ABSTRACT

The purpose of this work was to do an extensive study of the removal of zinc cations from dilute aqueous solution by foam fractionation. The system chosen was zinc - sodium dodecylbenzene sulphonate - sodium chloride. Equilibrium studies were performed for the determination of the surface excess of surfactant and the surface excess of zinc cations. The surface excess of surfactant was determined as a function of bulk surfactant concentration and the surface excess of zinc was determined as a function of bulk zinc concentration, electrolyte concentration, surfactant concentration and pH. These results were then expressed analytically and were used to predict the removal of zinc from a batch process.

Ion flotation was found to have a strong dependence on collector concentration. Batch removals by foam fractionation were found to reach a different limiting value for each collector ratio used. The ultimate fraction removed was found to be some function of the collector concentration, but the shape of the removal curves were not significantly affected.

It has also been shown that the Gibbs' Adsorption Isotherm does not apply to a dynamic system. Surface excess values many times higher than the Gibbs predicted values have been measured. The results bear no definite relation to either the Gibbs' value or to that for monomolecular adsorption.

The results of this investigation can be explained by the double layer concept as the mechanism for the ion flotation of zinc cations. The removal of zinc cations was found to be a function of the competition of zinc cations and other cations of the solution for the collector.

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. F.D.F. Talbot, the director of this thesis, for his encouragement and assistance throughout the course of this work.

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NOMENCLATURE

Γ_i	surface excess of component i
R	gas constant
a_i	activity of the i th component
γ	surface tension
C_i	concentration of component i
C_B	bulk concentration
C_F	foamate concentration
Q	volumetric flowrate of foamate on a gas free basis
d	bubble diameter
G	gas flowrate
NaDBS	sodium dodecylbenzene sulphonate
DBS^-	dodecylbenzene sulphonate anion
CR	collector ratio, defined as moles of collector to moles of zinc
D	distribution factor, defined as the surface excess divided by the bulk concentration
collingend	the substance removed by the collector
collector	surfactant which causes another substance to be effectively surface active

I. INTRODUCTION

Recently there has been a renewed interest in the separation or removal of components from solution using the technique known as foam separation. This technique is based upon the tendency of surface active solutes to concentrate at gas-liquid interfaces. Foam separation is used to concentrate or separate the components of a single, homogeneous, liquid phase and for this reason it is closest in principle to distillation, extraction and ion exchange.

Foam fractionation of metals is a recent development and only a few studies are available in the literature. Metal ions are in general not surface active and in order to employ foam separation as a means of removing them from solution, the metal ions must be made surface active. This is done by associating them with anionic surface active agents, organic chelating and complexing agents or other negatively charged materials exhibiting surface activity.

II. LITERATURE SURVEY

Foam Fractionation of Metals

Foam fractionation of inorganic cations by anionic surfactants in homogeneous systems was first reported in 1952 by Walling, Ruff and Thornton (1). They described the adsorption of inorganic ions by soluble anionic surfactant surface films (2). Their results indicated that surface films show a strong preferential adsorption of polyvalent ions even in homogeneous systems where the salts of the surfactant are completely soluble.

Following this in 1959, Schnepf et al. (3) studied the application of foam separation to the removal of metal ions from solution. They examined the system composed of Areskap 100, a commercial surfactant, and Sr^{++} in water solution using a circulatory foaming column, similar to a conventional vapour-liquid equilibrium still. Results were expressed in terms of enrichment ratio: the concentration of metal in the foam divided by the bulk concentration. Effects studied were pH, alkaline earth concentration, gas flow rate, foaming agent concentration and the effect of other metal ions. It was found that by increasing gas flow rate, enrichment decreased due to liquid entrainment. By increasing the foaming agent concentration, there was an initial rapid increase in strontium enrichment

ratio, followed by a rapid drop and finally a gradual decrease. The effect was interpreted in the following manner: as foaming agent is added up to a concentration sufficient to complex all the strontium present, enrichment increases to its maximum value. Further addition of foaming agent creates competition at the gas-liquid interface, between the excess foaming agent and the strontium-foaming agent complex, causing strontium enrichment ratio to decrease. It was found that the presence of heavier metal ions, Fe^{3+} and Al^{3+}, caused the enrichment to decrease and often precipitation of the surfactant occurred. Sodium ions interfered only at high concentrations. Barium and calcium interfered with strontium removal because of the similarity of the ions.

In that same year, 1959, Sebba introduced the first of the low gas-flow-rate foam separation techniques known as ion flotation (4). With this technique a surfactant of opposite charge to the ion is added in stoichiometric amounts, in such a manner that is exists as simple ions and not micelles. The surfactant reacts with the inorganic ion to form an insoluble soap and is levitated to the surface by gently bubbling to form a foam which collapses into an insoluble scum. This is a true flotation process involving the foam separation of a heterogeneous system as compared to homogeneous systems employing a partition process.

Further discussion of ion flotation of inorganic ions was published in 1960 (5). Other publications occurred in 1962 (6,7,8) and in 1965 (9,10). Sebba's technique was an innovation in foam technology because it suggested the feasibility of low-gas-flow rates without the use of tall columns.

In 1962, a compilation of various systems separable by foam fractionation appeared in "New Chemical Engineering Separation Techniques" by E. Rubin and E.L. Gaden (11). Among the various systems were included eighteen metals. Since then many more studies have been reported in the literature of foam separation.

Grieves and Wilson published their work in 1965 on the foam fractionation of an insoluble surfactant - metal ion salt. Dichromate was removed using ethylhexadecyl-dimethylammonium bromide, a quaternary ammonium surfactant, at high rates of gas flow, about 4300 ml per minute through a volume of 2 litres (12). Many of the operating and solution variables affecting ion removal by foam fractionation are interrelated and otherwise difficult to study in tall columns. By using a short column and low rates of gas flow it was possible to investigate individually these variables affecting the rate of separation. The results of such an investigation are described in their paper.

A comparison of variables in ion and precipitate flotation was published in 1966 by A.J. Rubin et al. (13). These two flotation techniques are compared by showing relative effects of collector concentration, gas flow rate and ionic strength. Other variables included are metal ion concentration, pH and temperature. The ion flotation investigated was the removal of a soluble copper (II) - sodium lauryl sulfate collector product. Copper hydroxide was removed by precipitate flotation also using sodium lauryl sulfate. Ion flotation was insensitive to temperature in the range 15° to 34°C., but generally more sensitive than precipitate flotation to the other variables. The rate and total removal by precipitate flotation were greater than ion flotation under all experimental conditions. Rate equations and mechanisms are also proposed in this paper. Application of a low flow rate process to the foam separation of bacteria and algae has also been discussed by Rubin (14,15,16,17).

Three years later, in 1969, A.J. Rubin and W.L. Lapp, published the results of experiments on the foam separation of lead (II) using sodium lauryl sulfate (18). Experiments were run as a function of time with gas flow rate, ionic strength, collector concentration and pH as parameters. Increasing gas flow rates increased the rate of removal without affecting the ultimate removal. The other

parameters did not affect the rate of removal but had a significant effect on the ultimate or steady state removal. Removals were found to decrease with increasing ionic strength at all pH values. This reduction was attributed to a decrease in the activity of the lead species and increased competition between cations for the collector. Removal was found to increase with increasing pH because of the stepwise hydrolysis of heavy metal ions with increasing pH. The effects of pH on foam separation of lead (II) at different collector ratio was interpreted by examining the hydrolysis of lead (II).

The only literature references to flotation of zinc cations are by Sebba (4) and Walling (2). Sebba briefly mentions that zinc, among various other cations, has been floated. Walling reports on the adsorption of cations by anionic foams and one of the cations is zinc, floated by N-palmitoyl methyl taurine. Beyond this there has been no further study on the flotation of zinc cations.

In 1971, F.D. Talbot and W.L. Dick published the results of their investigation on the use of an auxiliary ligand in the foam fractionation of copper with sodium lauryl sulfate (19). The purpose of the work 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 auxiliary ligand. Distribution factors were determined for copper as a function of pH, auxiliary ligand concentration, surfactant concentration, electrolyte concentration and bulk copper concentration. In general it was found that the ligand THPED (N,N,N',N'-tetrakis (2 - hydroxypropyl) ethylenediamine) improved the distribution factor significantly, particularily in the presence of much added NaCl and at low bulk copper concentrations.

The technique of foam separation is very suitable for concentrating species from extremely low aqueous concentrations of materials. With increasing pollution of lakes and rivers the necessity of a method to remove certain ions becomes self-evident. Before the advent of bio-degradable surfactants, foam separation was used to clean up alkyl benzene sulphonates (20). Foam fractionation was used on a large scale in several localities to remove detergents from municipal sewage (21). There techniques are very relevant to nuclear waste water. For example ^{89}Sr and ^{90}Sr could be concentrated preferentially from an aqueous solution by the technique of ion flotation. In the mining industry, trace quantities of Au^{3+}, Ag^{+}, Hg^{+} and $U_2(SO_4)_2^{2+}$ could be recovered from certain effluents by foam separation.

Foam separation also has important engineering implications. These methods utilize low rates of gas flow

producing a small volume of foam without tall columns or violent agitation of the surface phase. In general, the equipment used is of simple construction, readily lending itself to continuous automatic operation. It has not however been calculated whether it would be an economic proposition to float certain metallic ions on a large scale operation. For example, it has been found that the cost to float one pound of copper using alpha-sulphoalmitic acid is under one cent (U.S.)(22). A feature of this method is that the ion to be removed may be in ionic or complex form. Addition of a complexing agent would immediately result in a cost increase for the process. In many cases it has been found that the amount of collector needed to float a particular ion is more than the stoichiometric amount. This naturally affects the cost. It would then be necessary to recycle the collector for the process to become an economic proposition.

Most of the work on foam separation has been done on a batch scale. On an industrial scale, this approach is not feasible because a continuous process is necessary and the foam needs to be recycled to obtain good enrichment. To date no entirely satisfactory multi-stage piece of equipment has been designed (22).

III. THEORETICAL CONSIDERATIONS

The Process of Foam Fractionation

Foam separations are usually associated with the fractionation of naturally surface active materials, but it has also been applied to such diverse substances as micro-organisms, organic ions, metal ions and their precipitates. The foam separation of these materials may be accomplished by their reaction with a substance known as a collector which forms a surface active product.

The foam fractionation of metal ions is a foam fractionation process where the metal ion and the collector are attracted by simple ion pair formation or by weak co-ordination. When the metal ion and collector react to form a soluble product the process is termed ion flotation. Precipitation of the metal prior to addition of the collector results in precipitate flotation. Foam fractionation and ion flotation require stoichiometric or greater amounts of collector. With precipitate flotation the metal concentration may be in great excess over that of the collector, the limit being based on the surfactant requirements for a stable surface phase.

Rubin et al. (13) have concluded that homogeneous ion flotation is a process in which ions are removed by electrostatic and/or coordination interactions with the

collector as it is being removed from solution. The attachment of collector to the gas bubble is the primary mechanism of removal. This step is accompanied by neutralization of the collector charge by the metal and/or coordination between the two. This neutralization of the negatively charged surface creates a diffuse sub-layer which will contain an excess of cations in order to create electrical neutrality. This is the essence of the double layer theory. Removal of a specific component is a function of the competition of this component and the other components of the solution for the collector. It was also concluded that pH affects ion flotation by altering the composition of the solution and thereby altering the ionic competition.

The agent used to remove a particular ion from solution must have two characteristics; it must be surface active and, it must have some preferential attraction for the metal to be removed; an attraction exceeding or at least equalling that for other cations in the solution. The first requirement is not difficult to fulfill; a vast number of surface active materials and chelating agents are available. The second requirement is not so easily satisfied for all metallic ions. This can best be illustrated by an example. Consider a solution containing Na, Ca, and Fe salts from which it is

desired to remove Ca. The presence of Na would present little difficulty since almost all chelating or complexing agents have a much greater attraction for Ca than Na. But the presence of Fe complicates the situation since most known chelating and complexing agents preferentially attract the Fe rather than the Ca ions.

Whether or not a particular agent will remove a given ion from solution depends on many factors; the presence of other ions, their concentration, the relative stability of complexes formed, and the foaming power of the agent. Because of the large number of possible combinations of these factors in cases where foam separation appears attractive, few generalizations can be made regarding the procedure to be followed in a given case. Each application must be investigated separately.

The Gibbs Adsorption Isotherm

The separation obtained by foam fractionation depends in part on the extent and selectivity of adsorption at the bubble surface. In 1878, J. Willard Gibbs derived, from a rigorous thermodynamic treatment, the well known Gibbs Adsorption Isotherm. Under equilibrium conditions, the adsorption at a gas liquid interface is as:

$$\Gamma_i = -\frac{1}{RT}\,\frac{d\,\gamma}{d\,\ln a_i} \qquad (1)$$

Γ_i is the surface excess which is essentially the concentration of an adsorbed component at the surface in units such as g-mol per sq. cm. R is the gas constant, T the absolute temperature, a_i is the activity of the i th component and γ is the surface tension. For a nonionic surfactant in pure water at concentrations below the critical micelle concentration, a_i can be replaced with the concentration C_i. This yields equation (2) for the surfactant: (30).

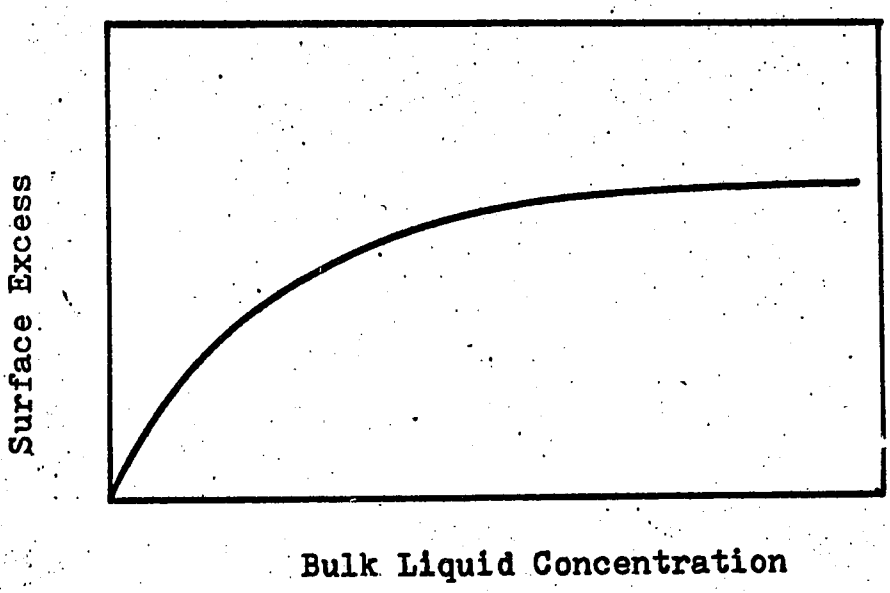
$$\Gamma_i = -\frac{1}{RT}\,\frac{d\,\gamma}{d\,\ln C_i} \qquad (2)$$

With a uni-univalent surfactant, the left hand side of equation (2) theoretically becomes $2\Gamma_i$. However the

presence of salts and certain other factors can suppress the coefficient.

Figure 1 shows a typical variation of the surface concentration. At very low concentrations, the curve is inclined straight through the origin. At higher concentrations it bends and tends to level off. The adsorption isotherm for many substances follow the general profile of Figure 1.

Figure 1- Typical Variation of Concentration at the Surface with Concentration in the Liquid



The surface concentration of the major surfactant in a foam usually corresponds to the level portion of the curve. This level portion is often taken as representing an adsorbed monolayer. The surface excess of the major surfactant in the foam is thus roughly independent of its concentration in the liquid. However, this approximate independence need not apply to minor surfactants or colligends which may be present. For adsorption of trace colligends the lower (inclined) linear portion of the curve applies. The adsorption of a colligend can be affected by the collector (surfactant) concentration. This can come about through an insufficiency of collector, but it may also come about by an excess of collector which may compete against the colligend-collector complex for the available surface.

The excess collector may form micelles which themselves are not adsorbed but which compete against the collector at the surface for the available colligend. In other words, the micelles in the liquid may adsorb some of the colligend by electrostatic attraction, thus reducing the colligend adsorbed at the surface.

Various methods have been proposed to determine the surface excess experimentally. One of the earliest methods involves measuring the performance of a foam

fractionating column operating in the simple mode, that is, operating as a single theoretical (equilibrium) stage. It can be used to determine surface concentrations for surfactants or colligends, with or without micelles (23).

