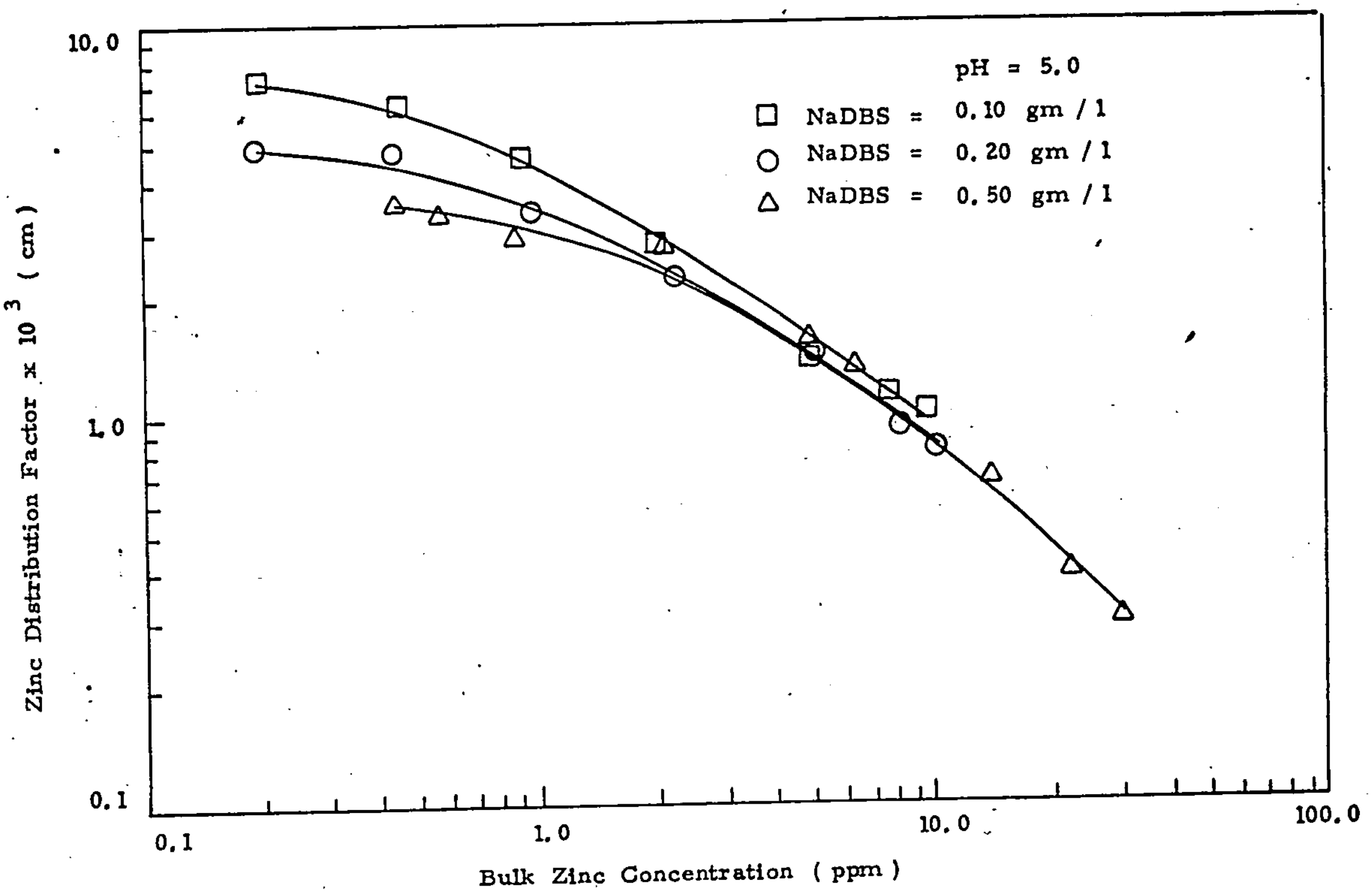

FIG. 7 - Zinc Distribution Factor versus Bulk Zn^{++} Concentration

by the gradual levelling off of the surface excess curve in Fig. 5 and approaching a surface excess of 1.4×10^{-10} g-mole / cm^2 .

Note that although the surface excess curves decrease with decreasing bulk Zn^{++} concentration as shown in Fig. 5 , the distribution factor curves in Fig. 6 increase . The reason for this is that for $\frac{\Gamma}{c}$, the c decreases more rapidly than Γ , and hence the ratio as a whole increases as c decreases .

In order to observe the trend of the distribution factor curves at high and low Zn^{++} concentrations, Fig. 6 was replotted in Fig. 7 on a log-log scale . Published distribution factor curves of Sr^{++} and UO_2^{++} also show the same pattern on a log-log scale (26 d , 34) .

With regard to the log-log scale , it is important to mention that the levelling off of the distribution factor curves at low bulk Zn^{++} concentration is due to the log scale characteristics . Very often this leads one to consider the curve to be horizontal at low Zn^{++} concentration . This is rather misleading because 1) a slight difference on the log scale may in most cases correspond to a great difference in the actual scale , and 2) this will be erroneous when one extrapolates the curve towards the lower Zn^{++} concentration . A very small slope upon the extrapolation means a much higher distribution factor . For example in Fig. 7 , if one extrapolates the distribution factor curve for zero Zn^{++} concentration , one has to extrapolate it up to infinity .

Effect of Collector Concentration on Surface Excess and Distribution Factor of Zn^{++}

From the previous section, in Fig. 5, it is noted that at lower bulk Zn^{++} concentration (less than 4 ppm), the surface excess of Zn^{++} is higher at lower collector concentration. Twelve data points from Fig. 5, together with experimental runs numbers 40 to 49 are plotted in Fig. 8 and Fig. 9 to show more clearly the effect of the bulk collector concentration. In this study, the lowest surfactant concentration used is 0.05 g / 1 (1.44×10^{-4} g-mole / 1) since the foam becomes unstable at surfactant concentration lower than this value. The pH used was 5.0. Experimental data are tabulated in Table V, Appendix A.

In Fig. 8, at 0.5 ppm (7.64×10^{-6} M) and 1.0 ppm (1.53×10^{-5} M), the surface excess of Zn^{++} increases as the collector concentration decreases. This same relationship has been reported for the foam fractionation of UO_2^{++} ($1.47 - 2.47 \times 10^{-6}$ M) and Sr^{++} ($4.5 \times 10^{-7} - 1.0 \times 10^{-6}$ M) using the collector Aresket 300 ($1 - 17 \times 10^{-3}$ M) (34). The effect of collector concentration becomes less significant at higher bulk Zn^{++} concentration. A closer observation of the 10 ppm Zn^{++} surface excess - collector concentration curve particularly shows that there is a slight increase initially and is followed by a gradual drop as the collector concentration increases. Further study was done using the same 10 ppm Zn^{++} concentration but at a pH of 2.0 (Run nos. 62 - 68). It is interesting that this curve also has a maximum as shown in Fig. 10. Similarly, the foam fractionation of Cu^{++} by NaLS and that of Zn^{++} by NaDBS, both in the presence of NaCl (0.01 g-mole / 1) (14, 15), show a maximum on their surface excess - collector concentration curves. It is therefore important to give an explanation to its occurrence.