Operation in The Simple Mode

Figure 2 shows a foam fractionating column operating in the simple mode. In the foam, the surfactant or colligend in question is found to be partly adsorbed at the bubble surfaces and partly in the interstitial liquid. This liquid is virtually identical with pool liquid if there is no coalescence of bubbles in the rising foam. A simple material balance yields:

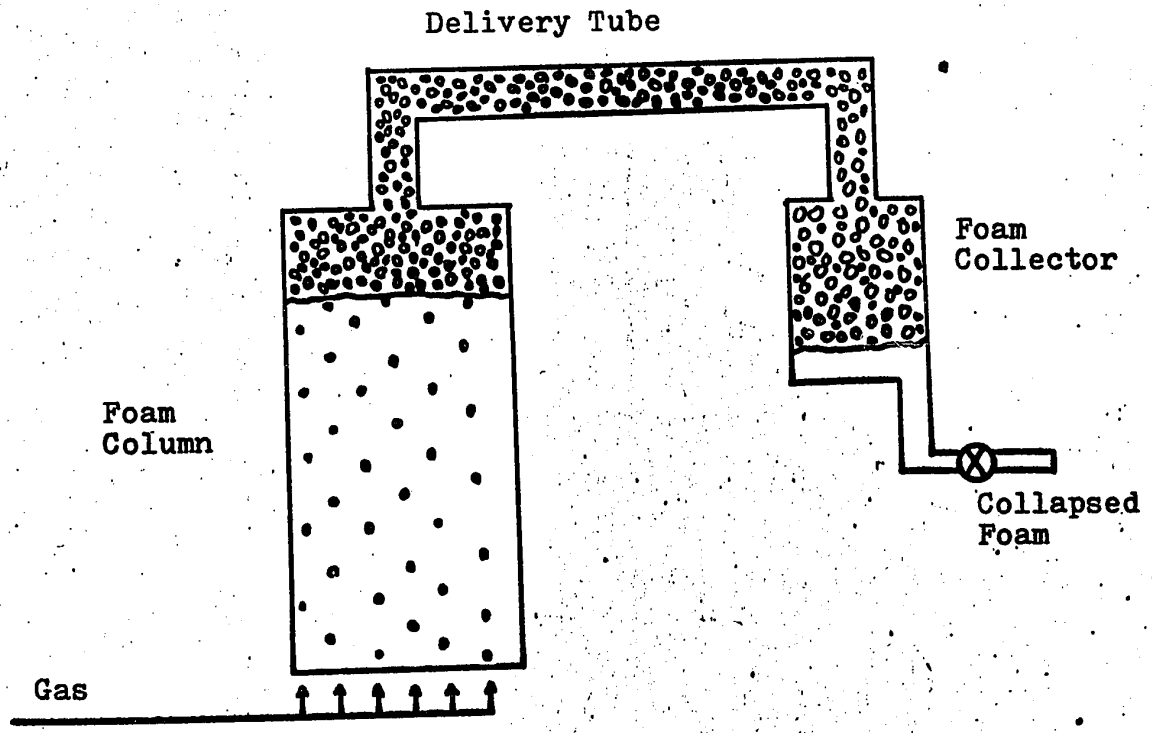
$$\Gamma = \frac{(C_F - C_B)Qd}{6G} \qquad (3)$$

where Γ denotes the surface excess in equilibrium with the liquid pool concentration C_B, C_F is the concentration in the collapsed foam, Q is the volumetric flowrate of foamate, G is the volumetric flowrate of gas and d/6 is the volume to surface ratio for a spherical bubble where d is the bubble diameter.

In order to determine the surface excess accurately by equation (3) the operation must be truly in the simple mode or in other words, the column must act as a single theoretical stage. This means the coalescence in the rising foam must be avoided or kept to a bare minimum. Such internal coalescence destroys surface and so

releases adsorbed material which flows back down through the rising foam. This rich drainage acts as an internal reflux which enriches the foam. While such enrichment is very useful under certain circumstances it is highly undesirable in the present context because it causes equation (3) to yield an erroneously high surface excess.

Figure 2-Foam Fractionation in the Simple Mode



Coalescence can be minimized by employing a high gas rate. This keeps the liquid content of the foam high which in turn keeps the films separating the foam bubbles relatively thick and more resistive to rupture. A high gas rate also holds down the residence time for the foam in the column; so does a very short height of foam. For this purpose a height of less than one inch is desirable. A short residence time minimizes the opportunity for film rupture and thus minimizes coalescence.

When the surface excess is determined by operation in the simple mode, collapsed foam can be recycled to maintain the pool concentration and hence the overall operation, at steady state. However, when the surface excess is measured for a colligend, recycle may not be the preferred technique because collector micelles which form in the foam may not dissociate fast enough upon dilution in the liquid pool. For this last case the surface excess can be determined alternatively from equation (4) which is derived by combining equation (3) with an overall material balance for the column.

$$\Gamma = \frac{(C_F - C_B)Fd}{6G} \qquad (4)$$

F is the feed rate and C_F is the feed concentration.

Bubble diameters in the foam can be measured photographically through the glass wall of the column. However, such measurements are subject to several sources of error including distortion of the individual bubbles at the wall, distortion of the distribution of bubble sizes at the wall, and the statistical bias inherent in sampling a size distribution at a plane rather than by count through its volume. The last two sources of error can be minimized by generating bubbles of fairly uniform size. This is accomplished by using a bubbler with identical orifices, such as a spinneret or simply a bubbler with a single orifice. Bubble diameters can also be measured photographically in the liquid pool, utilizing an external surrounding pool bounded by flat walls to eliminate optical distortion. If a single-orificed bubbler is employed, the bubble diameter can be determined by combining a stroboscopic count of the frequency with an external volumetric measurement of gas flow rate.

A bubbler immersion of one foot or more should ensure good contact. Prehumidifying the gas eliminates any spurious evaporative effects. A wide pool discourages vertical concentration gradients in the pool liquid. Such gradients are undesirable when measuring the surface excess since they lend uncertainty to C_B.

IV. APPARATUS AND EXPERIMENTAL PROCEDURES

Equilibrium and Batch Removal Cells

A single theoretical stage foam fractionating column was used to determine the surface excess. A batch procedure is used in order to avoid the possibility of micelle or precipitate formation in the recycled foamate. A schematic diagram of the apparatus is shown in Figure 3.

Details of the construction of the equilibrium stage have been published by Dick and Talbot (19). It should also be stated that for this particular apparatus, determination of the surface excess involves a maximum error of about ten percent and in many cases the error is less than this value. Experimental error of the independent variable is negligible. A sample error calculation is included in Appendix C. Oil free compressed air from cylinders was first reduced to six p.s.i.g., humidified, flow rate adjusted with a Matheson flowmeter (tube size R-2-15AA), then passed to the bubbler in the column. The column consisted of an inverted three liter separatory funnel with stopcock removed and replaced by a 18/9 Pyrex ball and socket joint to which was connected the delivery tube. Liquid depth was about 33 cm. above the bubbler and liquid height was controlled by a 500 ml. leveling bulb and adjusting screw. The bubbler consisted of five capillary tubes, 0.240 inches long and 0.007 inches i.d., which were

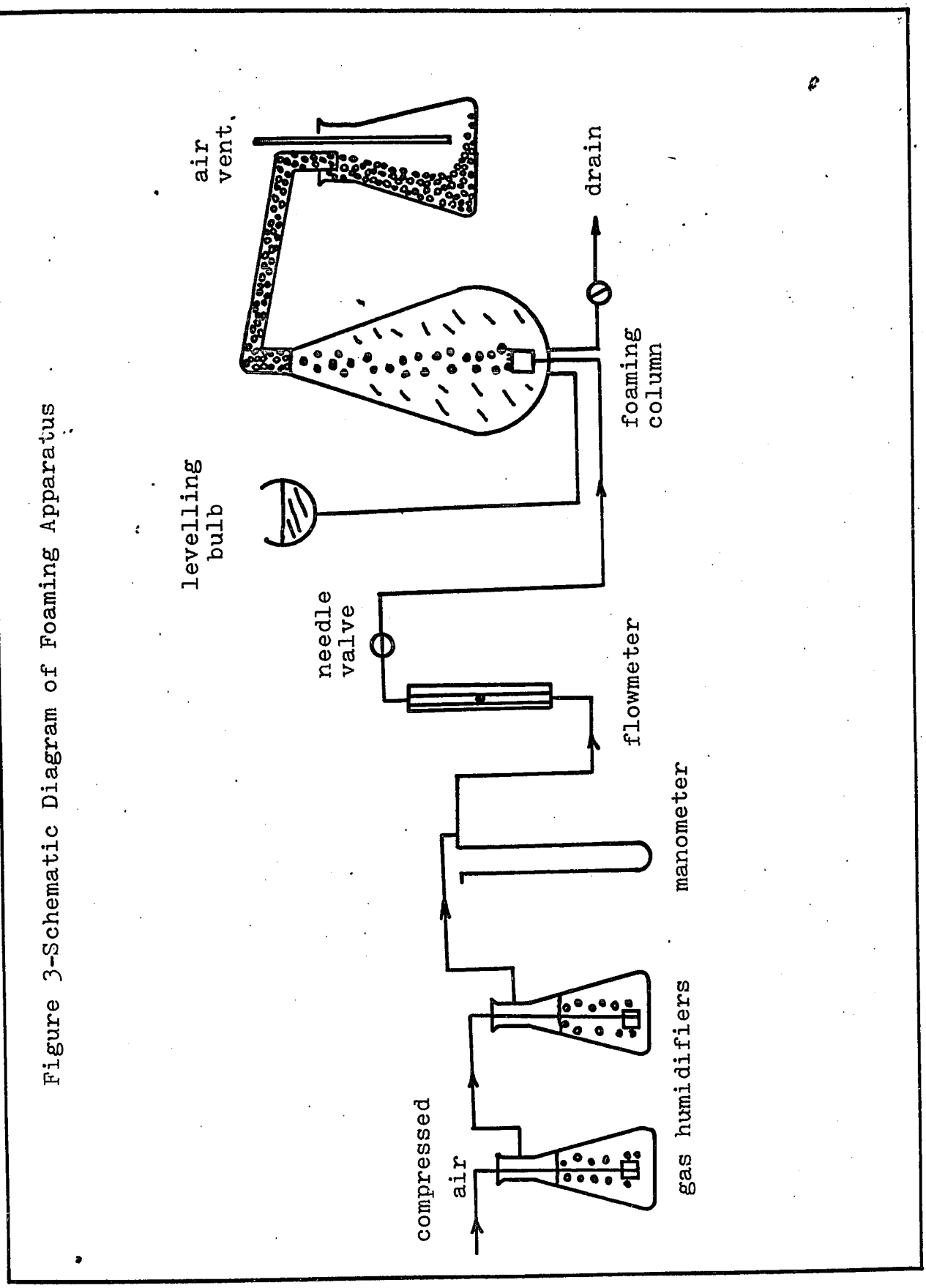


Figure 3-Schematic Diagram of Foaming Apparatus

imbedded in a teflon chamber. Foam was collected in a one liter erlenmeyer flask, with the foam delivery tube declined toward the collection flask.

All water used was distilled and passed through a Barnstead mixed bed ion exchange column, then stored in a glass vessel prior to use. All pH adjustments were carried out using normal HCl or NaOH. Measurements were made with an Ionalyzer model 801/digital pH meter.

For the batch removal runs a similar apparatus was used with the equilibrium column being replaced by a 4.6 cm. i.d. glass column, 40 cm. in height with a liquid depth of about 25 cm. A porous metal sparger was used to produce fine bubbles. The column was equipped with a side entry port from which one ml. samples were withdrawn for analysis.

Surface Tension Measurements

Surface tensions of aqueous solutions of NaDBS at room temperature, about 22°C., were measured with a Cenco Du Nouy Interfacial Tensiometer no. 70545 equipped with a platinum ring. Measurements were made in an evaporating dish which had been cleaned with a chromic acid solution and rinsed with the solution to be measured. The platinum ring was flamed before each measurement. The measurements were made within a short period in which the temperature of the room was unchanged. Three readings were averaged for each solution and reproducibility was within 0.3 dynes/cm.

Experimental Procedure and Analytical Methods

For each of the equilibrium runs, four liters of feed were prepared using the distilled water which was passed through the ion exchange column. After adding the required quantities of NaDBS, NaCl and zinc standard, the pH was adjusted to the desired values using NaOH or HCl.

Chemicals Used:

1. Certified Atomic Absorption Standard, Zinc Reference Solution 10,000 ppm, Fisher Scientific Company.

2. Sodium Dodecylbenzene Sulphonate, K and K Laboratories, Plainview, N.Y.

3. HCl, NaOH, NaCl, Research or Analytical grade.

Prior to charging the column the erlenmeyer receiver flask was weighed to 0.1 mg. and a feed sample was taken for analysis. The gas rate was then adjusted and the column filled via the levelling bulb. The liquid level was then adjusted to the mark and a final adjustment in the gas rate was made. When steady conditions were reached the erlenmeyer flask was placed in position and the timer started simultaneously. Following this the bubble rate was determined using a Type 1538-A Strobotac electronic stroboscope. After sufficient foamate was

collected for analysis the receiver was removed and the time noted. The receiver was then weighed and stoppered, allowing the foamate to break naturally over a period of about one week. After each run the column was drained through a stopcock in the bottom and the solution discarded. The column and levelling bulb were then rinsed thoroughly with distilled water and allowed to drain completely prior to the next run. Gas rate was maintained to prevent capillary wetting during the entire procedure of charging and washing the column.

Analysis for zinc was carried out using a Unicam Model SP90a Atomic Absorption Spectrophotometer. Analysis for NaDBS was carried out using the standard method of test for alkyl benzene sulphonate in industrial water and industrial waste water, ASTM Designation D2330-68. Briefly, the method consists of mixing the sample with an acidified aqueous solution of methylene blue and, any resulting hydrophobic complex which may be formed is extracted by serial chloroform washes. The combined chloroform extracts are washed with an acid solution which hydrolyzes and returns to the aqueous phase the fragments from many of the less stable complexes formed by potentially interfering substances. The intensity of the blue color, remaining in the chloroform extract is measured photometrically at a wavelength of 650

V. RESULTS AND INTERPRETATION

1. Surface Tension Measurements

Figure 4 shows the surface tension for the surfactant NaDBS. The tabulated values are in Table 2 in Appendix A. This type of surface tension versus concentration curve for an air-water system is typical of long chain ions. For dilute solutions the surface tension approaches that of water 72.8 dynes/cm. at 20°C., then there is a linear portion of the curve where the slope is constant, finally at higher concentrations the surface tension is again constant at about 30 dynes/cm.

We can calculate the maximum surface excess of NaDBS from the Gibbs equation for long chain ions.

For long chain ions:

$$\Gamma = -\frac{1}{2RT}\,\frac{d\,\gamma}{d\,\ln C}$$

From Figure 4 the maximum value of $d\gamma/d \ln C$ occurs on the linear portion of the curve. Here the value is -7.383 dyne/cm. Substitution in the Gibbs equation yields a value of 1.5×10^{-10} g-mol/cm.^{2} for the surface excess of NaDBS (see Appendix A). This corresponds to a

millimicrons and related to concentration of ABS by means of a calibration chart. A Bausch and Lomb Precision Spectrophometer no. 33-26-50 was used for the analysis.

A similar procedure was adopted for the batch removal runs. One liter of feed solution was prepared then the batch, 400 ml. was emptied into the column. The surfactant was injected into the column by a syringe through the entry port. The injection was taken as time zero. Samples were then withdrawn periodically from the entry port using a one ml. syringe.

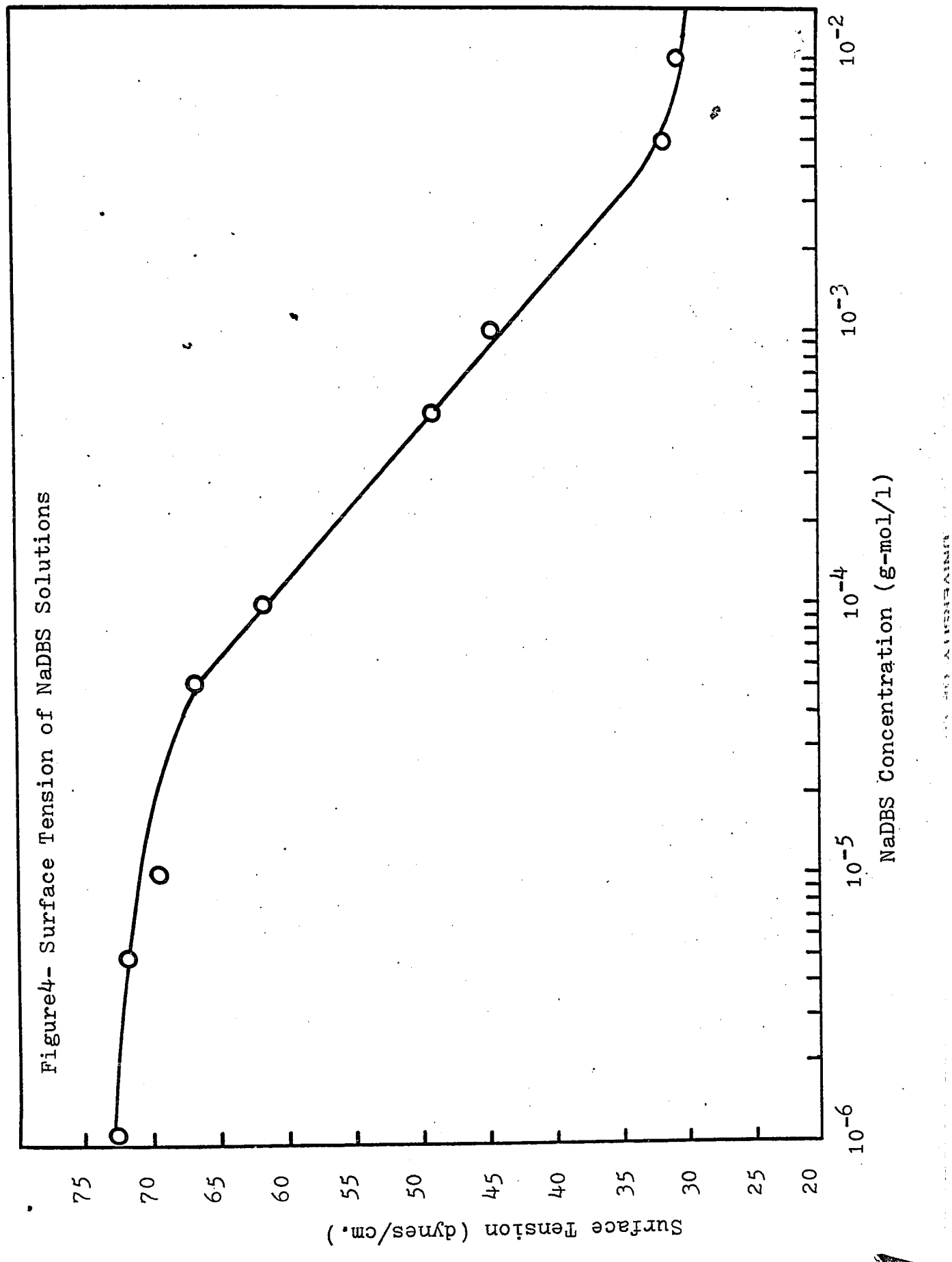


Figure4- Surface Tension of NaDBS Solutions

minimum surface area per molecule of 110.42 square angstroms. The corresponding values determined by Rubin and Jorne (24) are 3×10^{-10} g-mol/cm.^{2} and 57.8 square angstroms. On the strength of previous observations they determined their values without the factor "2" in the Gibbs equation, although according to theory this factor should have been used.

Another important piece of information which can be determined from the surface tension versus concentration curve is the critical micelle concentration (C.M.C.). The break in the surface tension curve is probably the best indication for the C.M.C. This occurs at 5×10^{-3} g-mol/l or 1.74 gm/l NaDBS concentration. The suggestion that micelles are deleterious to ion flotation has been made repeatedly by Sebba but this has been questioned by Rubin et al. (25) who found that aged collector solutions which contained micelles gave the same removals as others which had been freshly prepared. As micelles have been shown by Kresheck et al. (26) and Jaycock and Ottewill (27) to disintegrate very rapidly, it may be that their presence is not as important as was first thought, and that the effects on flotation attributed to them are due to increased concentrations of collector.

2. Equilibrium Stage Measurements of NaDBS

Figures 5, 6, and 7 show the results of the equilibrium stage measurements for the surface excess of NaDBS. These results are tabulated in Table 4, Appendix E and are listed as runs no. 1 to 24. For these runs the pH was kept constant at 5.0 ± 0.1.

The most striking observation is that these values are 6 to 8 times that predicted by Gibbs from surface tension measurements. The results can be interpreted in the following manner.

The rate of adsorption at a surface involves the rate of transfer of material to the surface by diffusion and convection and perhaps the rate of penetration of an oriented surface layer with an energy barrier. Calculations for this system and apparatus used indicate that diffusion is not the limiting process (see Appendix B). Indeed the time required to form a monolayer of surfactant has been calculated as 0.058 seconds, and the residence time of a bubble in the column is approximately 12 to 18 times that value. A bubble rate of 2400 bubbles per minute or 40 bubbles per second means that it requires 0.025 seconds for a bubble to form. This means that in 0.025 seconds approximately 43% of the diffusion has already taken place.

Figure 5-Surface Excess of NaDBS versus NaDBS Concentration

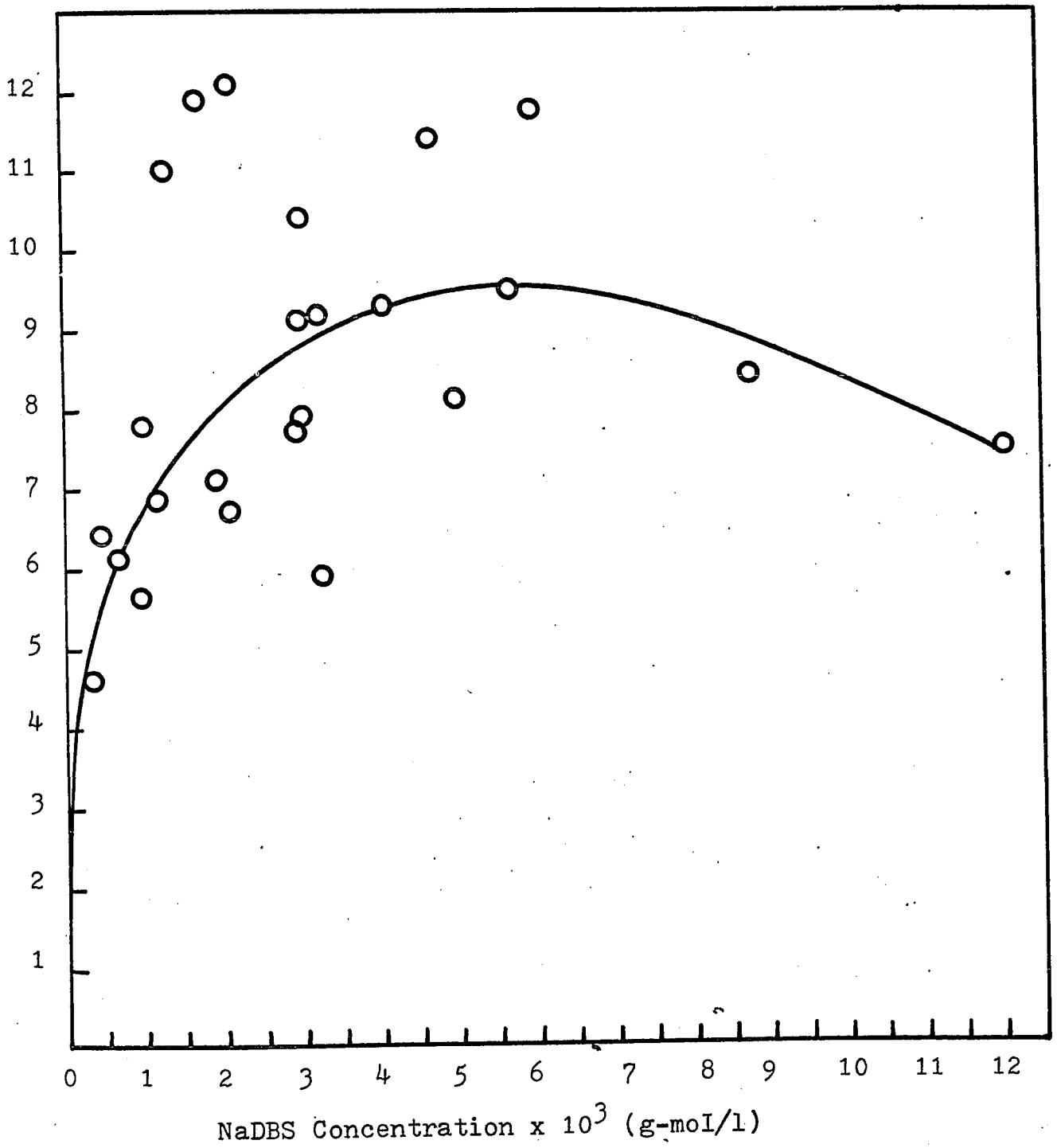


Figure 6- NaDBS Distribution Factor versus NaDBS Concentration

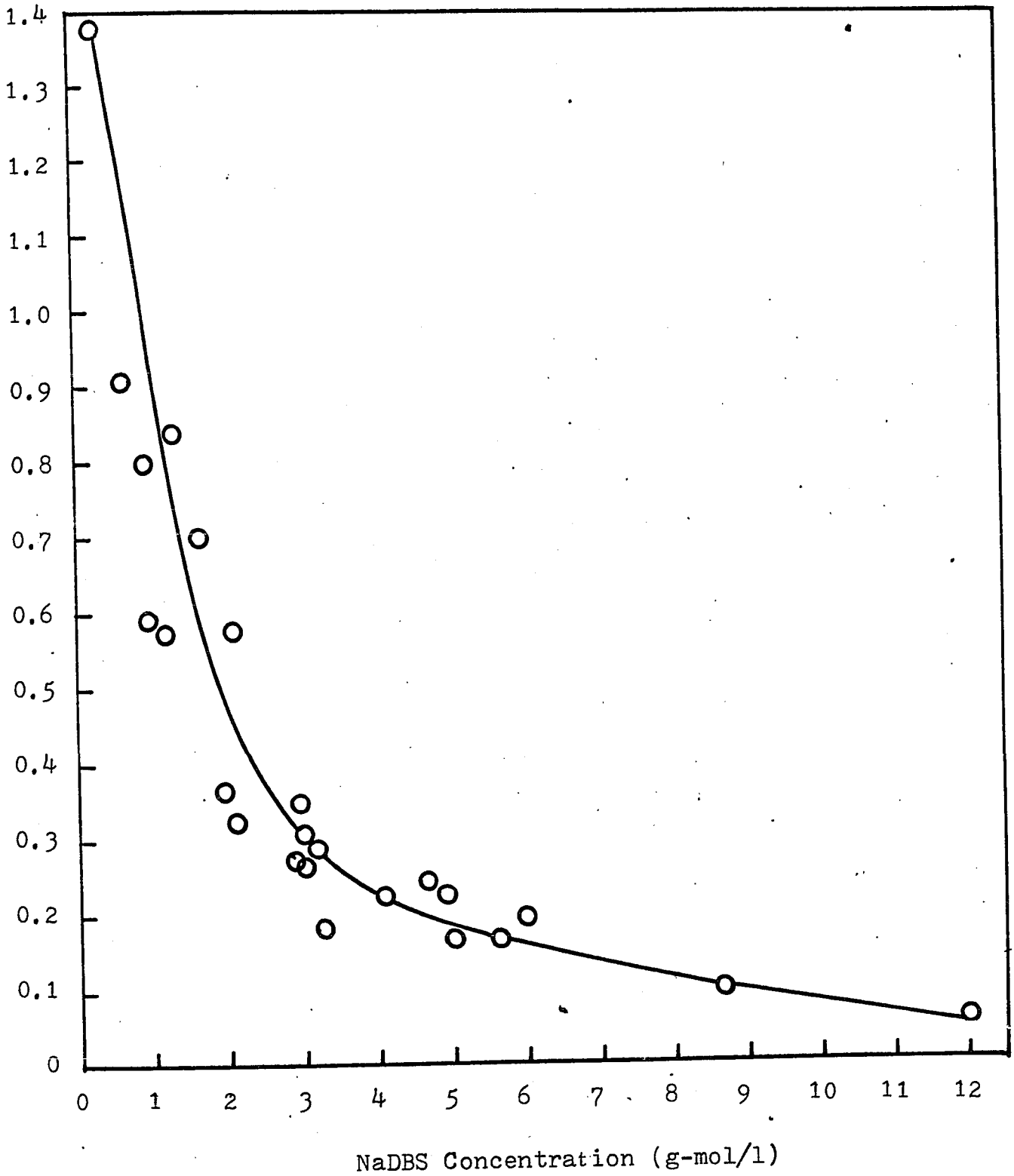
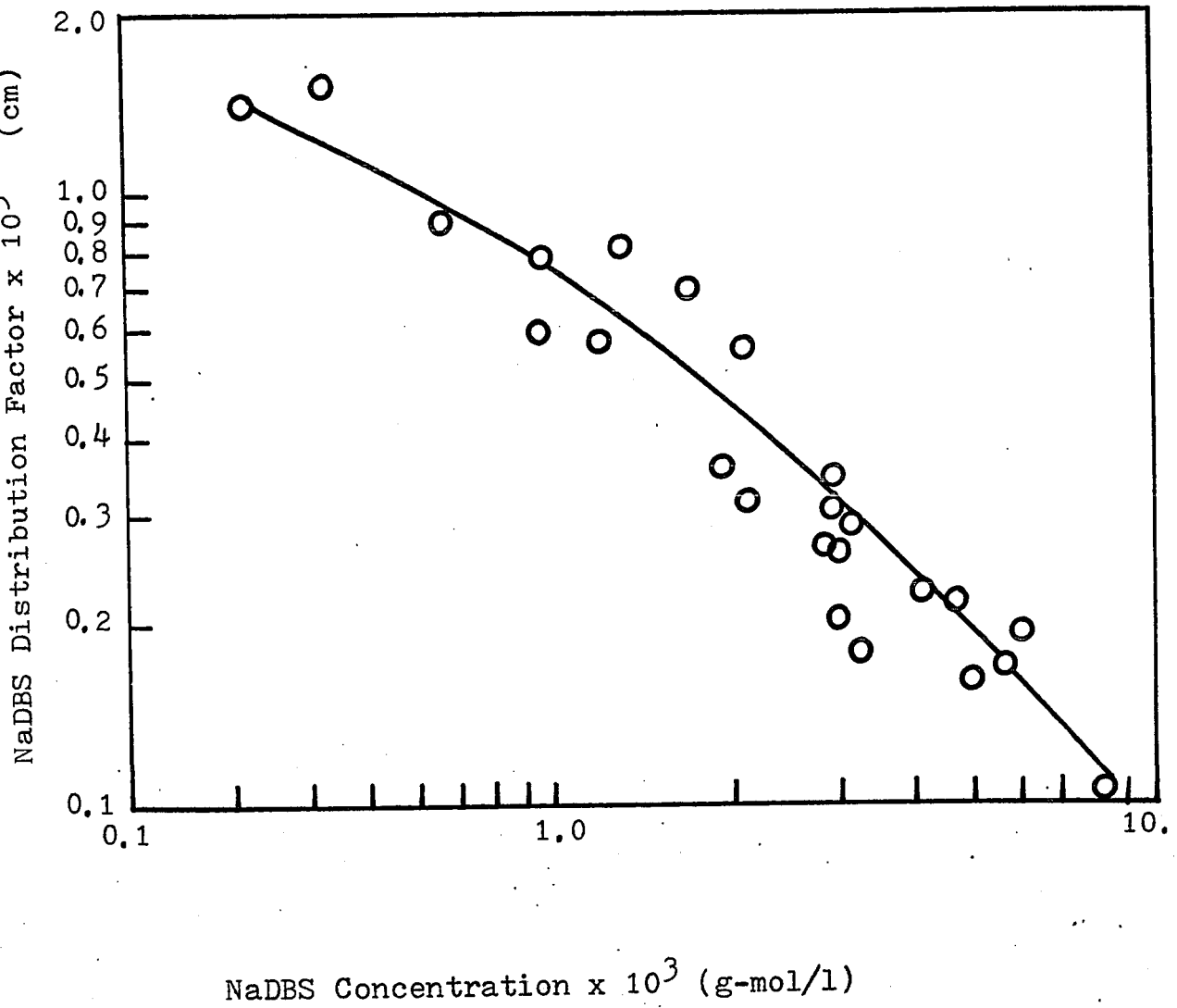


Figure 7- NaDBS Distribution Factor versus NaDBS Concentration



It would seem that convection is what limits the surface excess in this case. Prior to the perfecting of the microtome method of McBain and Humphreys (28) there had been many attempts to test the Gibbs equation experimentally. Many of these attempts gave results much higher than the theoretical values. This anomaly which appears to be due to the experimental method is partially explained by the movement of the surface of a rising bubble. The surface moves towards the rear of the moving bubble and carries with it adsorbed material which accumulates on this side, thus forming a multi-layer of surfactant. This type of movement has been studied experimentally by A.N. Frumkin and V.G. Levich (29). Thus these results, although definite and reproducible, bear no direct relation to the Gibbs' value or to that for monomolecular adsorption. It should be emphasized that in the development of his equation, Gibbs stated that one of the fundamental conditions was that the system under investigation be in complete thermodynamic equilibrium (30). In other words, Gibbs' equation strictly applies only to a static system and not a dynamic one.

When these high results for the surface excess were obtained a number of checks were made to ensure that these results were not due to experimental error. First, the analysis for NaDBS was duplicated using an entirely

different method from the standard ASTM method. The solution was buffered with a sodium acetate - acetic acid buffer at a pH of 4.75 and the absorbance was measured directly at 226 millimicrons, the peak in the absorption band for NaDBS. The analysis was in agreement. Second, bubble frequency was checked using a high speed camera and the results agreed with the stroboscope measurements. Finally a run was done with only half the liquid height as in the previous runs and again the results were in agreement. These checks verify the high adsorption values obtained for this dynamic system.