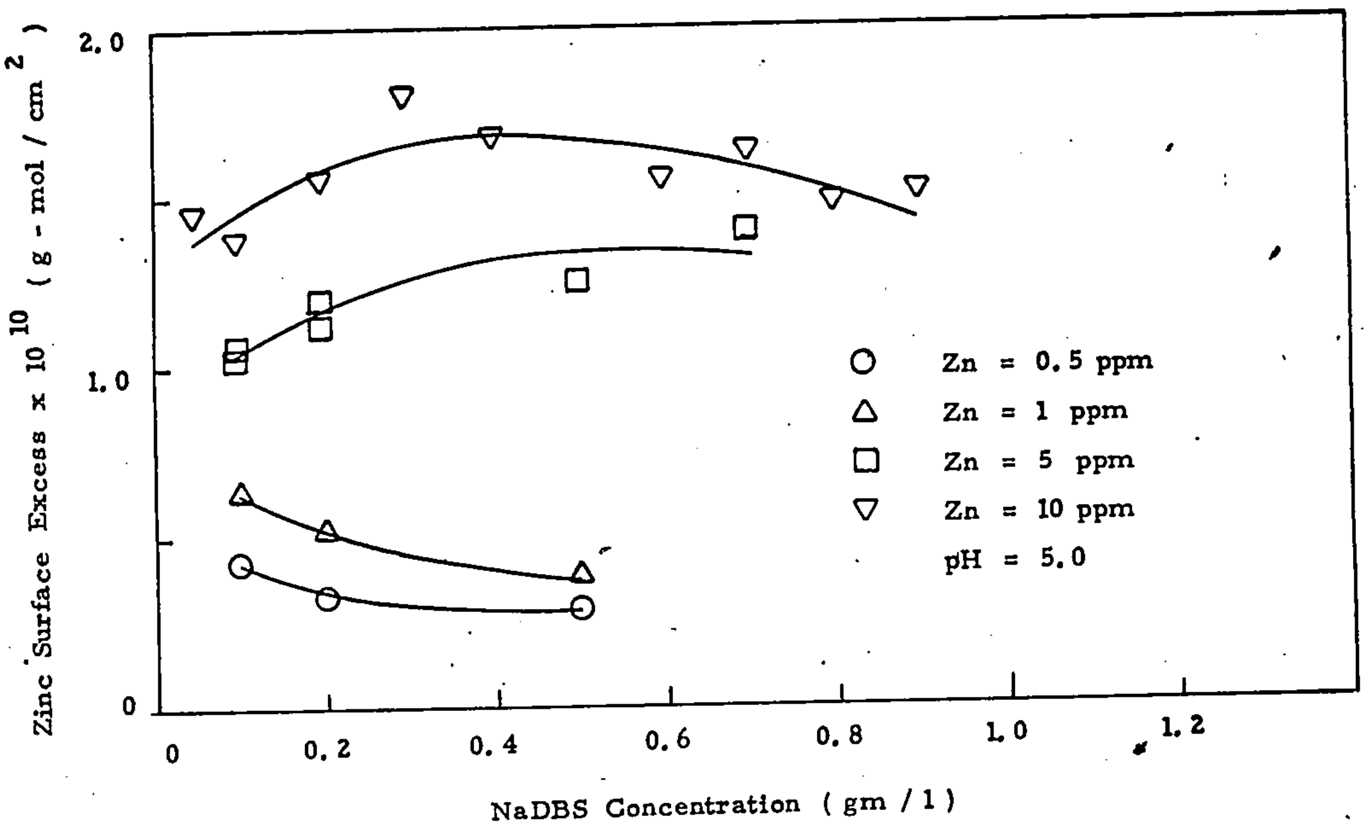

FIG. 8 - Zinc Surface Excess versus NaDBS Concentration

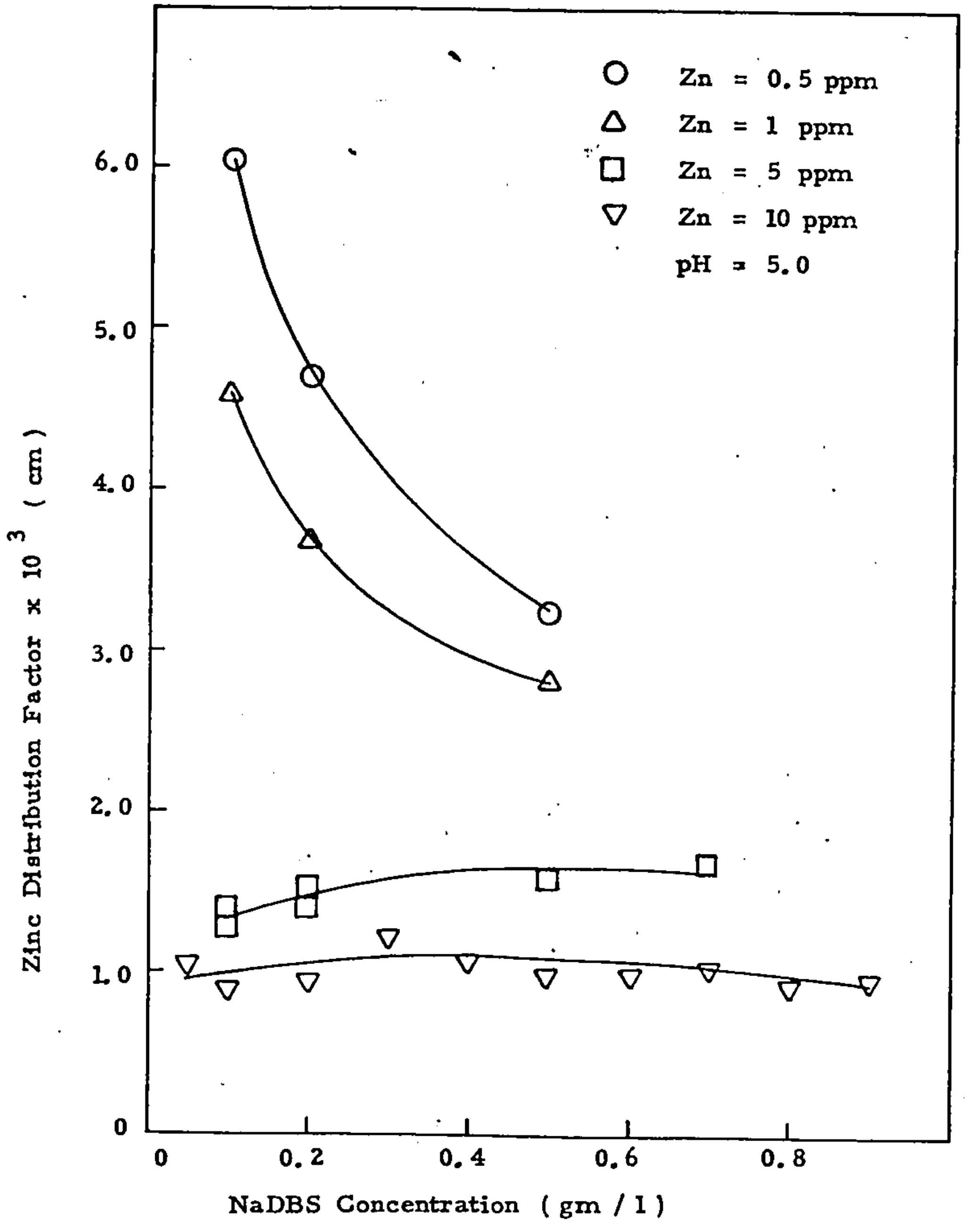

FIG. 9 - Zinc Distribution Factor versus NaDBS Concentration

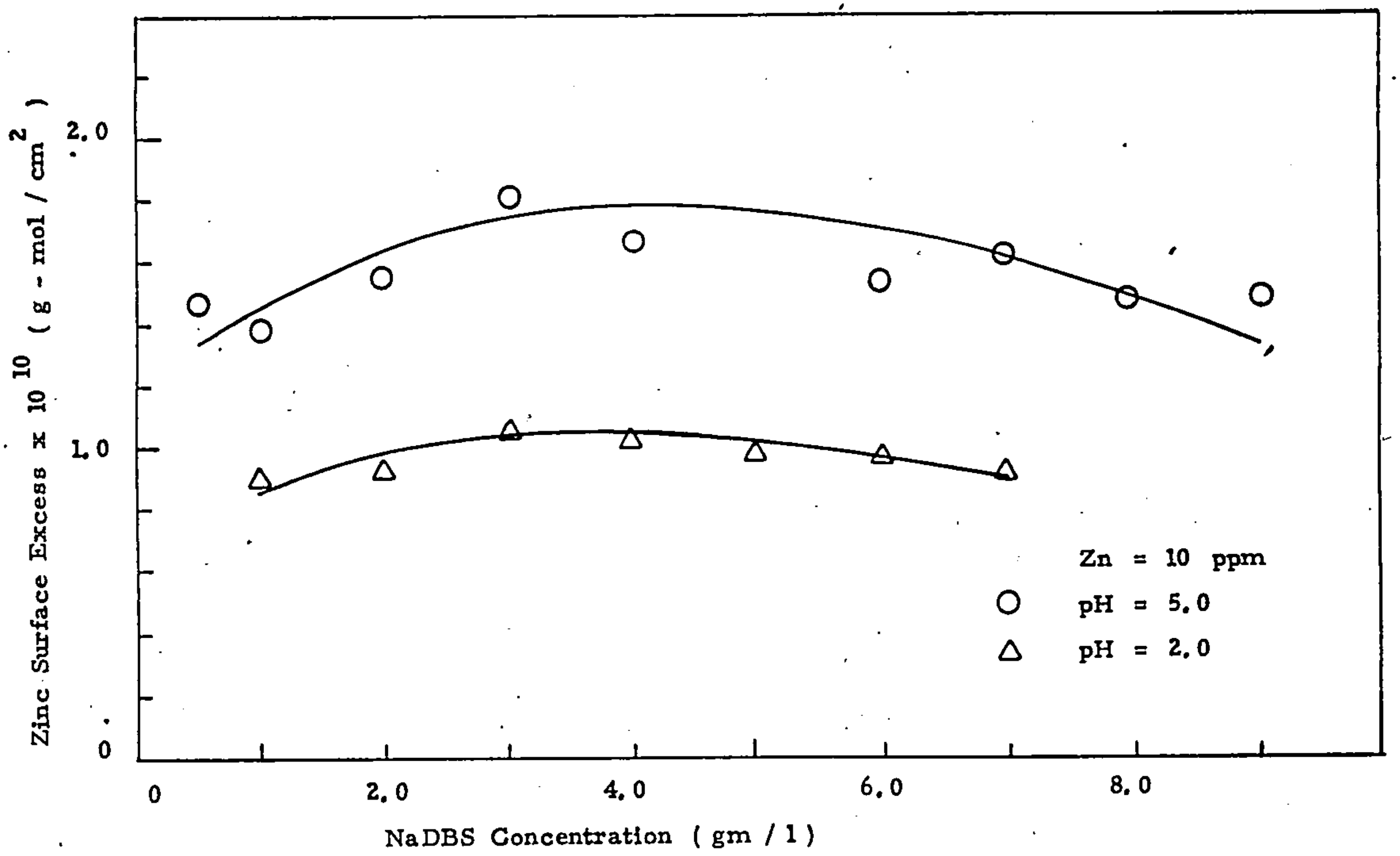

FIG. 10 - Zinc Surface Excess versus NaDBS Concentration at Different pH

At low collector concentration, the unoccupied bubble surfaces continually adsorb the collector as bulk collector concentration increases. This increase in " surface " collector is due to the presence of more " free " collector in the solution at higher bulk collector concentration. Although an increase in " surface " collector will tend to increase the adsorption of metallic Zn^{++}, this effect is counteracted by the increase of the " free " collector concentration and the Na^{+} cations that is associated with the collector.

The increase in the " free " collector will inhibit the foam fractionation of Zn^{++} by competing with the " surface " collector for the available metallic ions. The increase of Na^{+} cation will in turn compete with the very cation, Zn^{++}, that the collector intends to remove. Thus, the increased collector concentration will augment the competitive effect by increasing the number of competing ions and the " free " collector in the solution. Therefore the surface excess - collector concnetration curves in Fig. 8, for 0.5 ppm and 1.0 ppm of Zn^{++}, increases as the collector concentration decreases.

At high bulk Zn^{++} concentration, there will be sufficient Zn^{++} to lessen the competitive effect between the " free " and " surface " collector, and to suppress the competing effect of the cation that is associated with the collector, Hence the competing effects due to the increase in collector concentration will become less significant. One will therefore expect the maximum adsorption of the Zn^{++} to occur when the bubble surfaces are saturated with the surface collector. The adsorption of Zn^{++} will drop when the collector concentration increases to an extent that the Zn^{++} becomes insufficient in suppressing the " counter adsorption " effects. As a consequence, the competing effects reoccur and adsorption decreases as in Fig. 10.

Fig. 9 is a plot of Fig. 8 in terms of distribution factor. The order of the curves is reversed, i.e., D (10 ppm) $\langle$ D (5ppm) $\langle$ D (1 ppm) $\langle$ D (0.5 ppm). This is due to the definition of distribution factor in relation to surface excess, $D = \frac{\Gamma}{C}$. Although at high bulk Zn^{++} concentration, there is a slight maximum for the distribution factor curve, it is still of less significance as compared to the rapid increase in the distribution factor at 0.5 ppm and 1.0 ppm of Zn^{++} concentration. To conclude, the lowest surfactant concentration that will produce desirable foam properties should be used for maximum recovery and less collector consumption.

Effect of Alkali Metal Ions on the Removal of Zn^{++}

Experiments were conducted on the effect of alkali metal ions of various effective hydrated radius. For run nos. 62 to 80 only one particular kind of alkali metal ion was present, and from run nos. 56 to 61, the only cation in solution is H_3O^+. All the experimental results are tabulated in Table VI in Appendix A.

The solution for LiDBS and KDBS were prepared as follows. The required amount of NaDBS was weighed and dissolved in 2 liters of deionized distilled water. The solution was passed through a column of H_3O^+ cation exchanger to replace the sodium ions with the H_3O^+. The column was occasionally checked to ensure that no significant Na^+ were present in the eluant. KNO_3 or $LiNO_3$ that will produce the same gram - mole concentration as the DBS^- was added to the solution. The required amount of Zn^{++} standard was added and the solution was then made up to 4 liters with deionized distilled water. Finally the pH of the solution was adjusted to 2.0 with HNO_3.

Since the solution was made up of one particular kind of alkali metal ions and with the same molar concentration as the DBS^-, it can therefore be treated as if it were prepared from that particular alkali form of collector, e.g. Na^+ form, K^+ form, or Li^+ form.

Fig. 11 shows the effect of alkali metal ions on the distribution factor of Zn^{++}. The order of the curves is KDBS NaDBS LiDBS HDBS which is in the increasing order of the effective hydrated ionic radius. Table I (35) gives the values of their effective radius. This indicates that for the same valency, ions of smaller hydrated radius are more preferentially adsorbed on the surface and therefore are more competitive. H_3O^+ has the largest hydrated radius, and hence is the least competitive among them,

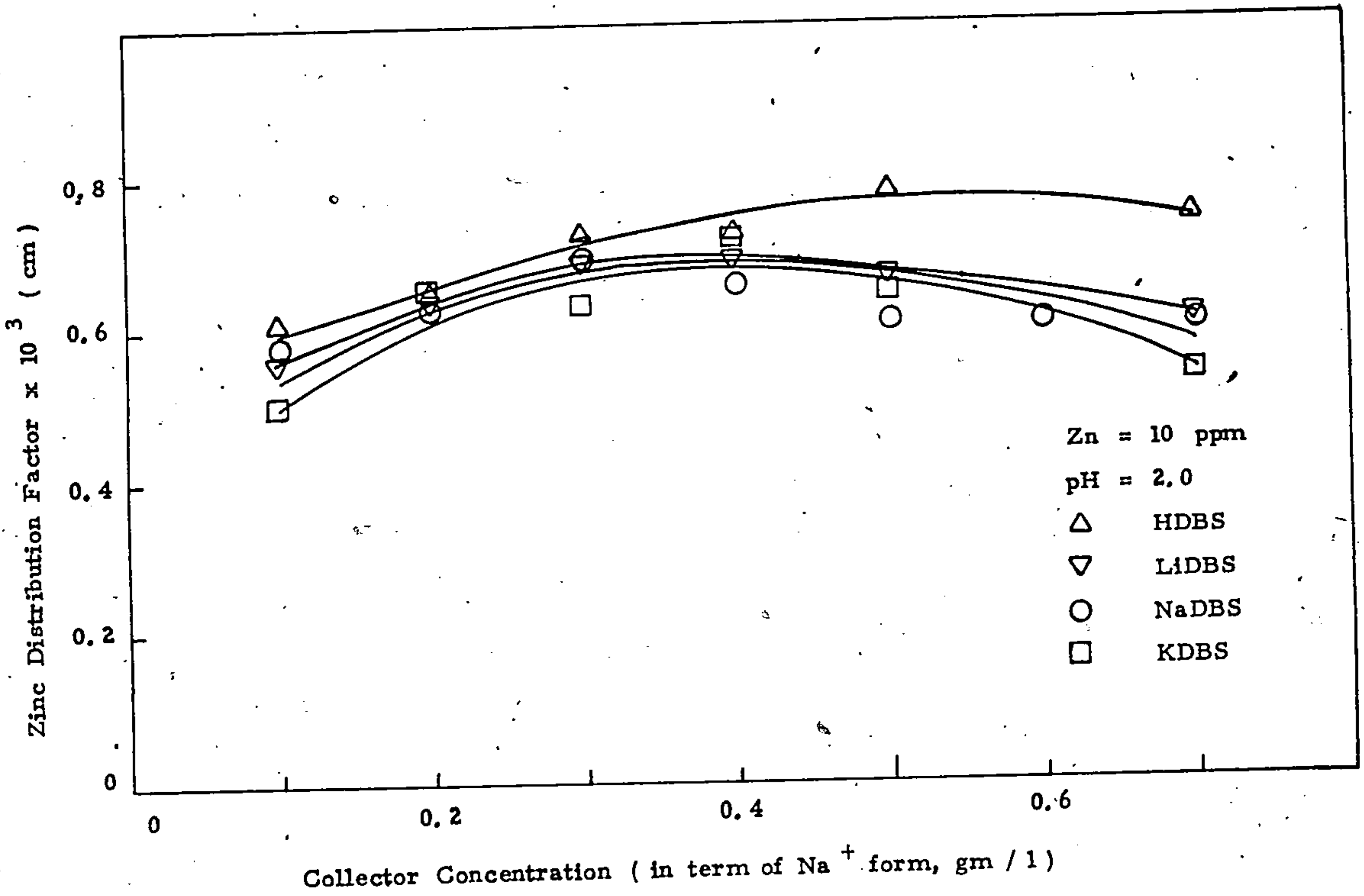

FIG. 11 - Zinc Distribution Factor versus Collector Concentration

Table I - The Effective Radii of Ions

Element	Effective Diameter of Unhydrated Ion x 10^{8} (cm)	Effective Radius of Hydrated Ion x 10^{8} (cm)
Li^+	0.8	5.3
Na^+	1.0	4.7
K^+	1.6	3.9

The effective radius of hydrated ion of H_3O^+ is taken as 9 x 10^{-8} cm.

and gives the highest distribution factor curve. A study on the foam fractionation of Cd^{++}, Cu^{++}, and Pb^{++} ions by NaDBS (16) showed the same order of preference of adsorption with hydrated radius.

This experimental result is supported by the modified theory of the Gouy - Chapman diffuse layer concept that was theoretically developed by J. Jorne and E. Rubin. The theory states that the mechanism for the removal of ions from the solution is that of electrostatic attraction and that selectivity depends on the charge and size of the hydrated ion.

The theoretical equations are quite lengthy and up to the present time no work has been done to check it quantitatively with this work.

CONCLUSIONS

The effects of 4 parameters on the zinc ion surface excess and zinc ion distribution factor were considered.

1 . The optimum pH range observed for 10 ppm bulk zinc ion concentration and 0.5 g/l of NaDBS was from 3.0 to 5.0.

2 . An increase in collector concentration at a lower zinc ion concentration (e.g. 0.5 ppm and 1.0 ppm) decreased the adsorption of zinc ion by the " surface " collector. An increase in collector concentration at a higher zinc ion concentration (e.g. 5 ppm and 10 ppm) was less significant in effect.

3 . The surface excess of zinc ion decreased with a decrease in the bulk zinc ion concentration, whereas the zinc ion distribution factor increased.

4 . The order of increasing effectiveness by the various forms of DBS for the removal of zinc ion is KDBS $<$ NaDBS $<$ LiDBS $<$ HDBS. This order is the same as that of increasing effective hydrated ionic radius. This finding is in agreement with the modified theory of Gouy-Chapman diffuse double layer concept.

Conditions suitable for foam fractionation of metal ions are :

1 . the operation at an optimum pH range ;
2 . the use of the lowest collector concentration that will give general desirable foam ;
3 . the use of low metal ion concentration ; and
4 . the use of collector whose cation is of larger hydrated radius.

RECOMMENDATION FOR FUTURE WORK

It is recommended that the present research work be extended to explore the feasibility of separating and recovering metal ions from complex aqueous solutions. Knowledge gained from this research concerning solution effects such as surfactant concentration, ionic equilibrium and ionic radius should be exploited. In addition to this, the possibility of the use of various auxiliary ligands and different surfactants should be studied.

The fundamental concepts of the foam separation of ions are interfacial and common to other separation techniques such as froth flotation, ion exchange and extraction. Some work should be done to consolidate the information of related fields to take advantage of existing knowledge.

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Appendix A

Table of Experimental Data and Calculated Results

Table II - Experimental Data.

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
1	0.50	2.045	10.5	16.5	2.790	97.614	12800
2	0.50	2.490	10.7	17.0	3.348	97.614	12588
3	0.50	2.594	10.7	17.0	3.632	97.614	12295
4	0.50	2.756	10.7	17.5	3.567	97.614	12337
5	0.50	2.861	10.7	17.5	3.343	97.614	12250
6	0.50	2.899	10.5	18.0	3.356	97.614	12400
7	0.50	3.224	10.5	18.3	3.535	97.614	12348
8	0.50	3.424	10.9488	21.2675	2.244	97.614	11320
9	0.50	3.791	10.9488	21.2675	2.312	97.614	12085
10	0.50	4.117	10.2	20.0	2.753	97.614	12190
11	0.50	4.505	10.1266	20.8352	2.205	97.614	11680
12	0.50	5.182	10.2	18.3	2.741	97.614	12850
13	0.50	5.785	9.8773	20.2111	2.106	97.614	11910
14	0.50	5.837	10.0	20.0	2.184	97.614	13320
15	0.50	6.575	10.9	19.3	2.291	97.614	11412

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
16	0. 50	6. 643	10. 1547	19. 439	2. 177	97. 614	11875
17	0. 50	7. 017	10. 7	17. 4	2. 831	97. 614	12835
18	0. 10	4. 975	10. 0457	20. 4047	1. 957	97. 614	10680
19	0. 10	5. 050	8. 0153	19. 2927	1. 830	97. 614	10560
20	0. 10	4. 996	4. 99927	12. 3431	2. 133	97. 614	10500
21	0. 10	4. 971	2. 10082	8. 5656	2. 003	97. 614	10740
22	0. 10	4. 964	0. 898651	6. 85951	1. 596	97. 614	11385
23	0. 10	4. 963	0. 457558	3. 00789	2. 466	97. 614	10910
24	0. 10	4. 962	0. 204453	1. 50061	2. 670	97. 614	11165
25	0. 20	5. 070	10. 6719	21. 2675	2. 188	97. 614	11125
26	0. 20	5. 070	8. 3822	15. 8043	2. 364	97. 614	10930
27	0. 20	4. 993	5. 17554	12. 3431	2. 331	97. 614	10850
28	0. 20	4. 993	2. 34411	7. 59834	2. 236	97. 614	10455
29	0. 20	5. 023	1. 02581	3. 87634	2. 666	97. 614	10380
30	0. 20	5. 010	0. 457558	2. 59064	2. 296	97. 614	10845

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
31*	0.50	4.91	0.354	3.101	1.232	120.00	12250
32*	0.50	5.03	0.584	5.009	1.188	124.31	12090
33*	0.50	4.94	0.906	6.983	1.170	124.31	12200
34*	0.50	5.01	2.190	20.505	0.8762	118.34	12740
35*	0.50	5.02	4.993	32.797	0.7829	118.34	12070
36*	0.50	5.09	6.435	33.291	0.8546	118.34	12980
37*	0.50	5.00	8.850	35.355	0.8895	118.34	12130
38*	0.50	5.00	15.100	46.467	0.7695	118.34	12120
39	0.20	5.034	0.20445	1.18683	2.337	97.614	11065
40	0.10	5.038	5.04665	12.1114	2.145	97.614	10730
41	0.20	5.009	5.12215	13.2191	2.232	97.614	11225
42	0.70	5.001	5.3505	9.9767	4.582	97.614	11585
43	0.05	5.003	8.98651	21.4404	1.769	97.614	11400
44	0.30	4.968	9.61029	25.6259	1.713	97.614	11605
45	0.40	4.976	9.99565	24.7516	1.750	97.614	12100

* Data from R. J. St Eloi (15).