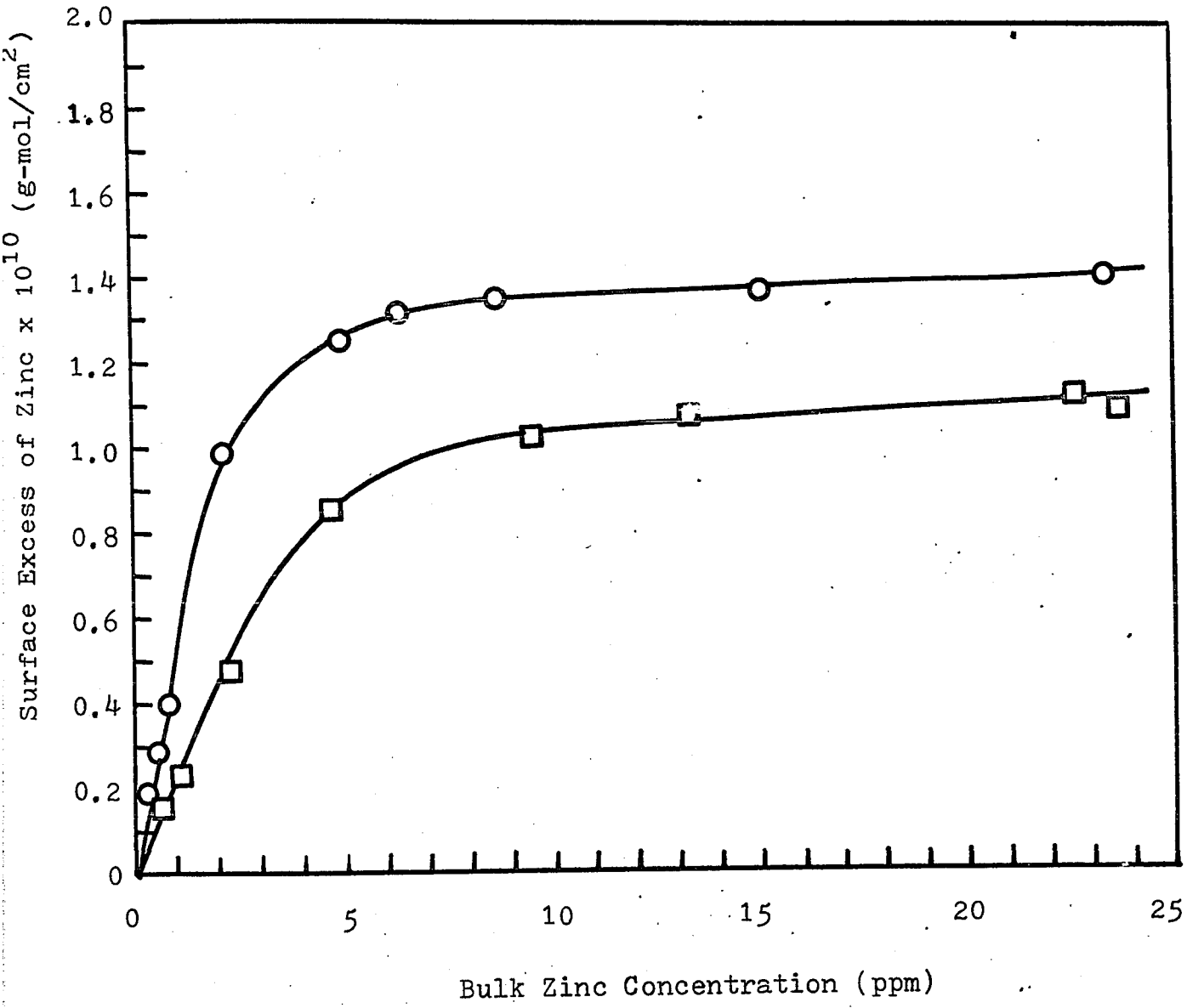
3a. Effect of Metal Ion Concentration

The effect of metal ion concentration is shown in Figures 8, 9, and 10 and is tabulated as runs 31 to 51 in Table 5, Appendix E. Two systems were studied, one with NaCl and one without NaCl. For both systems collector concentration and pH were held constant at 0.5 gm/liter and 5.0 respectively.

For the two systems we observe that the surface excess increases rapidly as the bulk zinc concentration increases. After 10 ppm the surface excess levels off at about 1.4×10^{-10} g-mol/cm.^{2} and 1.1×10^{-10} g-mol/cm.^{2} for the system without and with NaCl respectively. The significance of this result can be seen in Figure 9 which is a plot of the distribution factor, D, defined as the surface excess divided by the bulk concentration. As the bulk concentration decreases the distribution factor begins to rise rapidly. For concentrated solutions the distribution factors tend to zero assymptotically.

Since the inclined portion of the surface excess versus bulk concentration curve in Figure 8 is essentially linear, then the distribution factor must be constant. This is shown in Figure 10 which is a log-log plot of

Figure 8- Surface Excess of Zinc versus Bulk Zinc Concentration



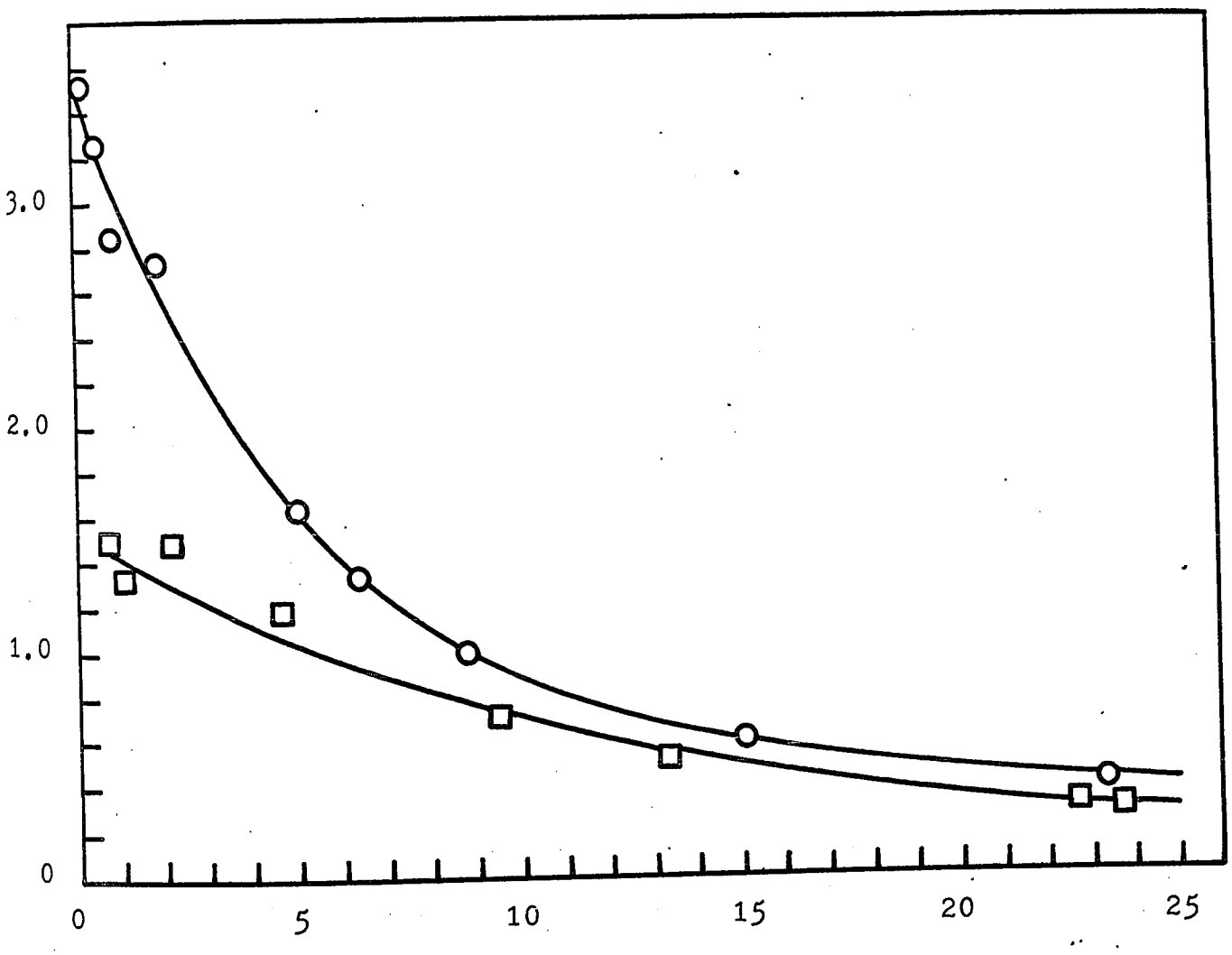
○ without NaCl

□ with 0.01 g-mol/l NaCl

pH = 5.0

NaDBS = 0.5 gm/l

Figure 9- Zinc Distribution Factor versus
Bulk Zinc Concentration



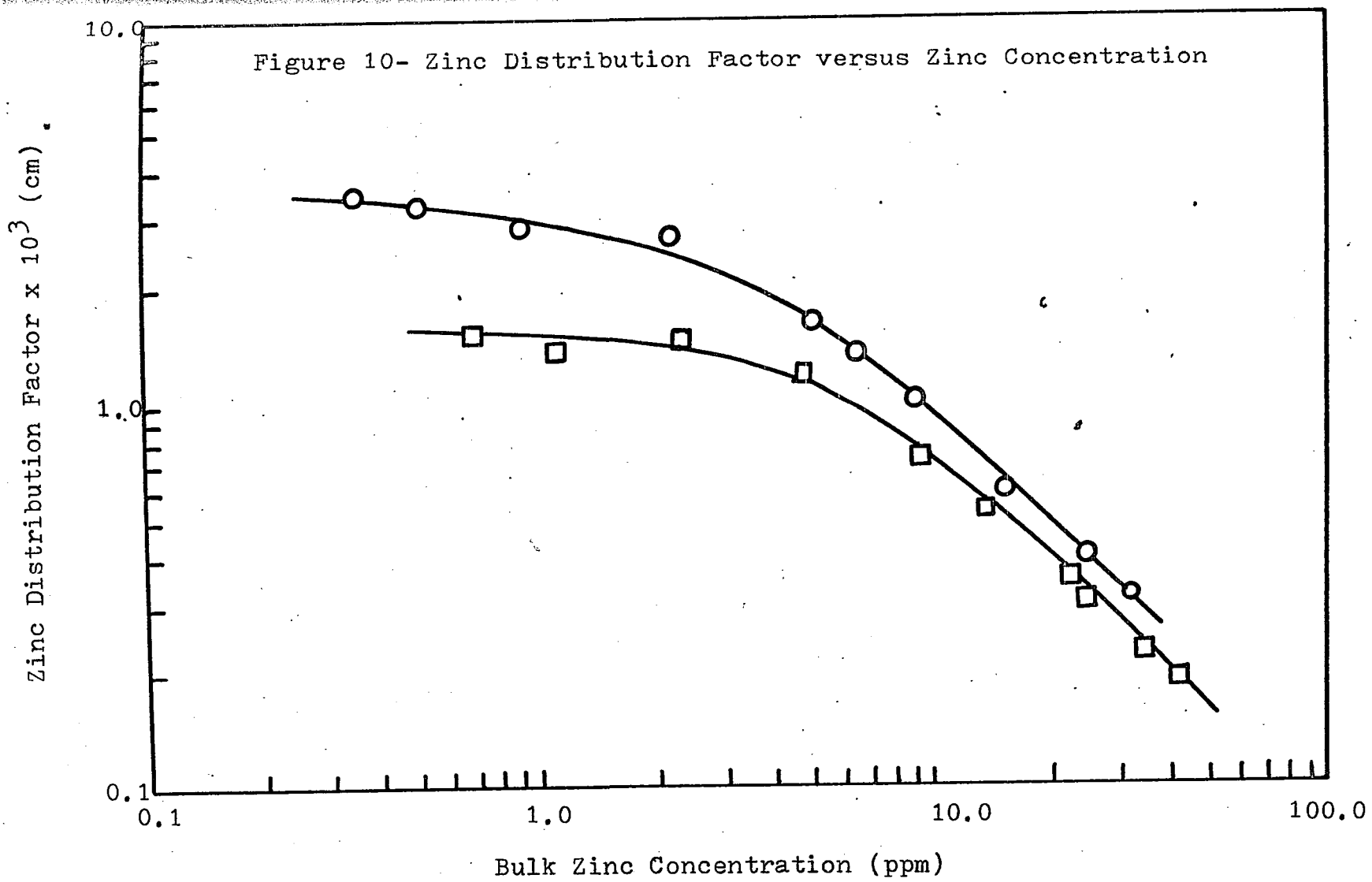
Bulk Zinc Concentration (ppm)

○ without NaCl

□ with 0.01 g-mol/l NaCl

pH=5.0
NaDBS=0.5 gm/l

Figure 10- Zinc Distribution Factor versus Zinc Concentration



○ without NaCl

□ with 0.01 g-mol/l NaCl

pH = 5.0 , NaDBS = 0.5 gm/l

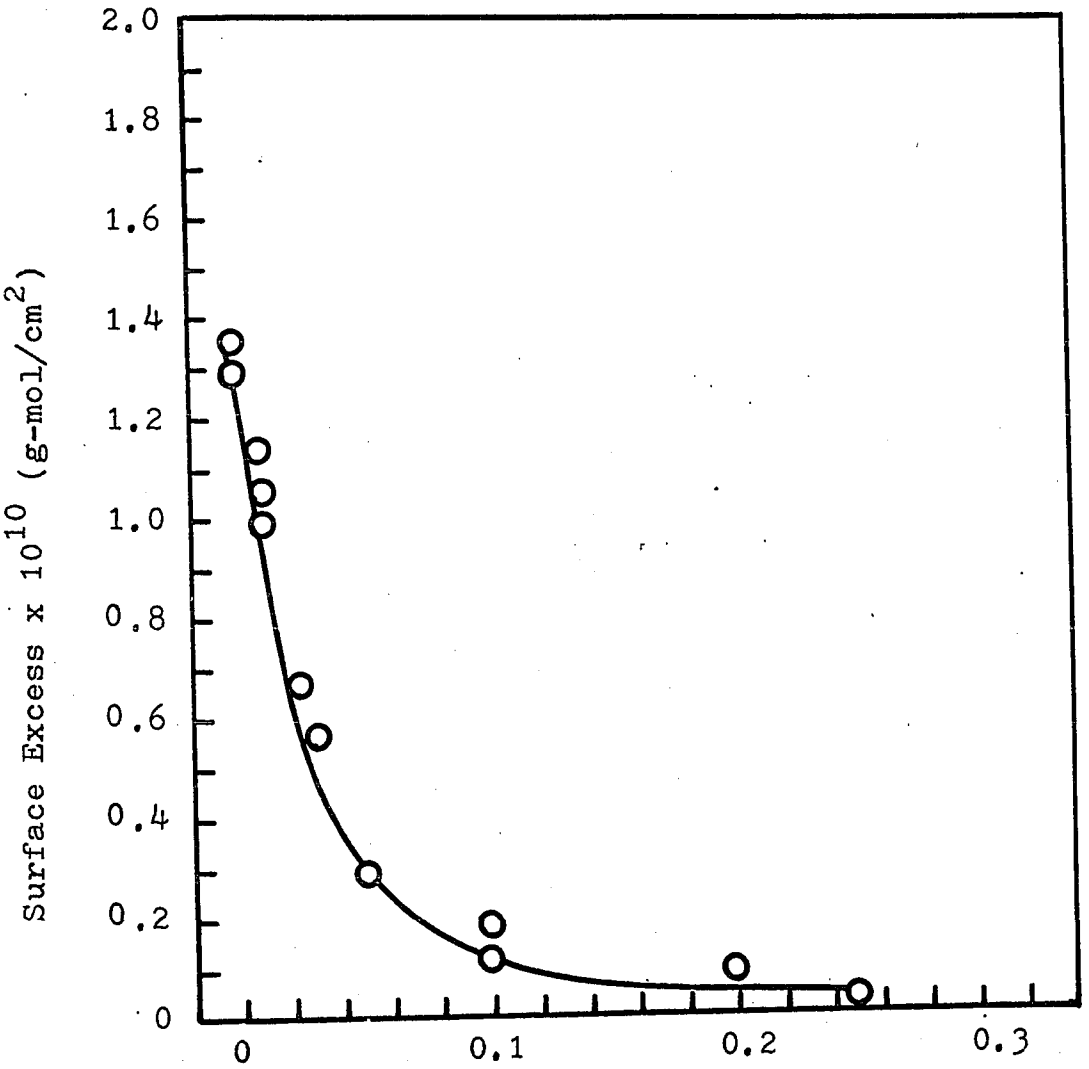
Figure 9. It shows that the distribution factors for the systems without and with NaCl level out at about 3.5×10^{-3} cm. and 1.5×10^{-3} cm. respectively.

3b. The Effect of Background Electrolyte Concentration

The effect of background electrolyte concentration can be seen in Figure 11 and is tabulated as runs 52 to 64 in Table 6, Appendix E. For these runs the zinc and surfactant concentrations were held constant at 10 ppm and 0.5 gm/liter respectively. The pH was adjusted to 5.0.

It is generally agreed that the presence of added electrolyte decreases the efficiency of ion flotation because of increased competition for the collector between the colligend and the added ions. For the zinc - NaDBS system the effects of added electrolyte are great. The surface excess drops exponentially from a maximum of 1.35×10^{-10} g-mol/cm.^{2} at zero NaCl concentration to 0.025×10^{-10} g-mol/cm.^{2} at 0.25 g-mol/liter NaCl concentration. 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. (31) for NaCl and many other electrolytes. The presence of added electrolyte alters the ionic competition for the collector as it is being removed from solution.

Figure 11- Surface Excess of Zinc versus
Electrolyte Concentration



Zinc = 10 ppm
NaDBS = 0.5 gm/l
pH = 5.0

3c. The Effect of pH

The effect of pH on the system is shown in Figure 12 and is tabulated as runs 65 to 80 in Table 7, Appendix E. For these runs the zinc, sodium chloride and collector concentrations were held constant at 10 ppm, 0.01 g-mol/liter and 0.5 gm/liter respectively.

In any system where there are acidic or basic components the pH will be an important parameter. There are three important aspects which must be considered in ion flotation. First, the initial pH will determine the nature of the process; that is ion flotation or precipitate flotation. Secondly, a change may occur in the ionization of the collector; for example the collector may lose its charge at high or low values of the pH. Third, flotation may be suppressed by the increased ionic strength which arises on adjusting the pH to high or low values. All of these effects can be observed in the zinc - NaDBS system. At low pH values, flotation is suppressed for two reasons. First, the collector loses its charge at low pH values. This is evident because of the equilibrium set up as follows:

$$NaDBS = Na^{+} + DBS^{-}$$

$$HDBS = H^{+} + DBS^{-}$$

The NaDBS is highly ionized so its concentration is small compared to that of DBS^{-}. The acid form is

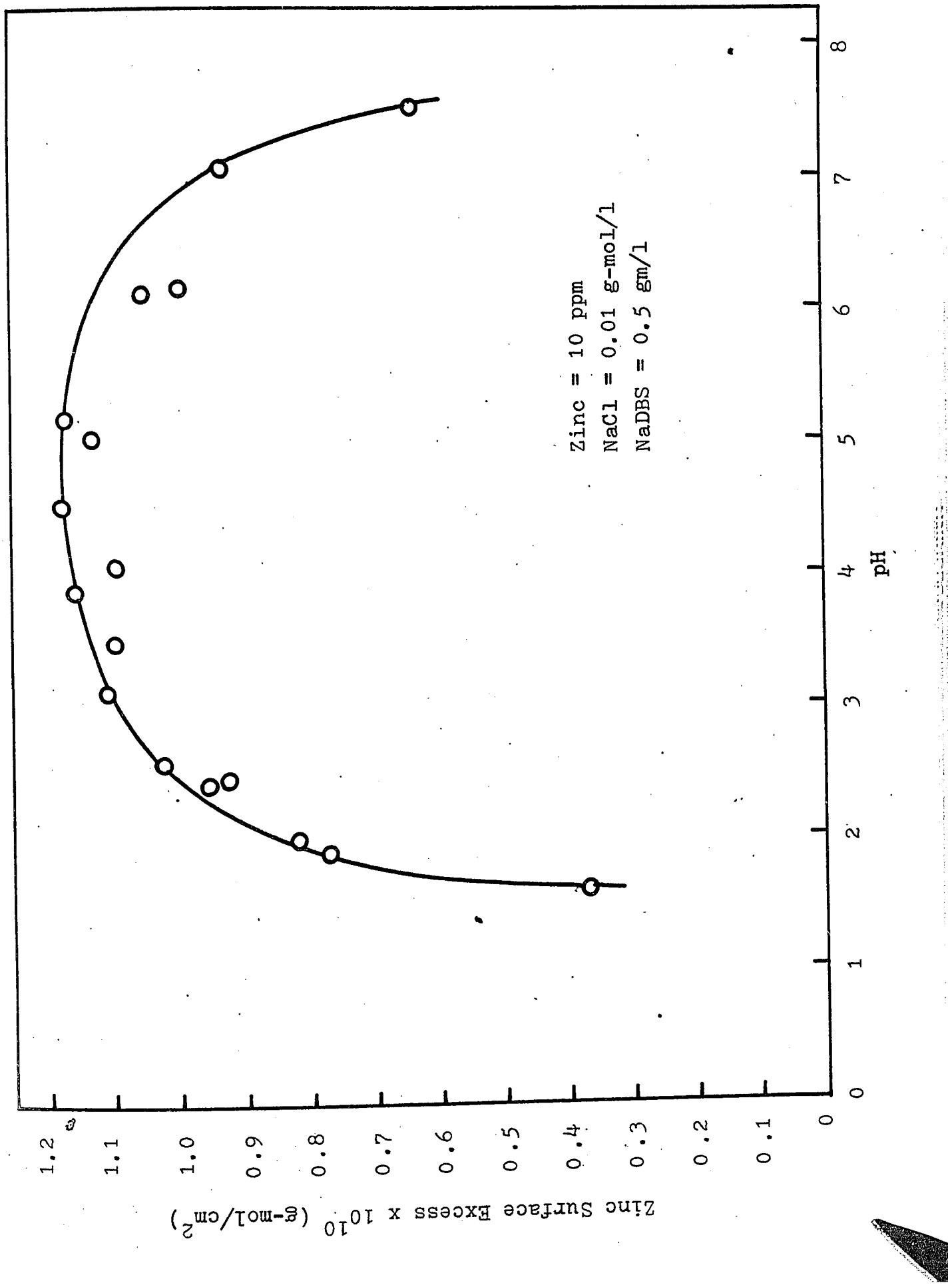


Figure 12- Surface Excess of Zinc versus pH

less highly ionized so that the DBS^- concentration is greatly reduced at low pH values. The net result is that the collector loses its charge and hence ceases to be a collector. In Figure 12 this is shown as the pH goes from 2.5 to 1.5 where the surface excess decreases exponentially . Also in this same pH range, flotation is suppressed by the increased ionic strength which arises on adjusting the pH to such extreme values.

At a pH of 7.0 the flotation process changes from ion flotation to precipitate flotation. The precipitation value of the pH is set by the solubility product of zinc hydroxide and the zinc concentration. These solubility products and incipient precipitation pH values are tabulated in Table 6, Appendix D.

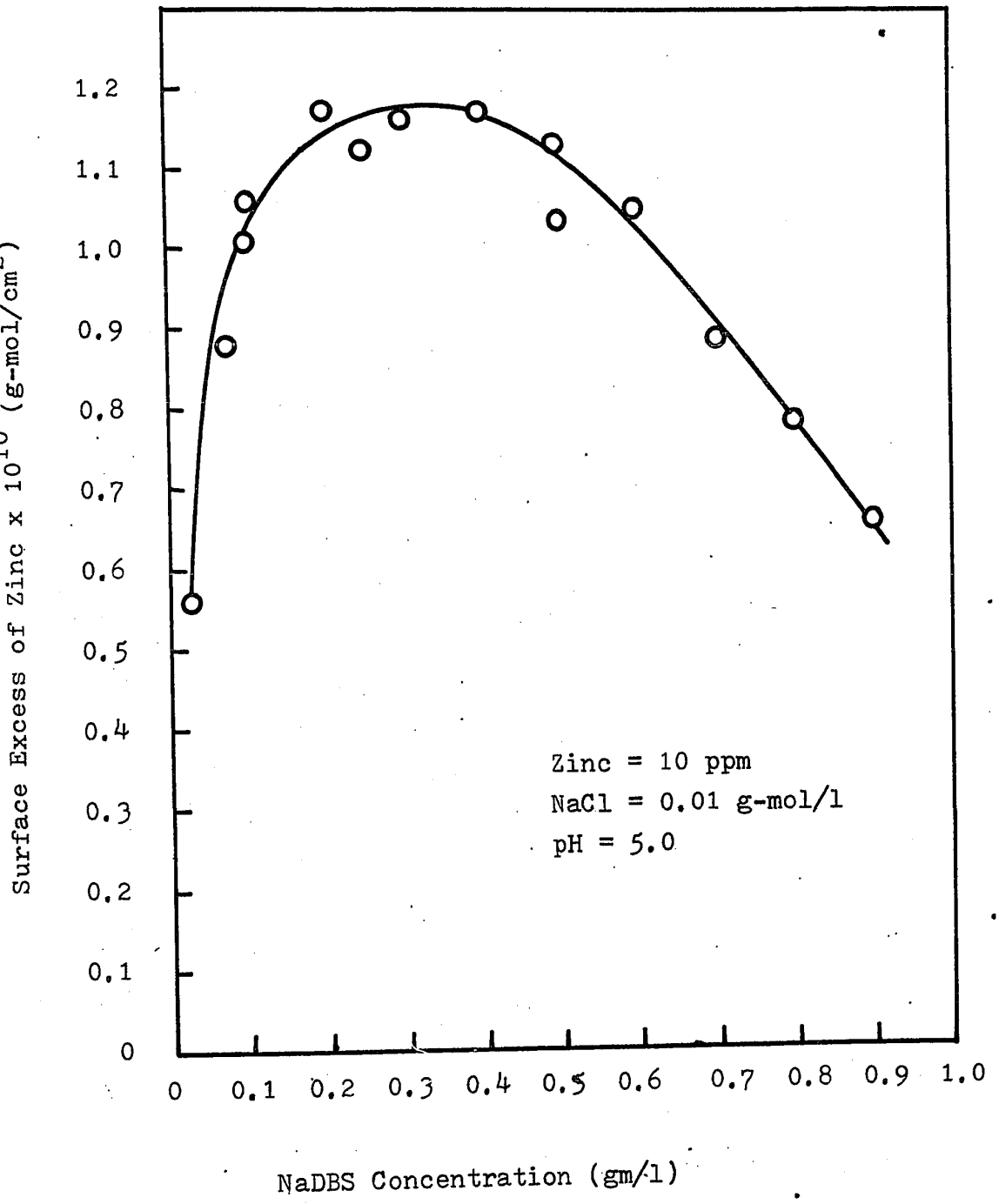
From Figure 12 we see that the optimum pH range for zinc flotation is between 3 and 6 with a surface excess of 1.1×10^{-10} g-mol/cm.^{2}

3d. The Effect of Collector Concentration

One of the leading advantages of ion flotation is the large volume reduction which occurs on collecting the colligend from a dilute solution and concentrating it in a small volume of foamate. The production of a large amount of foam is both unnecessary and undesirable. The extent to which foam forms depends on the collector concentration and it has been found that the presence of excess of collector inhibits flotation. This effect was first noticed by Lusher and Sebba (1965) (32) and subsequently by Davis and Sebba (1966) (33), Grieves and Bhattacharrya (1968) (34), Grieves et al. (1969) (35), Rose and Sebba (1969) (36) and Spargo and Pinfold (1970) (37).

When collector and colligend are present in the solution as ions there are two reasons for suppression. First, collector-colligend interactions in the bulk solution become more likely and adsorption of these species on the bubble surfaces becomes more difficult as the latter are crowded with collector. Second, if the collector concentration exceeds the critical micelle concentration, flotation will be impaired because colligend ions adsorb on the micelles, which are themselves unable to float because of their hydrophilic surfaces.

Figure 13- Surface Excess of Zinc versus NaDBS Concentration



Therefore in both cases, colligend is withheld from the bubbles and flotation is impaired.

The effect of collector concentration for the zinc - NaDBS system is shown in Figure 13 and tabulated as runs 81 to 94 in Table 8, Appendix E.

The maximum adsorption of colligend for this system is about 0.3 gm/liter NaDBS. Below this concentration the bubble surface is not completely packed with surfactant and hence maximum adsorption does not occur. Beyond 0.3 gm/liter no additional surfactant is adsorbed on the surface and any additional surfactant remains in the bulk solution and competes with that at the surface for the zinc ion. Also as the bulk concentration is increased the collector-colligend species will find it more difficult to be adsorbed on the bubble surface since the surface will be crowded with collector. In addition micelle formation may be occurring with increased collector concentration. Both of these effects combined cause a downward trend in the surface excess of colligend once the surfactant concentration is increased beyond 0.3 gm/liter.

4. Batch Foaming

In order to predict the removal of zinc from a batch solution, one must know the behaviour of the system in two ways. First, the dynamic behaviour of the system must be expressed analytically. This means one must know the surface excess of zinc as a function of pH, electrolyte concentration, bulk zinc concentration and surfactant concentration. Similarily the surface excess of surfactant must be known as a function of bulk surfactant concentration. Secondly, the physical performance of the batch cell must be known as related to liquid carry-over and surface generation rate. These two characteristics are dependent on cell geometry. Another important point is the realization that removal of zinc involves a dual mechanism; that is zinc is removed by attachment to the bubble surface and by liquid carry-over. When this information is obtained the amount of zinc removed can be calculated from equation (5):

$$R = S\Gamma_{Zn} + QX \qquad (5)$$

where R = amount of zinc removed

S = surface generation rate

Q = liquid over flow rate

Γ_{Zn} = surface excess of zinc

X = bulk zinc concentration.

A similar equation (6) can be used to predict the amount of surfactant removed.

$$R = S\Gamma_{DBS} + QY \qquad (6)$$

where R = amount of NaDBS removed

S = surface generation rate

Γ_{DBS} = surface excess of NaDBS

Q = liquid overflow rate

Y = surfactant concentration.

Therefore using equation (5) and (6) one can calculate the amount of solute removed as a function of time for a particular cell geometry. Knowing the total original amount of material present and the amount removed by the two mechanisms of surface activity and liquid carry-over one can calculate the new concentrations remaining and then repeat the calculation in a stepwise manner.

The adsorption of zinc ions can be described by equation (7):

$$\Gamma_{Zn} = \frac{k_1 X}{1 + k_2 X} \qquad (7)$$

where $k_1 = 11.5 \times 10^{-3}$ cm.

$k_2 = 79.2 \times 10^{6}$ cm.^{3}/g-mol

Equation (3) is a Langmuir type of isotherm which can often be used approximate equilibrium adsorption. Equation (8) describes the effect of sodium chloride on the system:

$$\Gamma_{Zn} = \Gamma_{Zn,max}\, 10^{-k_3(NaCl)} \qquad (8)$$

where $k_3 = 11.2$ l/g-mol and $\Gamma_{Zn,max}$ is the value of Γ_{Zn} at a given zinc concentration when there is no electrolyte in the system. That is, $\Gamma_{Zn,max} = \Gamma_{Zn}$ of equation (7). Equations (7) and (8) can be combined to give the surface excess of zinc as a function of both electrolyte and bulk zinc concentration, equation (9):

$$\Gamma_{Zn} = \frac{k_1 X}{1 + k_2 X}\, 10^{-k_3(NaCl)} \qquad (9)$$

The influence of pH on the system can be accounted for by multiplying equation (9) by the term $10^{-k_4(H_3O^+)}$ and this correction is valid provided the precipitation of zinc hydroxide has not begun, that is a pH of less than 7.5. The system now becomes equation (10):

$$\Gamma_{Zn} = \frac{k_1 X}{1 + k_2 X} 10^{-k_3(NaCl)} 10^{-k_4(H_3O^+)} \qquad (10)$$

where $k_4 = 24.4$ l/g-mol.

In a similar manner the effect of surfactant can be expressed by equation (11):

$$\Gamma_{Zn} = \Gamma_{Zn}^{\circ} \cdot \frac{k_5 Y}{1 + k_6 Y} \qquad (11)$$

where $k_5 = 137$ l/gm

$k_6 = 127$ l/gm

and $\Gamma_{Zn}^{\circ} = \Gamma_{Zn}$ of equation (10), that is the surface excess of zinc determined under the conditions for which the effect of surfactant was studies.

Thus the surface excess of zinc can now be expressed as a function of the four variables in equation (12):

$$\Gamma_{Zn} = \frac{k_1 X}{1 + k_2 X} \, 10^{-k_3 NaCl} \cdot 10^{-k_4 (H_3^+ 0)} \cdot \frac{k_5 Y}{1 + k_6 Y} \qquad (12)$$

The surface excess of surfactant is less complicated and can simply be expressed as equation (13):

$$\Gamma_{DBS} = \frac{k_7 Y}{1 + k_8 Y} \qquad (13)$$

where $k_7 = 73.8 \times 10^{-10}$

$k_8 = 6.52$

Y = NaDBS concentration gm/l

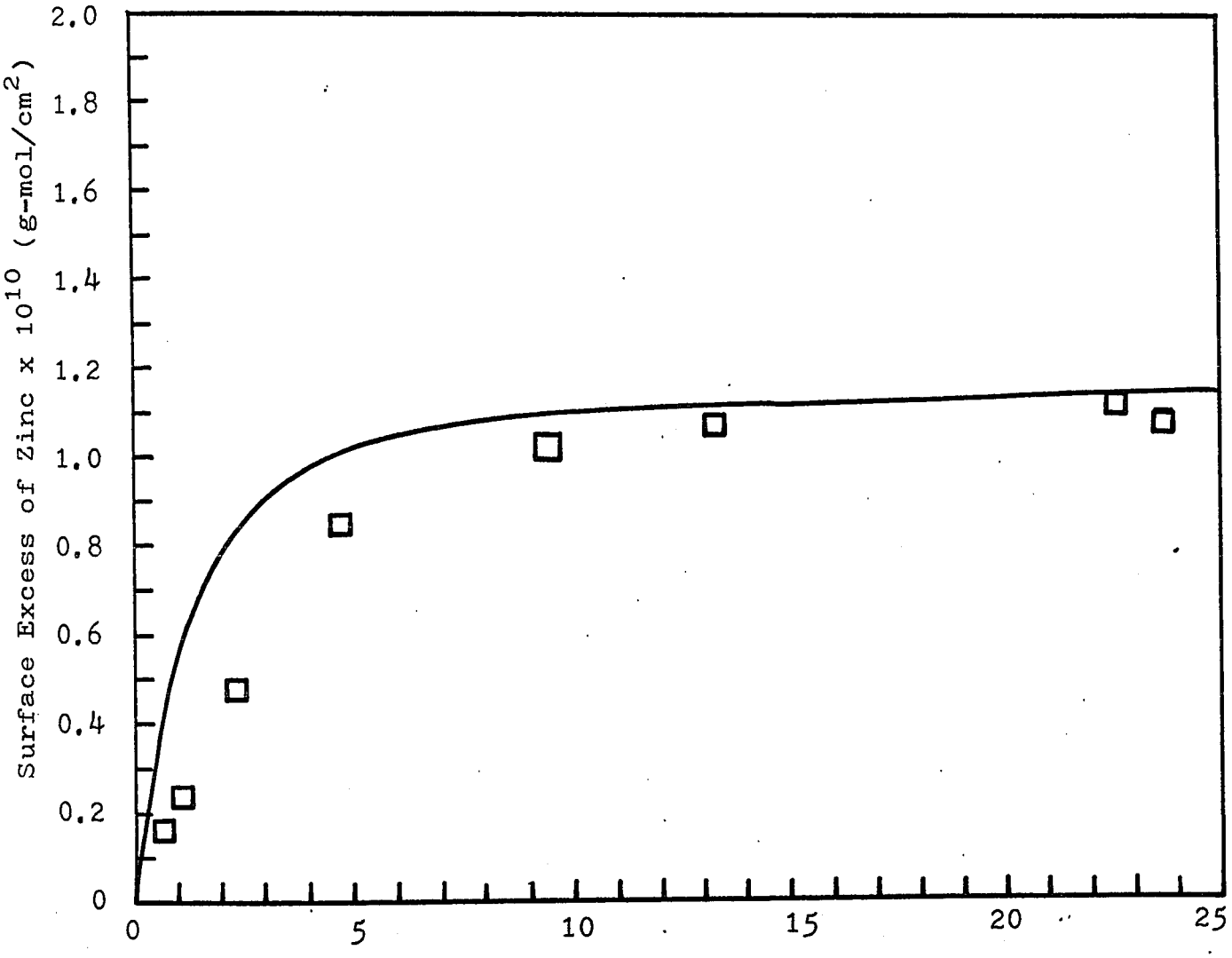
Γ_{DBS} = surface excess of NaDBS, g-mol/cm.^{2}.