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
46	0.60	4.972	9.9305	23.0048	1.890	97.614	13655
47	0.70	5.034	10.1547	17.9967	2.993	97.614	10015
48	0.80	4.960	10.1547	17.0129	3.128	97.614	10095
49	0.90	4.991	10.0009	17.7970	2.806	97.614	10095
50	0.10	2.087	10.1547	15.8773	2.317	97.614	10700
51	0.10	2.015	1.14112	4.49625	2.542	97.614	10535
52	0.10	2.023	5.41407	10.9345	2.311	97.614	10490
53	0.10	2.006	8.94279	14.7858	2.423	97.614	10905
54	0.10	2.018	0.608904	2.30004	2.359	97.614	10380
55	0.10	1.993	0.223144	1.09803	2.840	97.614	11295
56	0.10	2.050	10.3093	17.4021	2.012	97.614	10905
57	0.20	2.013	10.7771	17.7970	2.212	97.614	10425
58	0.30	2.010	10.7771	20.2984	1.900	97.614	11410
59	0.40	2.003	10.6205	18.4005	2.297	97.614	11645
60	0.50	1.995	10.4645	18.6048	2.294	97.614	11140

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
61	0.70	1.994	11.0927	19.98646	2.266	97.614	13215
62	0.40	2.068	10.1547	17.2068	2.175	97.614	11485
63	0.50	2.020	10.4645	18.1979	1.937	97.614	12275
64	0.20	2.089	10.0009	16.6291	2.069	97.614	10945
65	0.30	2.092	10.7771	17.0129	2.629	97.614	10070
66	0.60	2.011	10.4645	18.6048	1.959	97.614	14990
67	0.70	1.989	11.0927	17.4021	2.708	97.614	10070
68	0.70	2.092	10.7771	17.0129	2.629	97.614	15422
69	0.10	2.020	10.7771	15.7293	2.542	97.614	11430
70	0.20	2.031	10.7771	18.4005	2.131	97.614	11600
71	0.30	2.022	10.7771	17.0129	2.544	97.614	11810
72	0.40	2.012	10.7771	21.7369	1.652	97.614	11510
73	0.50	2.016	11.4112	20.2984	1.942	97.614	11805
74	0.70	2.010	11.8949	18.4005	2.722	97.614	20225
75	0.70	1.994	11.0927	17.797	2.589	97.614	15640

Run	NaDBS (gm / 1)	pH	X_B (ppm)	Y_F (ppm)	V_F (gm / min)	G (ml / min)	$\sum N$ (bpm)
76	0.50	2.012	11.0927	17.797	2.617	97.614	12355
77	0.40	1.930	10.7771	18.4005	2.278	97.614	12215
78	0.30	1.960	10.4645	16.6291	2.736	97.614	12060
79	0.20	1.986	10.4645	17.0129	2.350	97.614	11490
80	0.10	2.005	10.4645	15.5088	2.681	97.614	11740

Table III - Effect of pH on the Surface Excess and Distribution Factor of Zn^{++}.

Run	pH	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
1	2.045	0.9394	0.5849
2	2.490	1.190	0.7411
3	2.594	1.301	0.7950
4	2.756	1.378	0.8418
5	2.861	1.295	0.7909
6	2.899	1.428	0.8888
7	3.224	1.566	0.9751
8	3.424	1.539	0.9188
9	3.791	1.551	0.9261
10	4.117	1.539	0.9862
11	4.505	1.553	1.002
12	5.182	1.414	0.9065
13	5.785	1.426	0.9467
14	5.837	1.375	0.8986
15	6.575	1.275	0.7648
16	6.643	1.3217	0.8508
17	7.017	1.[illegible]87	0.7384

Feed Composition: Bulk Zn^{++} = 10 ppm

NaDBS = 0.5 gm / 1

Table IV - Effect of Bulk Zn^{++} Concentration on Surface Excess and Distribution Factor of Zn^{++}.

Run	X_B (ppm)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
18	10.0457	1.380	0.9021
19	8.0153	1.404	1.145
20	4.99927	1.067	1.396
21	2.10082	0.8759	2.726
22	0.898651	0.6310	4.590
23	0.457558	0.4230	6.044
24	0.204453	0.2310	7.387

Feed Composition. NaDBS = 0.10 gm / l
pH = 5.0

Run	X_B (ppm)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
25	10.6719	1.550	0.9496
26	8.3822	1.180	0.9200
27	5.17554	1.126	1.422
28	2.34411	0.8018	2.236
29	1.02581	0.5197	3.312
30	0.4576	0.3301	4.716
39	0.20445	0.1537	4.915

Feed Composition. NaDBS = 0.20 gm / l
pH = 5.0

Run	X_B (ppm)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
31*	0. 354	0. 191	3. 520
32*	0. 584	0. 291	3. 260
33*	0. 906	0. 392	2. 830
34*	2. 190	0. 926	2. 760
35*	4. 993	1. 250	1. 630
36*	6. 435	1. 320	1. 340
37*	8. 850	1. 350	0. 995
38*	15. 100	1. 380	0. 597

Feed Composition: NaDBS = 0. 50 gm / l
pH = 5. 0

Run	X_B (ppm)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
50	10. 1547	0. 8980	0. 5780
51	1. 14112	0. 5804	3. 325
52	5. 41407	0. 8697	1. 050
53	8. 94279	0. 9526	0. 6963
54	0. 608904	0. 2728	2. 929
55	0. 223144	0. 1652	4. 840

Feed Composition: NaDBS = 0. 10 gm / l
pH = 2. 0

Table V - Effect of Collector Concentration on Surface Excess and Distribution Factor of Zn^{++}.

Run	NaDBS (gm / 1)	$\times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
23	0.10	0.4230	6.044
30	0.20	0.3301	4.716
32*	0.50	0.291	3.260
	Feed Composition.	Bulk Zn^{++} Concentration = 0.5 ppm pH = 5.0	
22	0.10	0.6310	4.590
29	0.20	0.5197	3.312
33*	0.50	0.392	2.830
	Feed Composition.	Bulk Zn^{++} Concentration = 1 ppm pH = 5.0	
40	0.10	1.025	1.328
20	0.10	1.067	1.396
41	0.20	1.204	1.537
27	0.20	1.126	1.422
35*	0.50	1.250	1.630
42	0.70	1.398	1.708
	Feed Composition.	Bulk Zn^{++} Concentration = 5 ppm pH = 5.0	

Run	NaDBS (gm / l)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	D x 10^3 (cm)
43	0.05	1.461	1.062
29	0.10	1.380	0.9021
21	0.20	1.550	0.9496
44	0.30	1.808	1.230
45	0.40	1.679	1.098
37*	0.50	1.350	0.995
46	0.60	1.543	1.015
47	0.70	1.624	1.046
48	0.80	1.481	0.9535
49	0.90	1.511	0.9874

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm
pH = 5.0

50	0.10	0.8980	0.5780
64	0.20	0.9217	0.6025
65	0.30	1.133	0.6871
62	0.40	1.014	0.6529
63	0.50	0.9689	0.6052
66	0.60	0.9652	0.6029
67	0.70	0.9272	0.5464
68	0.70	1.133	0.6871

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm
pH = 2.0

Table VI- Effect of Alkali Metal Ions on the Removal of Zn^{++}.

Run	NaDBS (gm / l)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	$D \times 10^3$ (cm)
56	0.10	0.9601	0.6088
57	0.20	1.061	0.6435
58	0.30	1.200	0.7274
59	0.40	1.176	0.7241
60	0.50	1.247	0.7792
61	0.70	1.254	0.7393

NaDBS converted to HDBS

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm

pH = 2.0

50	0.10	0.8980	0.5780
64	0.20	0.9217	0.6025
65	0.30	1.133	0.6871
62	0.40	1.014	0.6529
63	0.50	0.9689	0.6052
66	0.60	0.9652	0.6029
67	0.70	0.9272	0.5464
68	0.70	1.133	0.6871
67 & 68	0.70	1.003	0.5997

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm

pH = 2.0

Run	NaDBS (gm / l)	$\Gamma \times 10^{10}$ (g - mol / cm^2)	D x 10^3 (cm)
69	0.10	0.8339	0.5058
70	0.20	1.071	0.6495
71	0.30	1.039	0.6305
72	0.40	1.197	0.7260
73	0.50	1.131	0.6479
74	0.70	0.9699	0.5330

NaDBS converted to KDBS

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm

pH = 2.0

80	0.10	0.8879	0.5546
79	0.20	1.018	0.6356
78	0.30	1.097	0.6855
77	0.40	1.125	0.6825
76	0.50	1.132	0.6674
75	0.70	1.036	0.610

NaDBS converted to LiDBS

Feed Composition: Bulk Zn^{++} Concentration = 10 ppm

pH = 2.0

Appendix B

Flowmeter Calibration

Flowmeter Calibration.

Flowmeter: Matheson # R - 2 - 15 A A
Upstream Pressure = 6 psig
Downstream Pressure = 3 psig

Table VII - Flowmeter Calibration

Reading	Air Flow Rate at STP (ml / min)
6.5	74.32
7.0	76.77
7.5	92.66
8.0	98.54
8.5	103.5
9.0	119.4
9.5	126.9
10.0	143.2
10.5	147.6
11.0	168.0
11.5	180.2
12.0	191.5
12.5	207.4
13.0	224.0
13.5	239.3
14.0	252.7
14.5	276.6
15.0	290.8

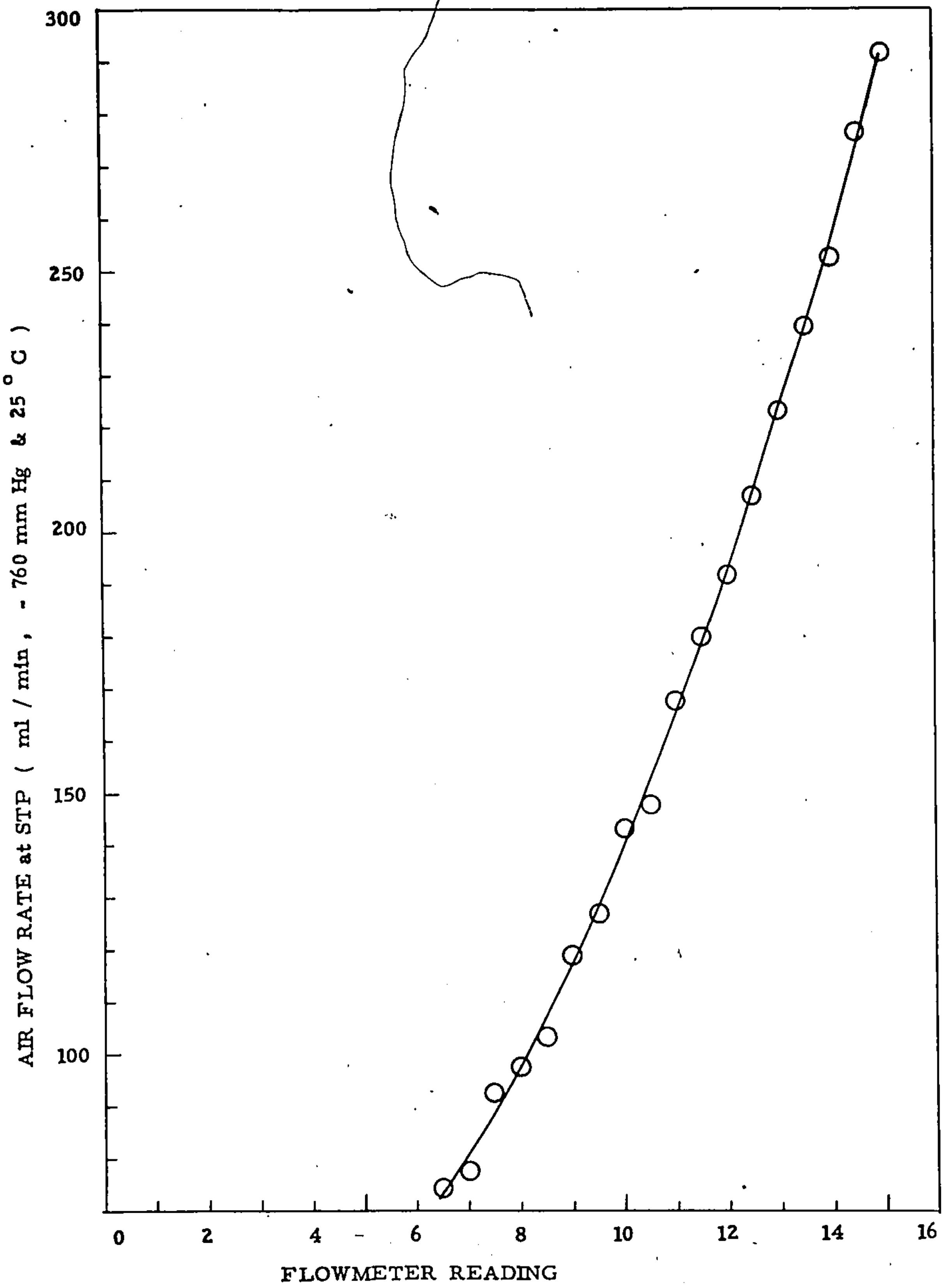


FIG. 12 - Air Flow Rate versus Flowmeter Reading

Appendix C

Calibration of Zn^{++} Concentration Curve

Absorption Measurements of Zn^{++} Concentration

Operating Conditions:

Wavelength = 213.9 mu

Slit Width = 0.4 mm

Fuel (Propane) = 400 cc / min

Fuel Pressure = 6.0 psig

Air = 5.0 l / min

Air Pressure = 40 psig

Burner Height = 1.2 cm

Sensitivity = 0.04 ppm

Table VIII - Calibration of Zn^{++} Concentration Curve

Zn^{++} Concentration (ppm)	% Transmittance
0	100.0
0.2	90.5
0.4	82.0
0.6	74.3
0.8	67.5
1.0	60.0
1.2	54.5
1.4	47.5
1.6	43.5
1.8	37.0
2.0	31.0

Zn^{++} Concentration (ppm)	% Transmittance
2.2	29.5
2.4	24.6
2.6	21.0
3.0	13.0
3.4	7.0
3.8	2.0
4.0	0.0

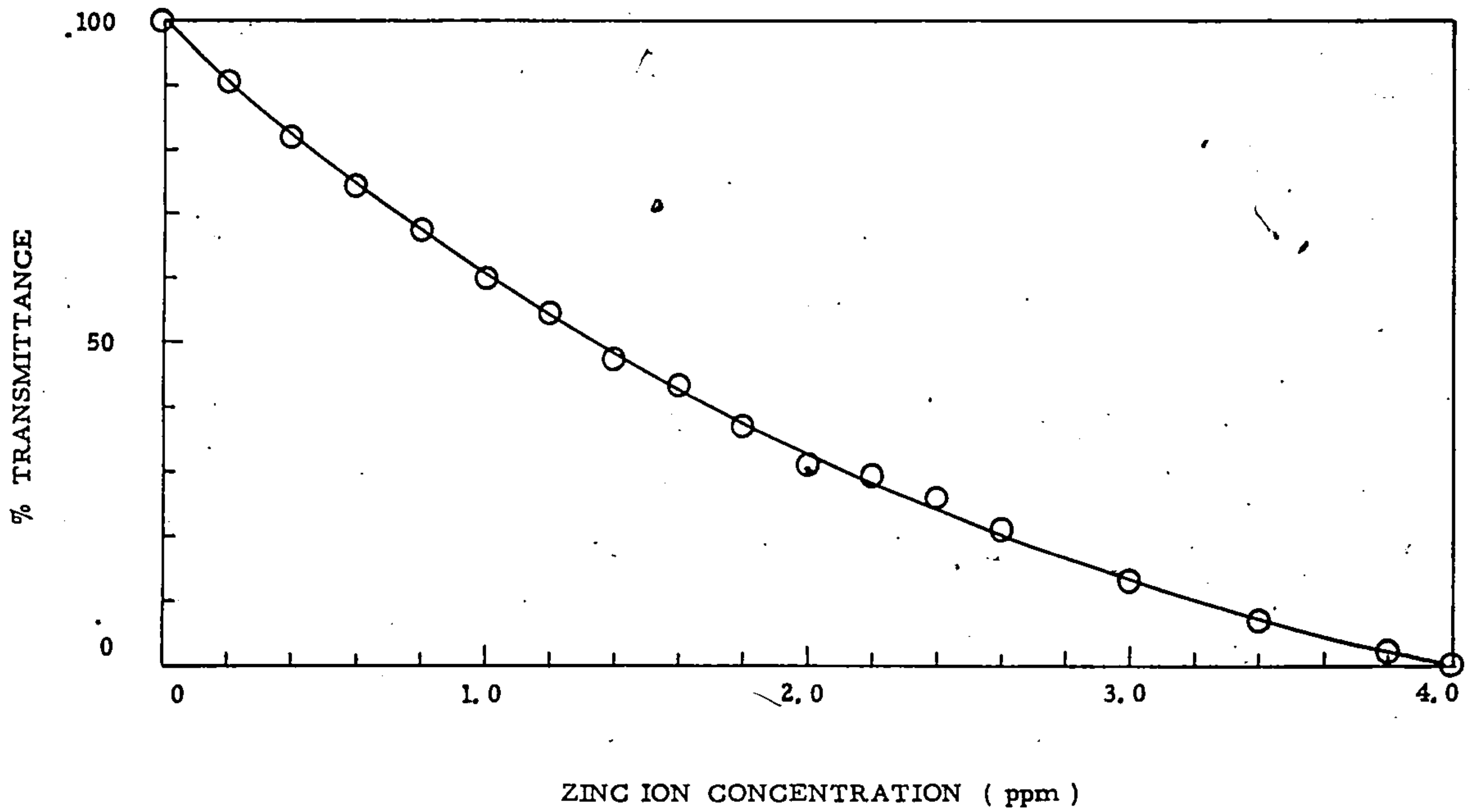


FIG. 13 - % Transmittance versus Zn^{++} Concentration

Appendix D

Calibration of Na^+ Concentration Curve

Emission Measurement of Na^+ Concentration

Operating Conditions:

Wavelength = 589.0 mu
Slit Width = 0.1 mm
Fuel (Propane) = 500 cc / min
Fuel Pressure = 6.0 psig
Air = 5.0 l / min
Air Pressure = 40 psig
Burner Height = 1.2 cm
Sensitivity = 0.04 ppm

Table IX - Calibration of Na^+ Concentration Curve

Na^+ Concentration (ppm)	% Emission
0	0
0.4	13.0
0.8	25.5
1.2	37.5
1.6	49.0
2.0	59.0
2.8	78.0
3.2	85.0
3.6	94.0
4.0	100.0

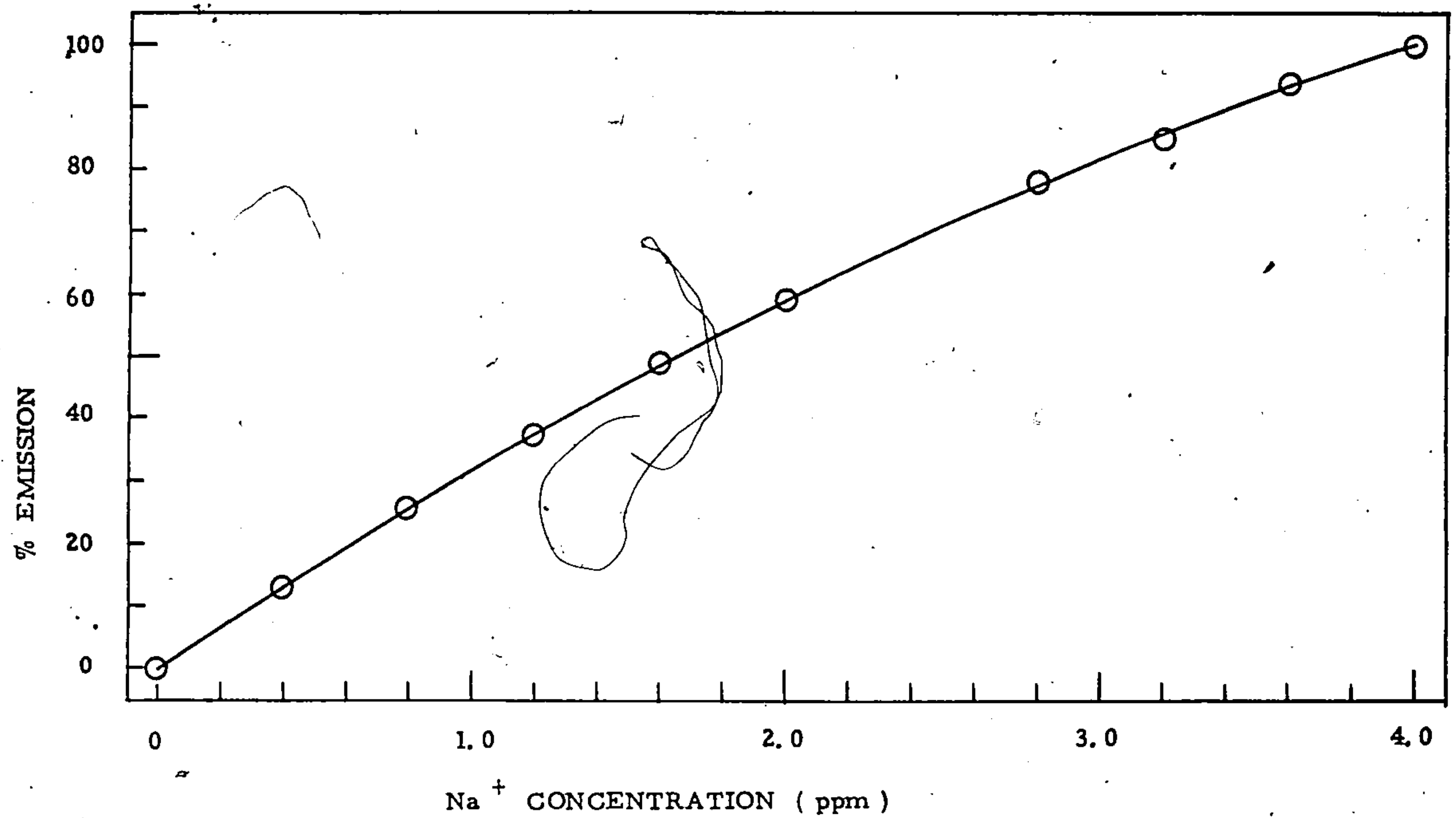


FIG. 14 - % Emission versus Na $^+$ Concentration

Appendix E

Calibration of NaDBS Concentration Curve

Absorbance of NaDBS

Table X - Calibration Curve for NaDBS Concentration.