The reason for such a simple expression for the surface excess of NaDBS can be argued as follows. It is the only surface active molecule in the system, and hence the surface excess will not depend on the presence of other ions which are not surface active, that is ions such as Zn^{++}, Na^+, Cl^-, H_3O and OH^-. This has been experimentally proven by doing runs with and without electrolyte. For this system, the results were identical.

Equations (12) and (13) have been calculated and compared to the experimental measurements of surface

Figure 14- Surface Excess of Zinc versus
Zinc Concentration

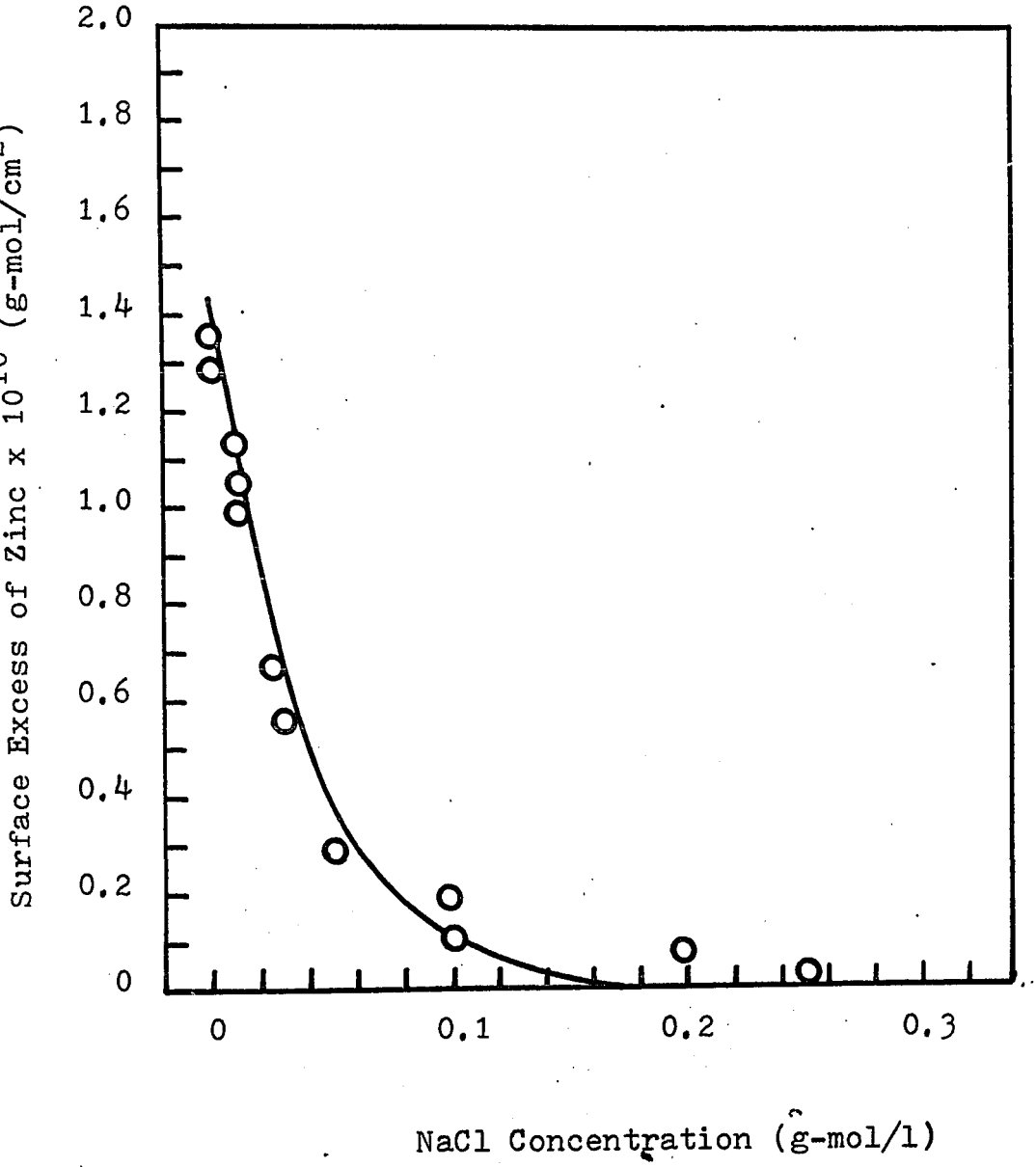
Calculated and Experimental Values



NaCl = 0.01 g-mol/l
NaDBS = 0.5 gm/l
pH = 5.0

Figure 15- Surface Excess of Zinc versus
Electrolyte Concentration

Calculated and Experimental Values



Zinc = 10 ppm
NaDBS = 0.5 gm/l
pH = 5.0

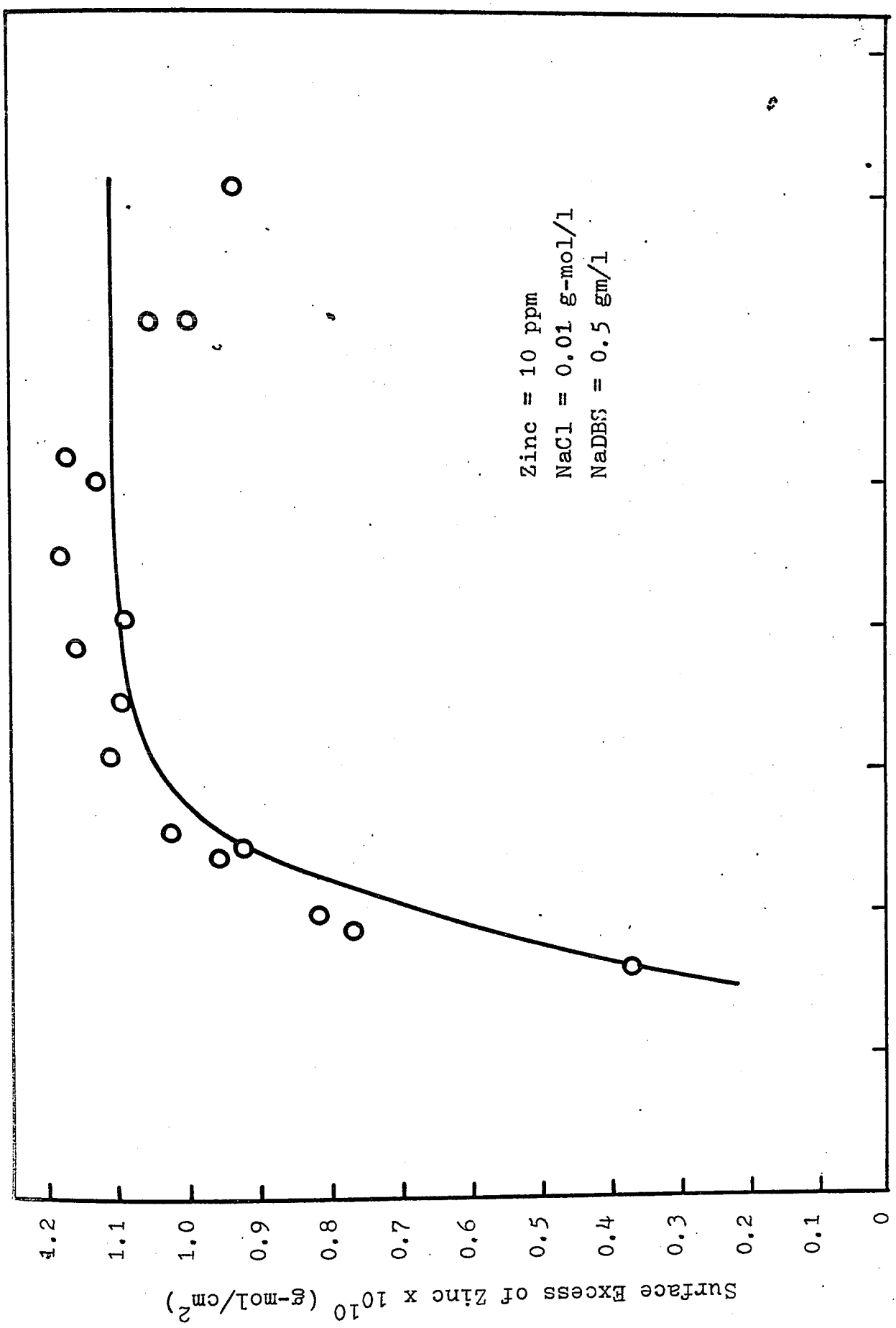
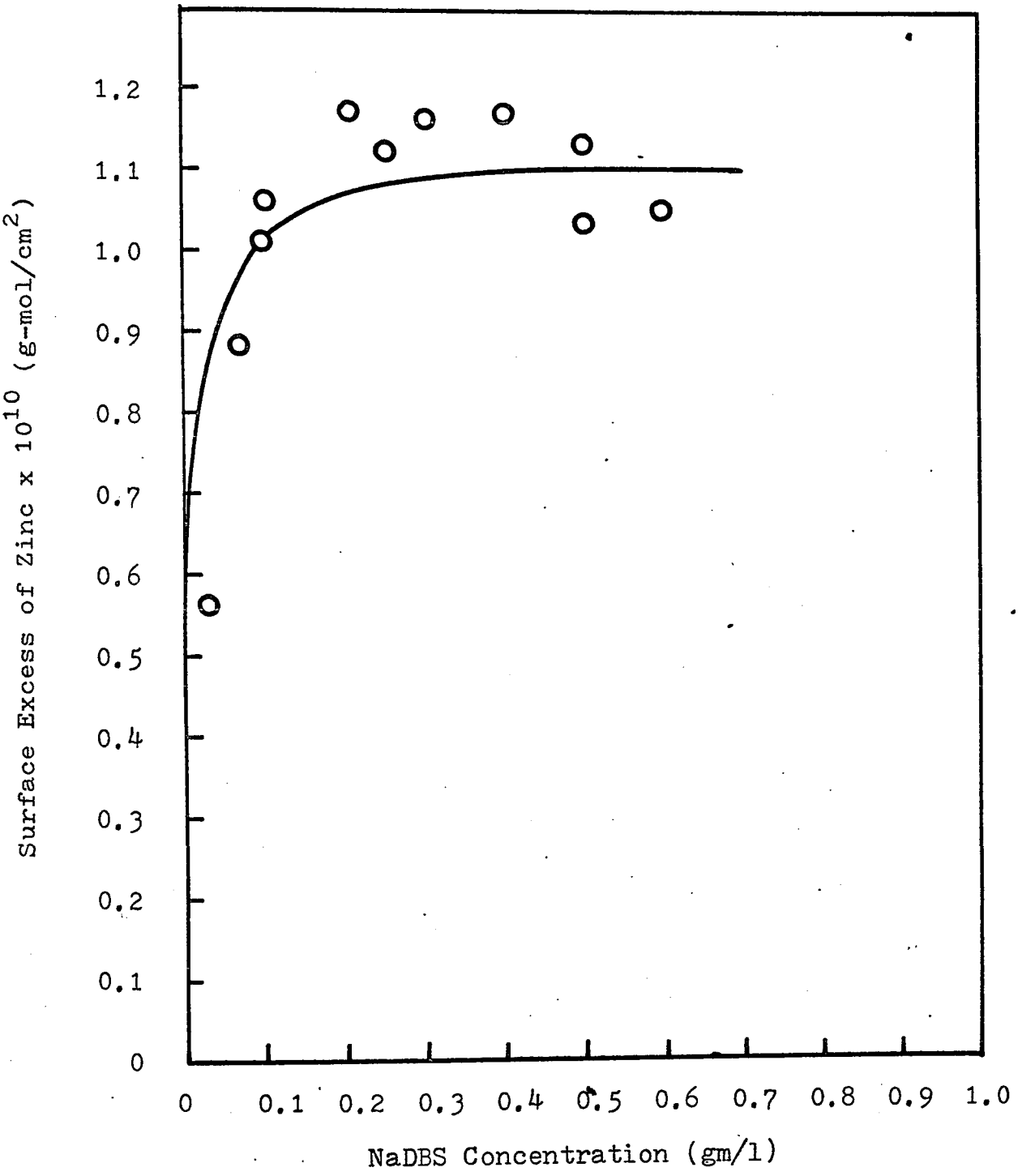


Figure 16-Surface Excess of Zinc versus pH, Calculated and Experimental Values

Figure 17- Surface Excess of Zinc versus NaDBS Concentration

Calculated and Experimental Values



Zinc = 10 ppm

NaCl = 0.01 g-mol/l

pH = 5.0

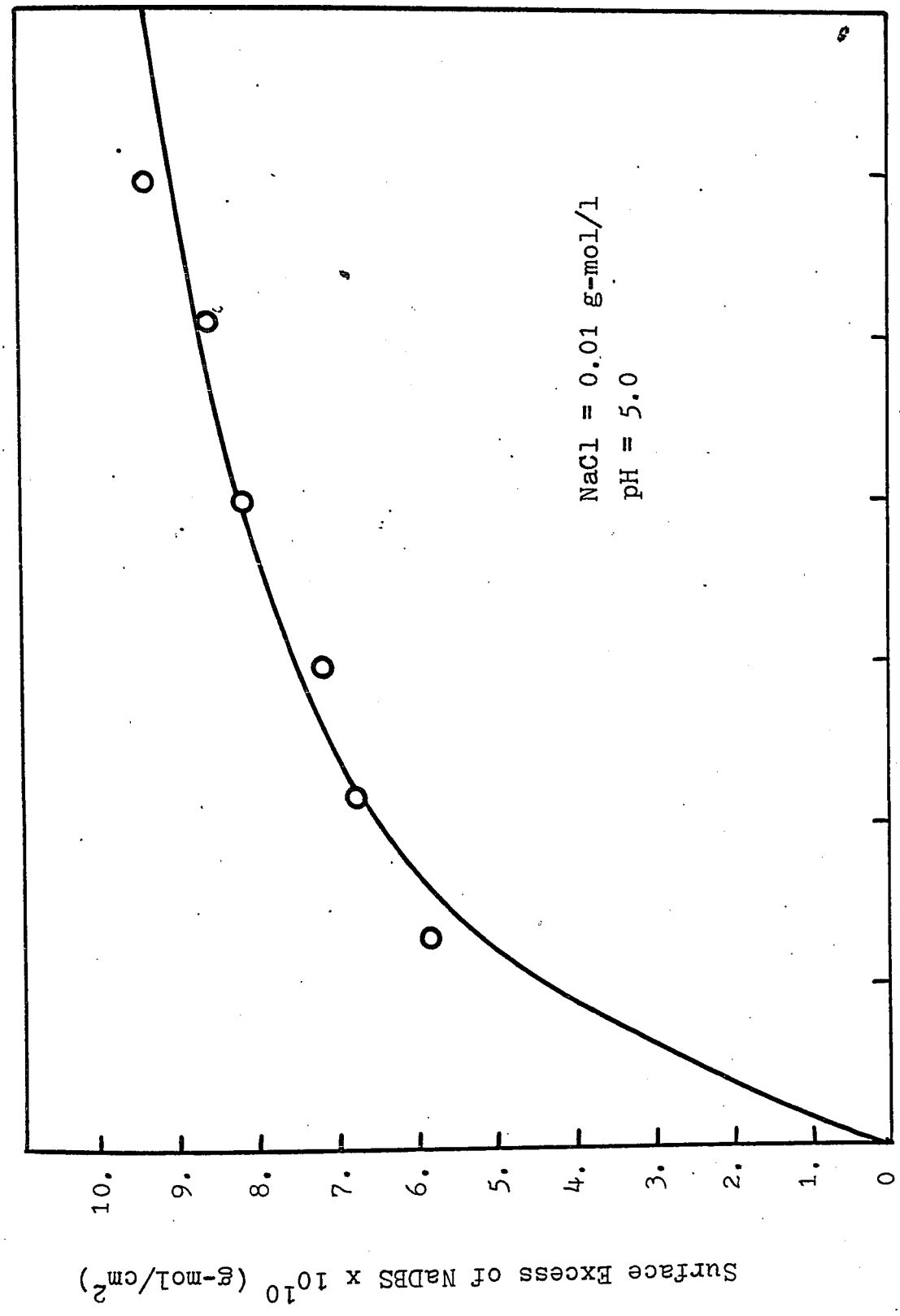


Figure 18- Surface Excess of NaDBS versus NaDBS Concentration

excess of zinc and NaDBS. The results are shown in Figures 14, 15, 16, 17 and 18.

What remains now is to determine the surface generation rate of the porous metal sparger used in the batch cell. This was estimated using an equation for foam overflow, developed by Lemlich. The equation was developed from theory for foam drainage and overflow and is equation (14):

$$Q = \frac{G^2 \mu}{Ag\rho d^2} \phi\left(\frac{\mu^3 G}{\mu_s^2 g \rho A}\right) \qquad (14)$$

where G = volumetric gas flowrate

Q = volumetric flow rate of foam overflow on a gas free basis

μ = liquid viscosity

A = horizontal cross sectional area of foam column

g = gravitational constant

ρ = liquid density

d = average bubble diameter

μ_s = surface viscosity

The function ϕ was evaluated theoretically in accordance with two alternatives regarding the detailed

relationship between the interstitial downflow and the bulk foam upflow. Complete details can be found in Lemlich's original work (38). In order to use equation (14) one must know the surface viscosity. Surface viscosity is the resistance of a monolayer to shear stress in the plane of the surface, similar to that in the bulk where a liquid is retarded in its flow by viscous forces. Surface viscosity was determined as follows: the bubbler from the equilibrium stage was used in the batch cell because it is possible to calculate the bubble diameter from a stroboscope count of bubble frequency and overall gas flowrate. Density ρ and viscosity μ are for the liquid in the capillaries and for dilute solutions these properties can be conveniently taken as those of the solvent water. Thus in equation (14) all the variables are known except μ_s which can be calculated directly.

This procedure was repeated for five concentrations and the results are shown in Table 1.

Table 1

Surface Viscosity versus Bulk Concentration

Surfactant Concentration (gm/1)	Surface Viscosity x 10^4 (dyne sec/cm)
0.10	0.23
0.20	0.60
0.30	0.57
0.40	0.51
0.50	0.54

From Table 1 we note that the surface viscosity does not vary appreciably over the concentration range 0.2 to 0.5 gm/litre. The low value of 0.23×10^{-4} dyne sec/cm can be attributed to coalescence in the foam and hence surface viscosity has no physical significance at this concentration of 0.1 gm/litre because a complete monolayer of surfactant has not formed. Lemlich has reported a value of the surface viscosity of essentially NaDBS solutions as 0.80×10^{-4} dyne sec/cm. This value was determined in the same manner as just outlined. Naturally any value of surface viscosity so determined incorporates not only any error in the data but also any limitations in the foam theory.

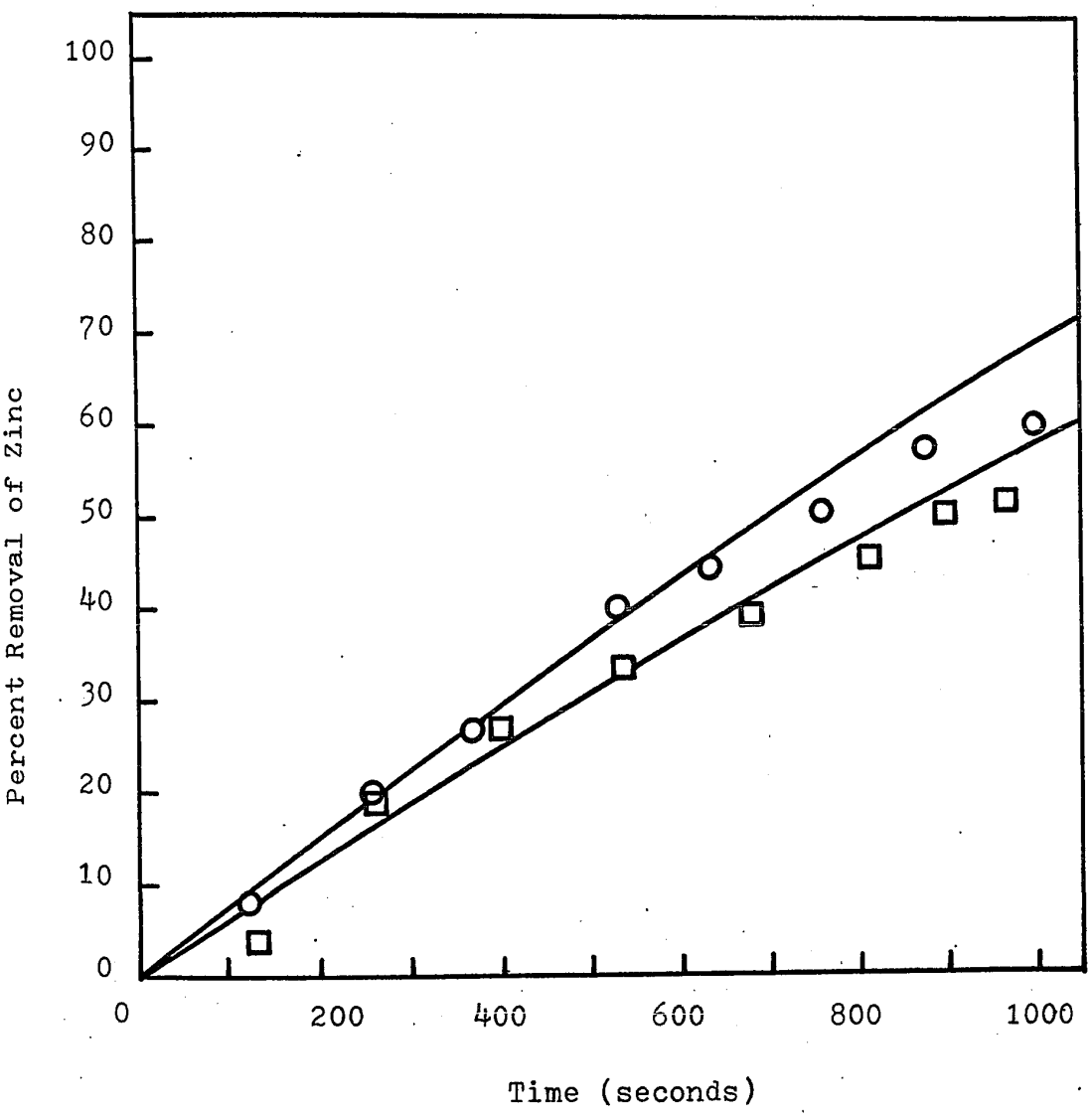
Taking an average surface viscosity of 0.55×10^{-4} dyne sec/cm. it is now possible to calculate the surface generation rate of the porous metal sparger used in the batch cell. This is done by using equation (14) and measuring the overflow rate of the batch column. Since the surface viscosity is known, the only unknown is d, the average bubble diameter. Once d is calculated and G is measured, it is possible to calculate the number of bubbles generated per second and hence the surface generation rate of the porous metal sparger in the batch cell.

As a test of the predicted removal rate, some batch removal experiments were performed at various collector ratios (moles of collector to moles of zinc) with and without electrolyte. These runs were performed with the same gas rate used in equation (14) so that the surface generation rate would be then known. All feed solutions were made to be 10 ppm zinc and initial pH of 5.0 ± 0.1. The collector was injected in a single injection from a freshly prepared solution with 0.4 ml of collector solution being equal to a collector ratio of 1.0.

The results of the experiments are shown in Figures 19, 20, and 21 and are tabulated in Tables 11 to 16, Appendix E. Also shown are the results predicted

Figure 19-Batch Removal at a Collector Ratio = 3

Calculated and Experimental Values



○ without NaCl

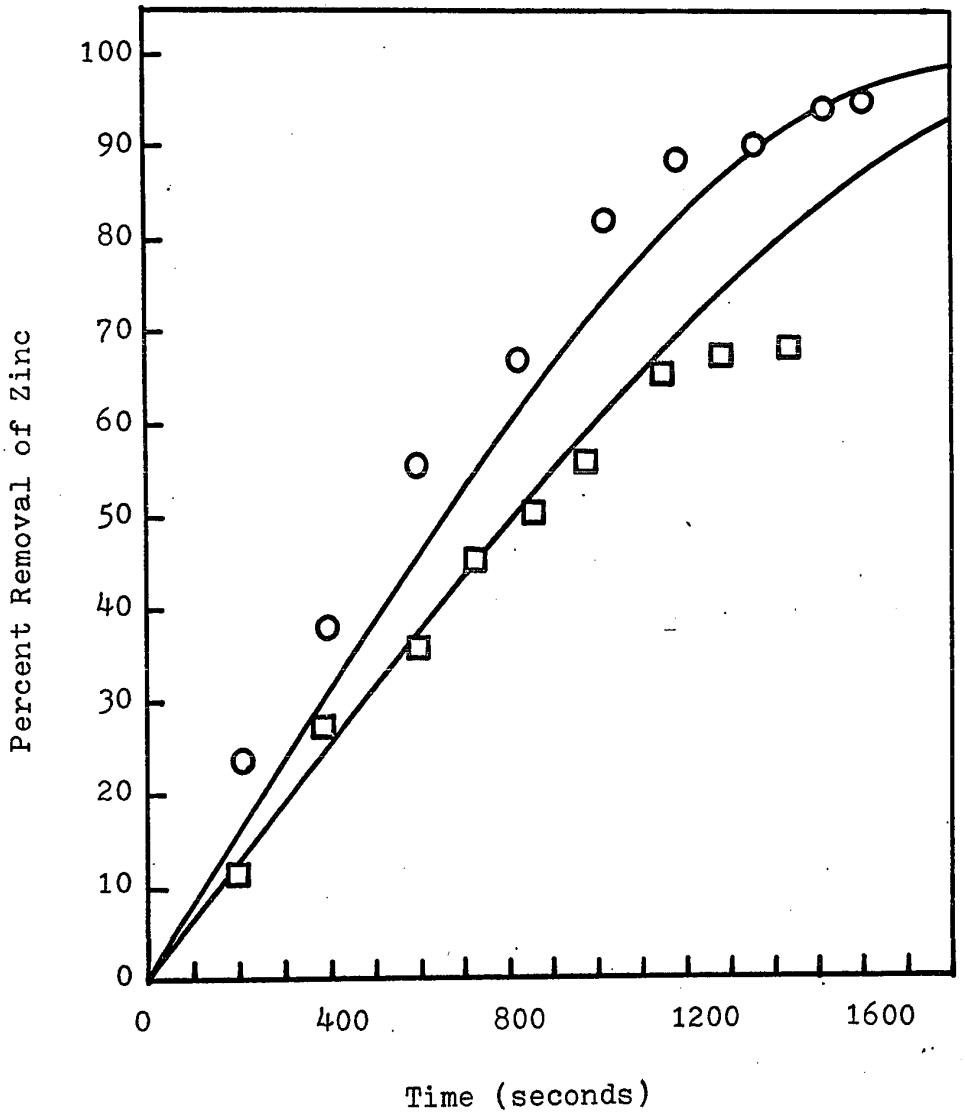
□ with 0.01 g-mol/l NaCl

pH = 5.0

10 ppm Zinc

Figure 20- Batch Removal at a Collector Ratio = 6

Calculated and Experimental Values



○ withiut NaCl

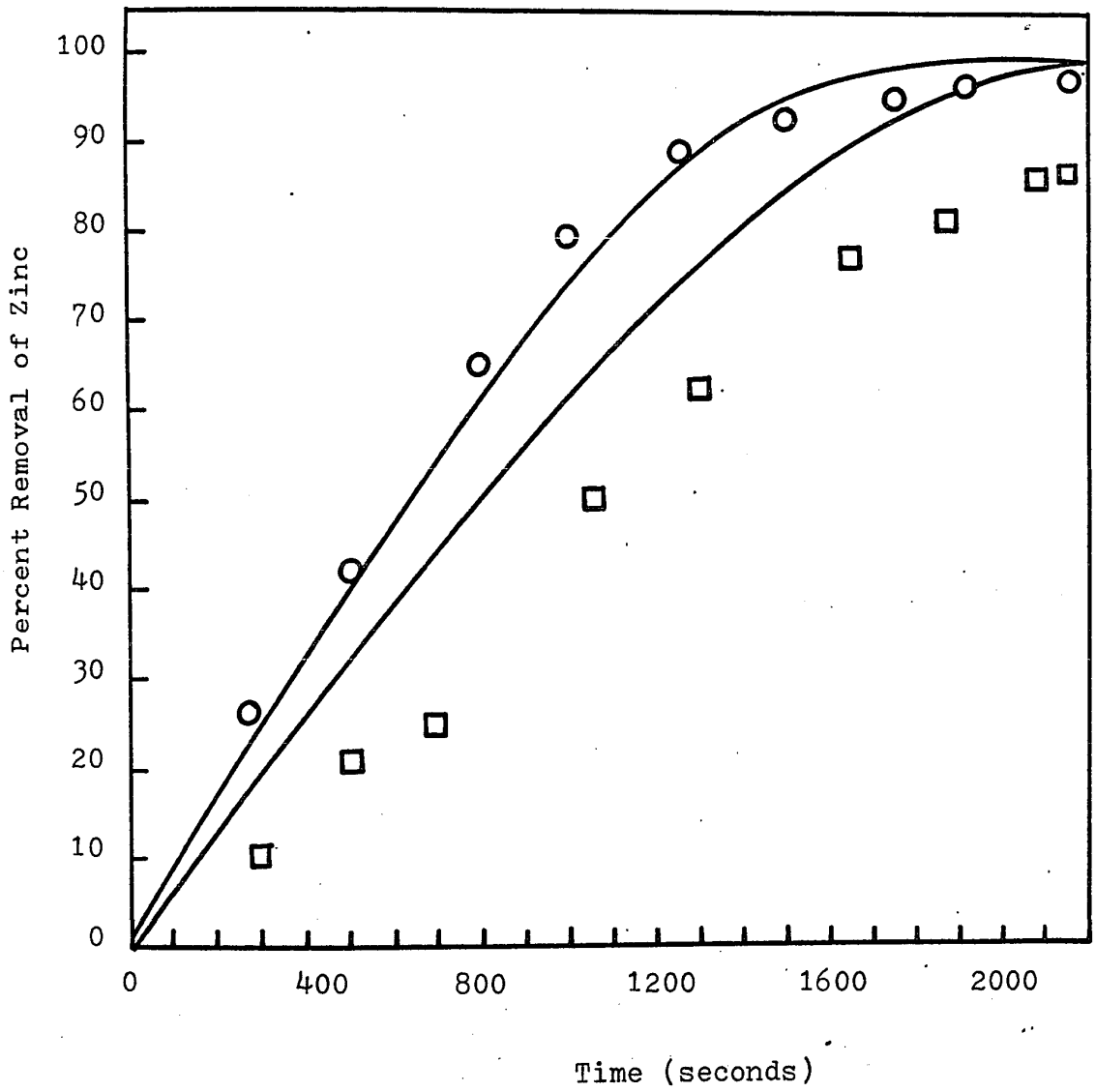
□ with 0.01 g-mol/l NaCl

pH = 5.0

10 ppm Zinc

Figure 21- Batch Removal at a Collector Ratio = 10

Calculated and Experimental Values



○ without NaCl

□ with 0.01 g-mol/l NaCl

pH = 5.0

10 ppm Zinc

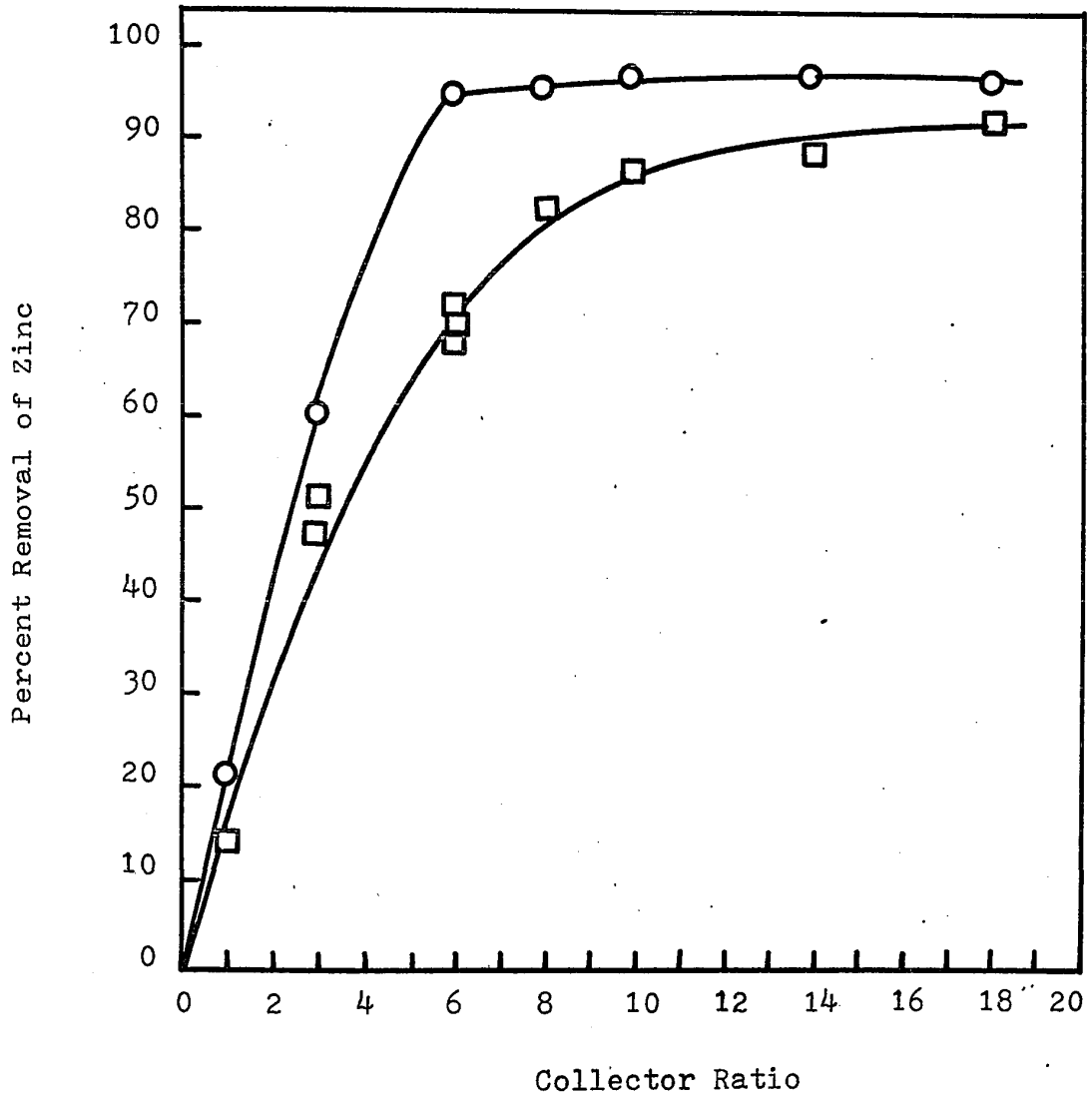
using the equilibrium data. In predicting the results it was assumed that pH and electrolyte concentration do not change appreciably during a batch run. This is reasonable since electrolyte is removed only by liquid carry-over and the concentration remains unchanged. Also electrolyte concentration does not appear to affect the surface excess of collector (compare runs 19 to 24 with runs 25 to 30 done under similar conditions). A change in pH of 1 or 2 units also will not affect the system (see Figure 12) and the pH was measured after a few runs and varied only about 1 unit. In general, agreement is within 15%. There is a practical limitation on the experimental runs and that is foam stability. At the end of a run when virtually all the collector is removed the foam becomes unstable, no longer supporting itself; this then is the termination of a run. This was visually observed to be about 0.08 gm/litre of surfactant. The prediction, on the other hand does not take this into account and so the removal continues at the same rate.