NaDBS Concentration (mg / l)	% Transmittance
0.0	100.0
0.5	87.3
1.0	81.5
2.0	72.0
3.0	57.4
4.0	43.7
5.0	38.8
6.0	32.7
7.0	29.5
8.0	24.3
9.0	22.5
10.0	18.8

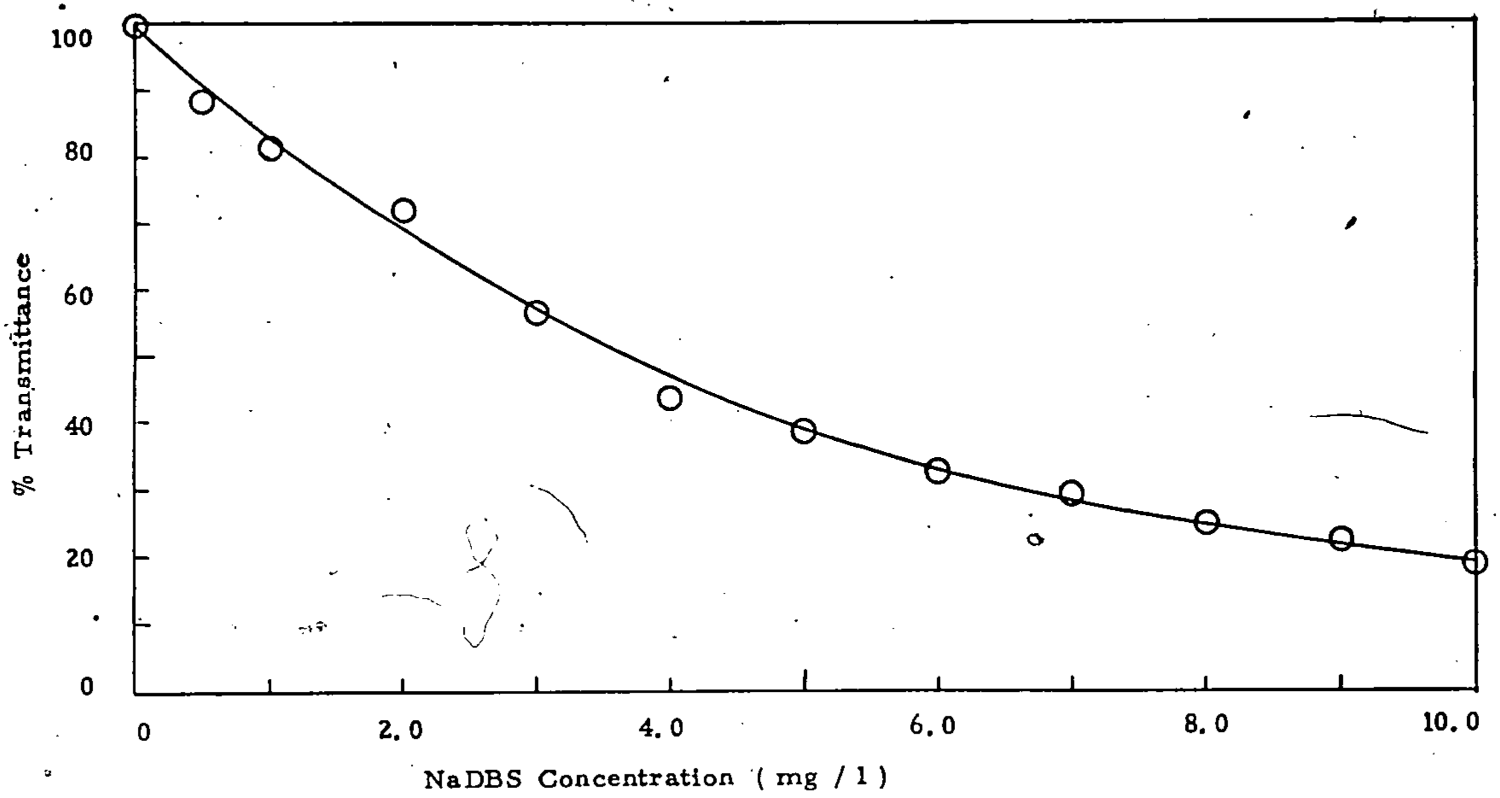


FIG. 15 - % Transmittance versus NaDBS Concentration

Appendix F

Surface Tension Measurements

Surface Tension Measurements.

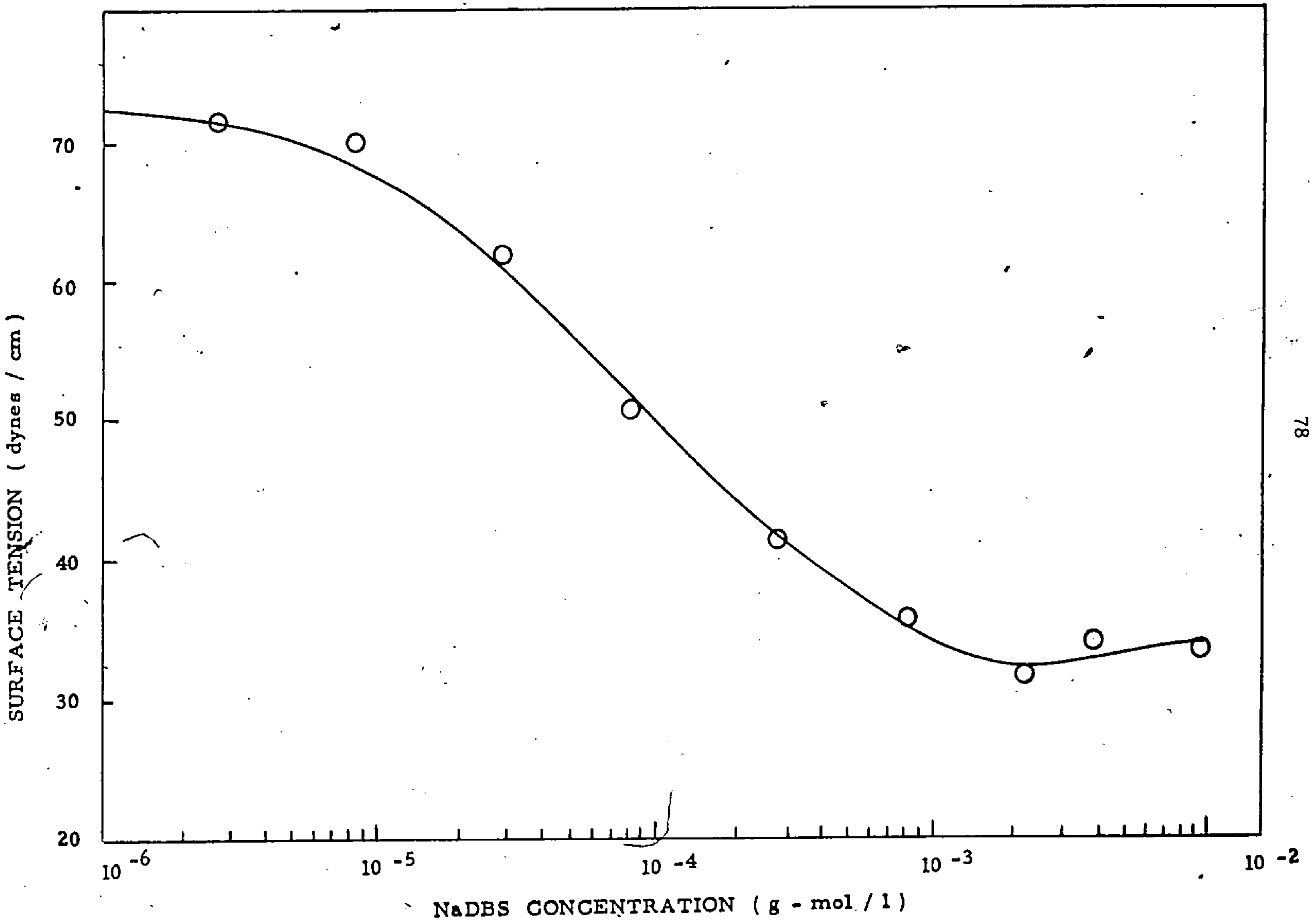
The surface tension of sodium dodecyl benzene sulfonate is dependent on the pH of the solution. Therefore it is necessary to consider the pH in its measurement. The surface tension - collector concentration diagram in Fig. 16 was constructed at pH of 2. 0.

The decrease of surface tension with increasing collector concentration is due to an increase of collector at the gas - liquid interface. The break in the curve is an indication of micelles formation. From the diagram, the critical micelles concentration of NaDBS at pH of 2. 0 is about 1×10^{-3} g - mol / l .

Table XI - Surface Tension Measurements at pH = 2. 0

NaDBS Concentration (g - mol / l)	Surface Tension (dynes / cm)
2.87×10^{-6}	71. 1
8.61×10^{-6}	69. 9
2.87×10^{-5}	62. 2
8.61×10^{-5}	53. 0
2.87×10^{-4}	41. 5
8.61×10^{-4}	35. 4
2.01×10^{-3}	31. 9
4.02×10^{-3}	35. 0
8.61×10^{-3}	34. 5

FIG. 16 - Surface Tension versus NaDBS Concentration



Appendix G

Computer Program for Least Squares Fit of Calibration Curves

```
502  REM      LEAST SOUARE FIT FOR LINEAR VARIABLE
504  REM      N9 = NO. OF CONST. ; M9 = NO. OF DATA SET
506  REM      DIM  X(M9,N9),Y(M9),A(N9,N9),B(N9),Z(M9),E(M9)
508  REM      DATA X(M9,0),Y(M9) LINES 745-900
510  REM      FUNTION GENERATION LINES 540-570
512  PRINT "NO. OF CONST."
514  INPUT N9
515  PRINT
516  PRINT "NO. OF DATA SET"
518  INPUT M9
519  PRINT
520  FOR I=1 TO M9
522    READ X[I, 0],Y[I]
540    LET X[I,1]=1
542    LET S1=1
544    FOR J=2 TO N9
546      LET X[I,J]=X[I, 0]*S1
548      LET S1=X[I,J]
550    NEXT J
572  NEXT I
574  FOR K=1 TO N9
576    FOR L=1 TO N9
578      LET S1= 0
580      FOR I=1 TO M9
582        LET S1=S1+X[I,K]*X[I,L]
584      NEXT I
586      LET A[K,L]=S1
588    NEXT L
589    LET S2= 0
590    FOR J=1 TO M9
592      LET S2=S2+X[J,K]*Y[J]
594    NEXT J
596    LET B[K]=S2
598  NEXT K
600  FOR I=1 TO N9
602    IF A[I,I]<1E-30 GOTO  606
604    GOTO  610
606    PRINT "ZERO IS THE VALUE OF A(";I;",";I;")"
608    GOTO  749
610    LET B[I]=B[I]/A[I,I]
612    LET C=A[I,I]
614    FOR J=1 TO N9
616      LET A[I,J]=A[I,J]/C
618    NEXT J
620    IF I=N9 GOTO  636
```

```
622  FOR K=I+1  TO N9
624    LET B[K]=B[K]-B[I]*A[K,I]
626    LET D=A[K,I]
628    FOR L=I  TO N9
630      LET A[K,L]=A[K,L]-A[I,L]*D
632    NEXT L
634  NEXT K
636  NEXT I
638  FOR J=N9  TO 1  STEP -1
640    IF J=1 GOTO  650
642    FOR K=J-1  TO 1  STEP -1
644      LET B[K]=B[K]-B[J]*A[K,J]
646      LET A[K,J]=A[K,J]-A[J,J]*A[K,J]
648    NEXT K
650  NEXT J
652  PRINT "COEFFICIENTS OF THE EQUATION ARE AS FOLLOWS"
654  FOR N=1  TO N9
656    PRINT N,A[N,N],B[N]
658  NEXT N
660  PRINT
662  PRINT "X VALUE","EXPT. Y","CALC. Y","% DIFF."
664  FOR L=1  TO M9
666    LET S1= 0
668    FOR K=1  TO N9
670      LET S1=S1+B[K]*X[L,K]
672    NEXT K
674    LET Z[L]=S1
676    LET S9=((Y[L]-Z[L])/Z[L])*100
678    LET E[L]= ABS (S9)
680    PRINT X[L, 0],Y[L],Z[L],E[L]
682  NEXT L
690  GOTO  1000
700  GOTO  740
740  END
1000  PRINT
1001  PRINT
1002  PRINT
1019  PRINT "READING","    PPM"
1020  FOR I=1  TO 1001
1030    LET X9=(I/10)-.1
1035    LET Y9=B[1]
1040    FOR N=2  TO N9
1050      LET Y9=Y9+B[N]*((X9)↑(N-1))
1060    NEXT N
1070    PRINT X9,Y9
1080  NEXT I
1100  GOTO  740
```

Appendix H

A Sample Computer Print Out of Calibration Curve

```
NO. OF CONST.
5
NO. OF DATA SET
18
COEFFICIENTS OF THE EQUATION ARE AS FOLLOWS
 1              1              3.97342
 2              1             -8.39473E-2
 3              1              9.48083E-4
 4              1             -7.85751E-6
 5              1              2.80103E-8

X VALUE         EXPT. Y        CALC. Y          % DIFF.
 100            0              3.04031E-3       100
 90.5           .2             .196041          2.01954
 82             .4             .398681          .330854
 74.3           .6             .600725          .120673
 67.5           .8             .791609          1.05993
 60             1              1.01548          1.52406
 54.5           1.2            1.18949          .883165
 47.5           1.4            1.42553          1.79072
 43.5           1.6            1.56925          1.95972
 37             1.8            1.81979          1.08747
 31             2              2.07395          3.56572
 29.5           2.2            2.14154          2.72978
 24.6           2.4            2.37535          1.03787
 21             2.6            2.56131          1.51037
 13             3              3.02587          .855034
 7              3.4            3.42962          .863699
 2              3.8            3.80926          .243084
 0              4              3.97342          .668821
```

READING	PPM
0	3.97342
.1	3.96503
.2	3.95667
.3	3.94832
.4	3.93999
.5	3.93168
.6	3.92339
.7	3.91512
.8	3.90686
.9	3.89863
1	3.89041
1.1	3.88221
1.2	3.87403
1.3	3.86587
1.4	3.85773
1.5	3.8496
1.6	3.8415
1.7	3.83341
1.8	3.82534
1.9	3.81729
2	3.80925
2.1	3.80124
2.2	3.79324
2.3	3.78526
2.4	3.7773
2.5	3.76935
2.6	3.76143
2.7	3.75352
2.8	3.74563
2.9	3.73776
3	3.7299
3.1	3.72206
3.2	3.71424
3.3	3.70644
3.4	3.69865
3.5	3.69088
3.6	3.68313
3.7	3.6754
3.8	3.66768
3.9	3.65999
4	3.6523
4.1	3.64464
4.2	3.63699
4.3	3.62936
4.4	3.62175
4.5	3.61415
4.6	3.60657
4.7	3.59901
4.8	3.59146
4.9	3.58393
5	3.57642

READING	PPM
5.1	3.56892
5.2	3.56144
5.3	3.55398
5.4	3.54654
5.5	3.53911
5.6	3.53169
5.7	3.5243
5.8	3.51692
5.9	3.50955
6	3.50221
6.1	3.49487
6.2	3.48756
6.3	3.48026
6.4	3.47298
6.5	3.46571
6.6	3.45846
6.7	3.45122
6.8	3.44401
6.9	3.4368
7	3.42962
7.1	3.42244
7.2	3.41529
7.3	3.40815
7.4	3.40103
7.5	3.39392
7.6	3.38682
7.7	3.37975
7.8	3.37269
7.9	3.36564
8	3.35861
8.1	3.35159
8.2	3.34459
8.3	3.33761
8.4	3.33064
8.5	3.32369
8.6	3.31675
8.7	3.30982
8.8	3.30292
8.9	3.29602
9	3.28914
9.1	3.28228
9.2	3.27543
9.3	3.2686
9.4	3.26178
9.5	3.25498
9.6	3.24819
9.7	3.24141
9.8	3.23465
9.9	3.22791
10	3.22118

READING	PPM
10.1	3.21446
10.2	3.20776
10.3	3.20107
10.4	3.1944
10.5	3.18774
10.6	3.1811
10.7	3.17447
10.8	3.16786
10.9	3.16125
11	3.15467
11.1	3.1481
11.2	3.14154
11.3	3.13499
11.4	3.12846
11.5	3.12195
11.6	3.11545
11.7	3.10896
11.8	3.10248
11.9	3.09602
12	3.08958
12.1	3.08315
12.2	3.07673
12.3	3.07032
12.4	3.06393
12.5	3.05755
12.6	3.05119
12.7	3.04484
12.8	3.0385
12.9	3.03218
13	3.02587
13.1	3.01957
13.2	3.01329
13.3	3.00702
13.4	3.00076
13.5	2.99452
13.6	2.98829
13.7	2.98207
13.8	2.97586
13.9	2.96967
14	2.9635
14.1	2.95733
14.2	2.95118
14.3	2.94504
14.4	2.93891
14.5	2.9328
14.6	2.9267
14.7	2.92061
14.8	2.91454
14.9	2.90848
15	2.90243

READING	PPM
15.1	2.89639
15.2	2.89037
15.3	2.88435
15.4	2.87836
15.5	2.87237
15.6	2.8664
15.7	2.86043
15.8	2.85448
15.9	2.84855
16	2.84262
16.1	2.83671
16.2	2.83081
16.3	2.82492
16.4	2.81905
16.5	2.81318
16.6	2.80733
16.7	2.80149
16.8	2.79567
16.9	2.78985
17	2.78405
17.1	2.77825
17.2	2.77248
17.3	2.76671
17.4	2.76095
17.5	2.75521
17.6	2.74948
17.7	2.74375
17.8	2.73805
17.9	2.73235
18	2.72666
18.1	2.72099
18.2	2.71533
18.3	2.70967
18.4	2.70403
18.5	2.69841
18.6	2.69279
18.7	2.68718
18.8	2.68159
18.9	2.67601
19	2.67043
19.1	2.66487
19.2	2.65932
19.3	2.65379
19.4	2.64826
19.5	2.64274
19.6	2.63724
19.7	2.63174
19.8	2.62626
19.9	2.62079
20	2.61533

READING	PPM
20.1	2.60988
20.2	2.60444
20.3	2.59901
20.4	2.59359
20.5	2.58818
20.6	2.58279
20.7	2.5774
20.8	2.57203
20.9	2.56666
21	2.56131
21.1	2.55597
21.2	2.55063
21.3	2.54531
21.4	2.54
21.5	2.5347
21.6	2.52941
21.7	2.52413
21.8	2.51886
21.9	2.5136
22	2.50835
22.1	2.50311
22.2	2.49788
22.3	2.49266
22.4	2.48745
22.5	2.48225
22.6	2.47706
22.7	2.47188
22.8	2.46671
22.9	2.46155
23	2.4564
23.1	2.45126
23.2	2.44613
23.3	2.44102
23.4	2.43591
23.5	2.43081
23.6	2.42572
23.7	2.42063
23.8	2.41556
23.9	2.4105
24	2.40545
24.1	2.40041
24.2	2.39538
24.3	2.39035
24.4	2.38534
24.5	2.38034
24.6	2.37534
24.7	2.37036
24.8	2.36538
24.9	2.36041
25	2.35546

READING	PPM
25.1	2.35051
25.2	2.34557
25.3	2.34064
25.4	2.33572
25.5	2.33081
25.6	2.32591
25.7	2.32101
25.8	2.31613
25.9	2.31126
26	2.30639
26.1	2.30153
26.2	2.29669
26.3	2.29185
26.4	2.28702
26.5	2.2822
26.6	2.27738
26.7	2.27258
26.8	2.26779
26.9	2.263
27	2.25822
27.1	2.25345
27.2	2.24869
27.3	2.24394
27.4	2.2392
27.5	2.23446
27.6	2.22974
27.7	2.22502
27.8	2.22031
27.9	2.21561
28	2.21092
28.1	2.20624
28.2	2.20156
28.3	2.1969
28.4	2.19224
28.5	2.18759
28.6	2.18295
28.7	2.17831
28.8	2.17369
28.9	2.16907
29	2.16446
29.1	2.15986
29.2	2.15527
29.3	2.15068
29.4	2.1461
29.5	2.14154
29.6	2.13698
29.7	2.13242
29.8	2.12788
29.9	2.12334
30	2.11881

READING	PPM
30.1	2.11429
30.2	2.10978
30.3	2.10527
30.4	2.10077
30.5	2.09628
30.6	2.0918
30.7	2.08732
30.8	2.08286
30.9	2.0784
31	2.07395
31.1	2.0695
31.2	2.06506
31.3	2.06064
31.4	2.05621
31.5	2.0518
31.6	2.04739
31.7	2.04299
31.8	2.0386
31.9	2.03422
32	2.02984
32.1	2.02547
32.2	2.02111
32.3	2.01675
32.4	2.0124
32.5	2.00806
32.6	2.00373
32.7	1.9994
32.8	1.99508
32.9	1.99077
33	1.98646
33.1	1.98217
33.2	1.97787
33.3	1.97359
33.4	1.96931
33.5	1.96504
33.6	1.96078
33.7	1.95652
33.8	1.95227
33.9	1.94803
34	1.9438
34.1	1.93957
34.2	1.93534
34.3	1.93113
34.4	1.92692
34.5	1.92272
34.6	1.91852
34.7	1.91434
34.8	1.91015
34.9	1.90598
35	1.90181

READING	PPM
35.1	1.89765
35.2	1.89349
35.3	1.88934
35.4	1.8852
35.5	1.88106
35.6	1.87693
35.7	1.87281
35.8	1.86869
35.9	1.86458
36	1.86048
36.1	1.85638
36.2	1.85229
36.3	1.84821
36.4	1.84413
36.5	1.84005
36.6	1.83599
36.7	1.83193
36.8	1.82787
36.9	1.82383
37	1.81979
37.1	1.81575
37.2	1.81172
37.3	1.8077
37.4	1.80368
37.5	1.79967
37.6	1.79566
37.7	1.79166
37.8	1.78767
37.9	1.78368
38	1.7797
38.1	1.77573
38.2	1.77176
38.3	1.76779
38.4	1.76384
38.5	1.75988
38.6	1.75594
38.7	1.752
38.8	1.74806
38.9	1.74413
39	1.74021
39.1	1.73629
39.2	1.73238
39.3	1.72847
39.4	1.72457
39.5	1.72068
39.6	1.71679
39.7	1.71291
39.8	1.70903
39.9	1.70515
40	1.70129

READING	PPM
40.1	1.69742
40.2	1.69357
40.3	1.68972
40.4	1.68587
40.5	1.68203
40.6	1.6782
40.7	1.67437
40.8	1.67054
40.9	1.66673
41	1.66291
41.1	1.6591
41.2	1.6553
41.3	1.6515
41.4	1.64771
41.5	1.64392
41.6	1.64014
41.7	1.63636
41.8	1.63259
41.9	1.62883
42	1.62506
42.1	1.62131
42.2	1.61756
42.3	1.61381
42.4	1.61007
42.5	1.60633
42.6	1.6026
42.7	1.59888
42.8	1.59515
42.9	1.59144
43	1.58773
43.1	1.58402
43.2	1.58032
43.3	1.57662
43.4	1.57293
43.5	1.56924
43.6	1.56556
43.7	1.56188
43.8	1.55821
43.9	1.55454
44	1.55088
44.1	1.54722
44.2	1.54357
44.3	1.53992
44.4	1.53627
44.5	1.53263
44.6	1.529
44.7	1.52537
44.8	1.52174
44.9	1.51812
45	1.5145

READING	PPM
45.1	1.51089
45.2	1.50728
45.3	1.50368
45.4	1.50008
45.5	1.49649
45.6	1.4929
45.7	1.48931
45.8	1.48573
45.9	1.48216
46	1.47858
46.1	1.47502
46.2	1.47145
46.3	1.4679
46.4	1.46434
46.5	1.46079
46.6	1.45724
46.7	1.4537
46.8	1.45017
46.9	1.44663
47	1.4431
47.1	1.43958
47.2	1.43606
47.3	1.43254
47.4	1.42903
47.5	1.42552
47.6	1.42202
47.7	1.41852
47.8	1.41502
47.9	1.41153
48	1.40805
48.1	1.40456
48.2	1.40108
48.3	1.39761
48.4	1.39414
48.5	1.39067
48.6	1.38721
48.7	1.38375
48.8	1.38029
48.9	1.37684
49	1.3734
49.1	1.36995
49.2	1.36651
49.3	1.36308
49.4	1.35965
49.5	1.35622
49.6	1.3528
49.7	1.34938
49.8	1.34596
49.9	1.34255
50	1.33914

READING	PPM
50.1	1.33573
50.2	1.33233
50.3	1.32894
50.4	1.32554
50.5	1.32215
50.6	1.31877
50.7	1.31539
50.8	1.31201
50.9	1.30863
51	1.30526
51.1	1.30189
51.2	1.29853
51.3	1.29517
51.4	1.29181
51.5	1.28846
51.6	1.28511
51.7	1.28176
51.8	1.27842
51.9	1.27508
52	1.27175
52.1	1.26842
52.2	1.26509
52.3	1.26176
52.4	1.25844
52.5	1.25513
52.6	1.25181
52.7	1.2485
52.8	1.2452
52.9	1.24189
53	1.23859
53.1	1.23529
53.2	1.232
53.3	1.22871
53.4	1.22542
53.5	1.22214
53.6	1.21886
53.7	1.21558
53.8	1.21231
53.9	1.20904
54	1.20577
54.1	1.20251
54.2	1.19925
54.3	1.19599
54.4	1.19274
54.5	1.18949
54.6	1.18624
54.7	1.183
54.8	1.17976
54.9	1.17652
55	1.17329

READING	PPM
55.1	1.17006
55.2	1.16683
55.3	1.16361
55.4	1.16038
55.5	1.15717
55.6	1.15395
55.7	1.15074
55.8	1.14753
55.9	1.14432
56	1.14112
56.1	1.13792
56.2	1.13473
56.3	1.13153
56.4	1.12834
56.5	1.12516
56.6	1.12197
56.7	1.11879
56.8	1.11561
56.9	1.11244
57	1.10927
57.1	1.1061
57.2	1.10293
57.3	1.09977
57.4	1.09661
57.5	1.09345
57.6	1.0903
57.7	1.08715
57.8	1.084
57.9	1.08085
58	1.07771
58.1	1.07457
58.2	1.07144
58.3	1.0683
58.4	1.06517
58.5	1.06205
58.6	1.05892
58.7	1.0558
58.8	1.05268
58.9	1.04956
59	1.04645
59.1	1.04334
59.2	1.04023
59.3	1.03713
59.4	1.03403
59.5	1.03093
59.6	1.02783
59.7	1.02474
59.8	1.02165
59.9	1.01856
60	1.01547

READING	PPM
60.1	1.01239
60.2	1.00931
60.3	1.00623
60.4	1.00316
60.5	1.00009
60.6	.997021
60.7	.993954
60.8	.990892
60.9	.987831
61	.984773
61.1	.981718
61.2	.978666
61.3	~~.975616~~
61.4	.972569
61.5	.969525
61.6	.966484
61.7	.963444
61.8	.960409
61.9	.957375
62	.954344
62.1	.951316
62.2	.948291
62.3	.945268
62.4	.942247
62.5	.93923
62.6	.936214
62.7	.933202
62.8	.930194
62.9	.927186
63	.92418
63.1	.921179
63.2	.918181
63.3	.915183
63.4	.912189
63.5	.909197
63.6	.906208
63.7	.903221
63.8	.900238
63.9	.897257
64	.894279
64.1	.891302
64.2	.888328
64.3	.885357
64.4	.882389
64.5	.879422
64.6	.876459
64.7	.873499
64.8	.870539
64.9	.867583
65	.86463

READING	PPM
65.1	.86168
65.2	.858732
65.3	.855785
65.4	.852841
65.5	.8499
65.6	.846963
65.7	.844026
65.8	.841093
65.9	.838161
66	.835235
66.1	.832309
66.2	.829385
66.3	.826465
66.4	.823546
66.5	.82063
66.6	.817716
66.7	.814805
66.8	.811896
66.9	.808991
67	.806088
67.1	.803185
67.2	.800288
67.3	.797391
67.4	.794497
67.5	.791605
67.6	.788717
67.7	.785831
67.8	.782947
67.9	.780066
68	.777187
68.1	.77431
68.2	.771436
68.3	.768565
68.4	.765695
68.5	.762828
68.6	.759964
68.7	.757102
68.8	.754242
68.9	.751385
69	.748531
69.1	.745678
69.2	.742829
69.3	.73998
69.4	.737136
69.5	.734294
69.6	.731455
69.7	.728616
69.8	.725781
69.9	.722948
70	.720118

READING	PPM
70.1	.717291
70.2	.714465
70.3	.711641
70.4	.708821
70.5	.706004
70.6	.703187
70.7	.700374
70.8	.697563
70.9	.694755
71	.691948
71.1	.689145
71.2	.686344
71.3	.683545
71.4	.680748
71.5	.677955
71.6	.675163
71.7	.672375
71.8	.669589
71.9	.666805
72	.664023
72.1	.661244
72.2	.658467
72.3	.655692
72.4	.65292
72.5	.650151
72.6	.647383
72.7	.64462
72.8	.641858
72.9	.639098
73	.63634
73.1	.633585
73.2	.630833
73.3	.628084
73.4	.625337
73.5	.622592
73.6	.619849
73.7	.617111
73.8	.614373
73.9	.611636
74	.608904
74.1	.606176
74.2	.603448
74.3	.600722
74.4	.598
74.5	.59528
74.6	.592561
74.7	.589846
74.8	.587134
74.9	.584423
75	.581717

READING	PPM
75.1	.579012
75.2	.57631
75.3	.57361
75.4	.570911
75.5	.568216
75.6	.565523
75.7	.562835
75.8	.560146
75.9	.557462
76	.55478
76.1	.5521
76.2	.549422
76.3	.546748
76.4	.544076
76.5	.541407
76.6	.53874
76.7	.536075
76.8	.533414
76.9	.530755
77	.528096
77.1	.525443
77.2	.522792
77.3	.520144
77.4	.517497
77.5	.514853
77.6	.512213
77.7	.509575
77.8	.506938
77.9	.504304
78	.501674
78.1	.499046
78.2	.496422
78.3	.4938
78.4	.491179
78.5	.488561
78.6	.485946
78.7	.483334
78.8	.480724
78.9	.478118
79	.475514
79.1	.472913
79.2	.470315
79.3	.467719
79.4	.465127
79.5	.462536
79.6	.459949
79.7	.457364
79.8	.454782
79.9	.452202
80	.449625

READING	PPM
80.1	.447052
80.2	.444481
80.3	.441911
80.4	.439346
80.5	.436783
80.6	.434223
80.7	.431666
80.8	.429113
80.9	.42656
81	.424012
81.1	.421464
81.2	.418921
81.3	.416381
81.4	.413844
81.5	.41131
81.6	.408777
81.7	.40625
81.8	.403724
81.9	.4012
82	.39868
82.1	.396163
82.2	.393647
82.3	.391137
82.4	.388628
82.5	.386122
82.6	.38362
82.7	.381119
82.8	.378623
82.9	.376128
83	.373639
83.1	.371152
83.2	.368666
83.3	.366184
83.4	.363706
83.5	.361229
83.6	.358757
83.7	.356287
83.8	.353821
83.9	.351357
84	.348897
84.1	.346441
84.2	.343985
84.3	.341534
84.4	.339085
84.5	.336639
84.6	.334197
84.7	.331759
84.8	.329324
84.9	.326891
85	.324463

READING	PPM
85.1	.322034
85.2	.319612
85.3	.317194
85.4	.314778
85.5	.312363
85.6	.309954
85.7	.307547
85.8	.305143
85.9	.302742
86	.300345
86.1	.29795
86.2	.295561
86.3	.293174
86.4	.290791
86.5	.288409
86.6	.286033
86.7	.283659
86.8	.281286
86.9	.278919
87	.276555
87.1	.274195
87.2	.271838
87.3	.269485
87.4	.267135
87.5	.264789
87.6	.262444
87.7	.260104
87.8	.257768
87.9	.255436
88	.253106
88.1	.25078
88.2	.248456
88.3	.246138
88.4	.243821
88.5	.24151
88.6	.239202
88.7	.236897
88.8	.234596
88.9	.232298
89	.230004
89.1	.227714
89.2	.225428
89.3	.223144
89.4	.220866
89.5	.218591
89.6	.216319
89.7	.21405
89.8	.211786
89.9	.209525
90	.207268

READING	PPM
90.1	.205014
90.2	.202764
90.3	.200519
90.4	.198276
90.5	.196039
90.6	.193805
90.7	.191575
90.8	.189347
90.9	.187124
91	.184906
91.1	.18269
91.2	.18048
91.3	.178272
91.4	.17607
91.5	.17387
91.6	.171674
91.7	.169483
91.8	.167296
91.9	.165112
92	.162931
92.1	.160758
92.2	.158587
92.3	.15642
92.4	.154256
92.5	.152097
92.6	.149941
92.7	.147792
92.8	.145644
92.9	.143501
93	.141364
93.1	.139231
93.2	.137101
93.3	.134975
93.4	.132854
93.5	.130737
93.6	.128624
93.7	.126515
93.8	.12441
93.9	.122311
94	.120214
94.1	.118123
94.2	.116035
94.3	.113954
94.4	.111877
94.5	.109803
94.6	.107734
94.7	.105669
94.8	.103607
94.9	.10155
95	9.95016E-2

READING	PPM
95.1	9.74526E-2
95.2	9.54123E-2
95.3	9.33747E-2
95.4	.091342
95.5	8.93126E-2
95.6	8.72884E-2
95.7	.085268
95.8	8.32515E-2
95.9	8.12435E-2
96	7.92389E-2
96.1	7.72357E-2
96.2	7.52411E-2
96.3	7.32498E-2
96.4	7.12605E-2
96.5	6.92792E-2
96.6	6.73013E-2
96.7	6.53296E-2
96.8	6.33621E-2
96.9	.061398
97	5.94411E-2
97.1	5.74894E-2
97.2	5.55401E-2
97.3	5.35946E-2
97.4	5.16586E-2
97.5	4.97236E-2
97.6	4.77962E-2
97.7	4.58732E-2
97.8	4.39539E-2
97.9	4.20413E-2
98	4.01325E-2
98.1	3.82261E-2
98.2	3.63293E-2
98.3	3.44343E-2
98.4	3.25456E-2
98.5	3.06644E-2
98.6	2.87848E-2
98.7	2.69141E-2
98.8	2.50454E-2
98.9	2.31814E-2
99	2.13251E-2
99.1	1.94731E-2
99.2	1.76253E-2
99.3	1.57838E-2
99.4	.013948
99.5	1.21179E-2
99.6	1.02916E-2
99.7	8.47006E-3
99.8	6.65665E-3
99.9	4.84753E-3
100	3.04174E-3