5. Effect of Collector Concentration on Removal

The effect of collector concentration on ion flotation is shown in Figure 22 and tabulated in Table 10 in Appendix E. For Figure 22, the collector ratios were varied from 1 to 18. Ion flotation is seen to have a strong dependence on collector concentration. Removal of zinc was observed to reach a different limiting value for each collector ratio. The ultimate removal is some function of the collector ratio but the shape of the removal curves is not affected significantly by the collector concentration as seen from Figures 19, 20, and 21.

For the system without electrolyte the ultimate removal, approximately 96% is reached after a collector ratio of 6, or 3 times the stoichiometric amount of surfactant required. After a collector ratio of 6 the system approaches the 100% removal asymptotically. For the system with electrolyte there is about 70% removal at a collector ratio of 6. A collector ratio of 6 corresponds to a surface excess ratio of NaDBS to Zn of about 6 also, for this system. Once again this shows the sensitivity of ion flotation to the presence of inorganic electrolytes. At higher collector ratios, this system approaches the 100% removal asymptotically.

Figure 22- Percent Removed versus Collector Ratio



○ without NaCl

□ with 0.01 g-mol/l NaCl

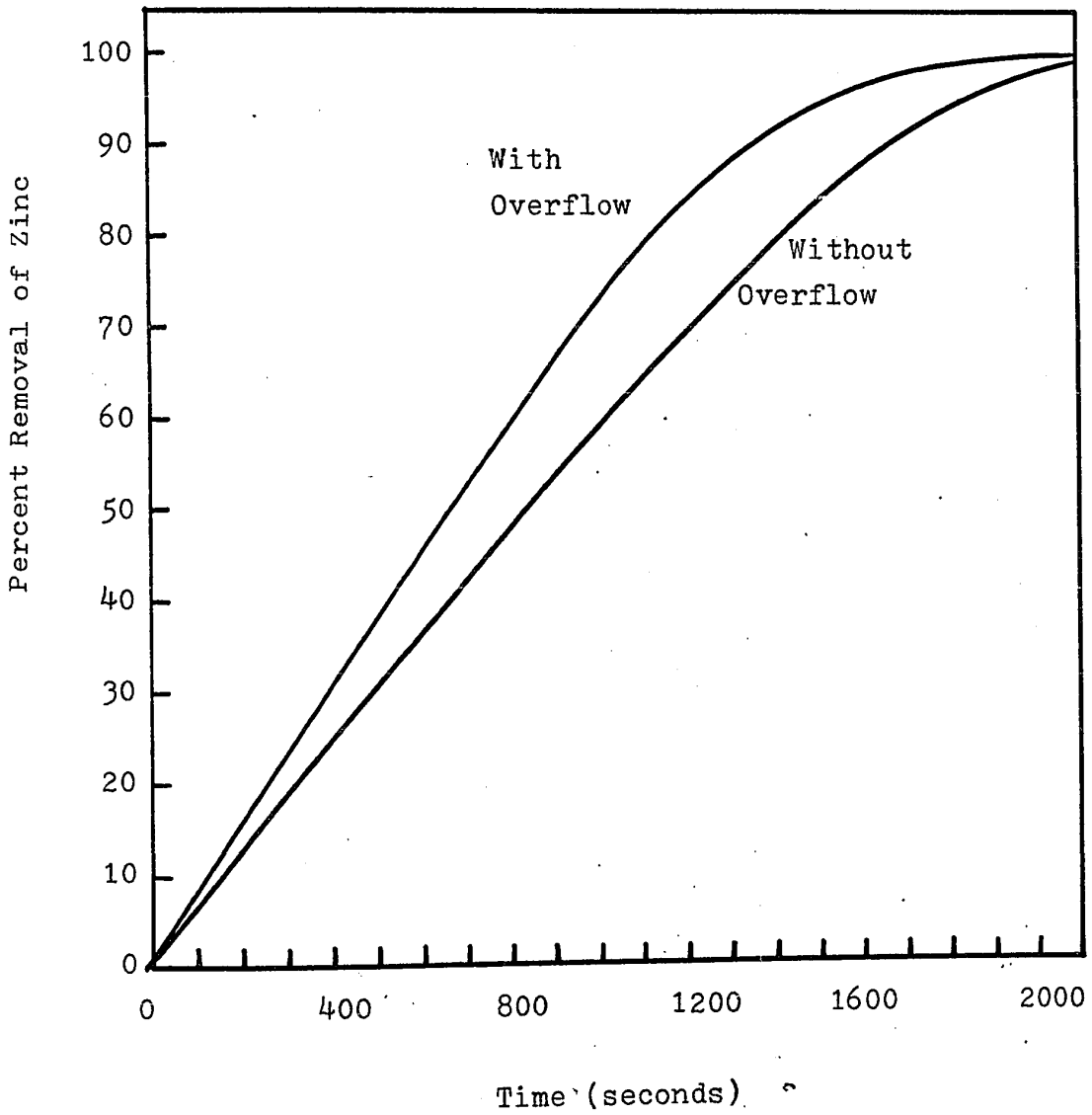
pH = 5.0

10 ppm Zinc

6. Effect of Overflow on the Simulation of a Batch Run

To show the importance of liquid carry-over in the foam, two simulation runs were executed, one with overflow (this is equivalent to a wet foam) and the other without overflow (dry foam). The results are shown in Figure 23. The run with overflow shows a much higher removal rate throughout the run. Once again this illustrates that solute is removed by two mechanisms, surface excess and bulk carry-over. Of course the process should be conducted in such a manner that a product of the least possible volume and the highest possible solute concentration would be finally obtained. This is equivalent to producing a very dry foam. There are a number of means of doing this. Looking at equation (14), although not entirely obvious, by doubling the horizontal cross sectional area of the column, the foam overflow rate is approximately halved. Similarily a lower gas rate would allow for better drainage thus producing a dryer foam. To this end an attempt was made using the batch column to carry out a run which would produce a dry foam. This was done by injecting the surfactant at a constant rate, the rate of injection being equal to the rate of removal. Since the surface excess is known as a function of concentration and the surface generation rate is known, the rate of removal and hence the injection rate can be calculated. The surfactant

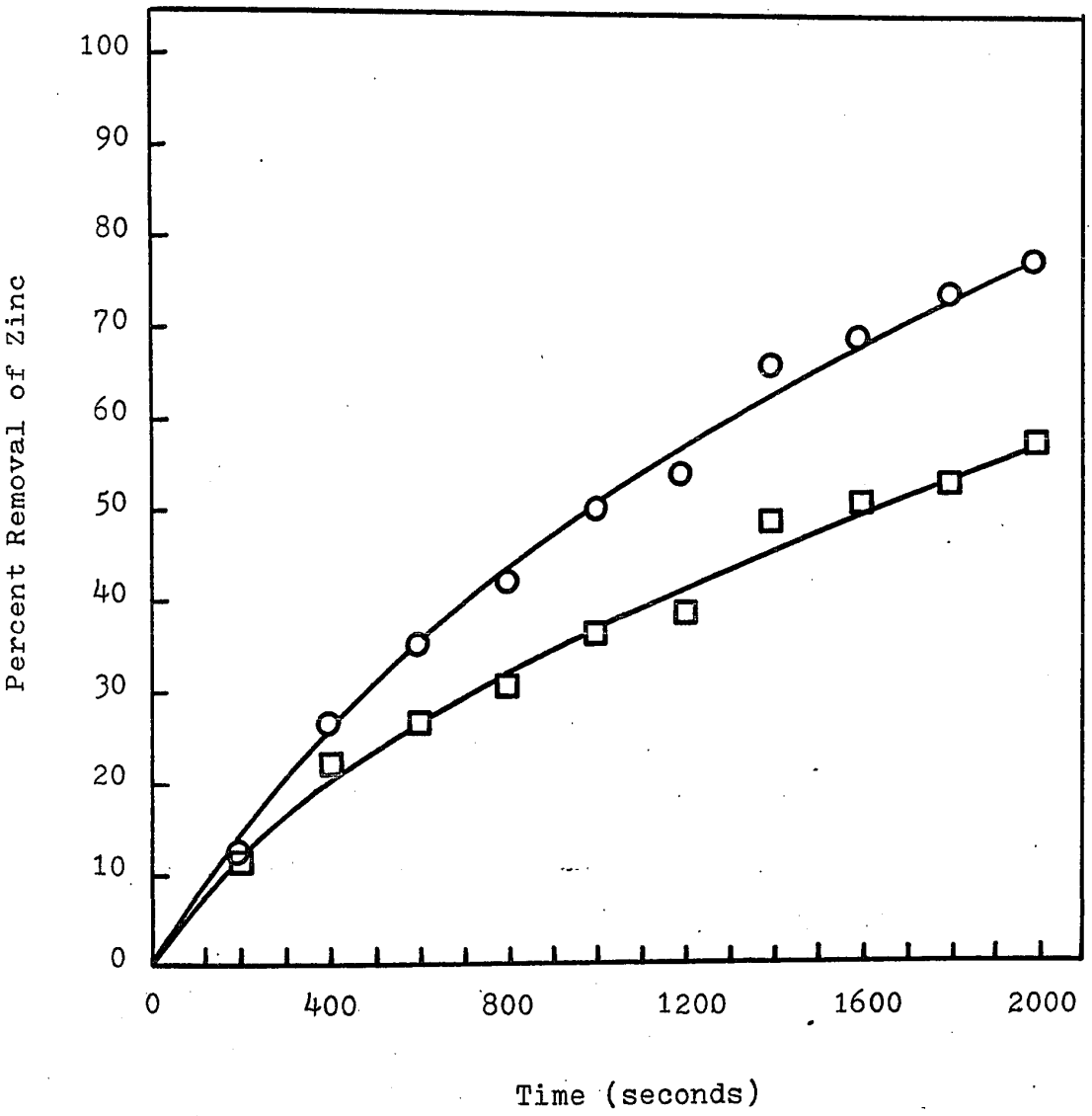
Figure 23- Effect of Liquid Overflow on the Simulation of a Batch Removal



Simulation Conditions: 10 ppm Zinc
0.01 g-mol/l NaCl
collector ratio = 6
pH = 5.0

solution was injected in the sample port by a Perpex Peristaltic Pump LKB 10200 at a rate of 2.33 mls. per minute. Run BR-9 was done at a collector concentration of 0.10 gm/liter and run BR-10 at 0.05 gm/liter. Both runs are shown in Figure 24 and both runs were terminated after 2000 seconds. The total amount of collector injected in run BR-9 corresponds to a collector ratio of 6.22 and for run BR-10 this is 3.11. From Figure 22 this should give 95% and 63% removal respectively but only 78% and 58% removal were obtained. Also it was visually observed that the foam collapsed quite readily at these low concentrations. This means that a monolayer was not present, and hence the best removal rate was not obtained. By increasing the surfactant concentration we increase carry-over because of increasing foam stability. A low gas flow rate would produce a dry foam but the flow rate would have to be so low that the time for complete surfactant removal would be prohibitive.

Figure 24- Batch Removal at Constant Collector Concentration



○ Collector Concentration = 0.1 gm/l

□ Collector Concentration = 0.05 gm/l

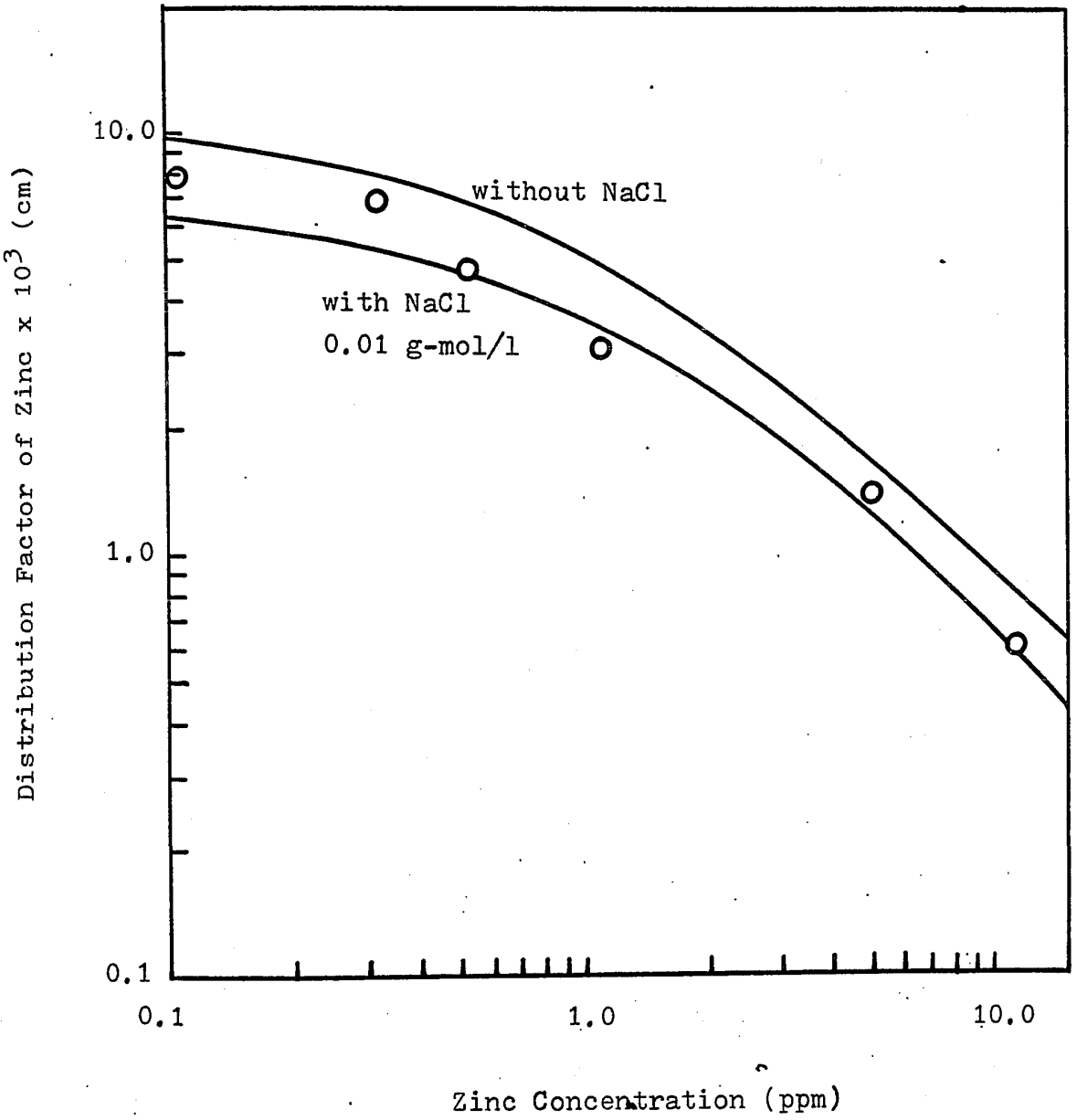
10 ppm Zinc
pH = 5.0
no NaCl

7. Effect of Low Surfactant Concentration on Distribution Factors for Zinc

From the simulations of runs with collector ratios of 6 and 10 it was observed that towards the ends of these runs the distribution factor reached a limiting value of 6 to 9 at a zinc concentration of 0.1 ppm or less. This was contrary to what was previously measured, the distribution factor for zinc being 3.5×10^{-3} cm. and 1.5×10^{-3} cm., without and with electrolyte respectively at a collector concentration of 0.5 gm/liter. In the simulation, both zinc and collector concentrations are being decreased simultaneously. In order to check the validity of this phenomena, the distribution factor for zinc was determined in the equilibrium cell at a concentration of 0.05 gm/liter which is ten times less than that of the previous determinations.

The results are shown in Figure 25 and tabulated as runs 95 to 100 in Table 5, Appendix E. Immediately one sees that the results verify those of the simulation. The zinc distribution factor reaches a value of 8.0×10^{-3} cm. at 0.1 ppm Zn. These results are supported by a similar study in France by J. Arod (39). He found that the distribution factor for strontium increased with constant lower surfactant concentrations at low strontium concentrations. At higher strontium concentrations, there was no significant variation in the distribution factor, with surfactant concentration.

Figure 25- Zinc Distribution Factor versus Zinc Concentration at Low Collector Concentration Calculated and Experimental Values



O experimental conditions: 10 ppm Zinc
0.05 gm/l NaDBS
pH = 5.0
no NaCl

——— simulation conditions: 10 ppm Zinc
Collector Ratio = 6
pH = 5.0

It is interesting to note that this result was discovered because of the simulation. Only after did a literature search verify the result.

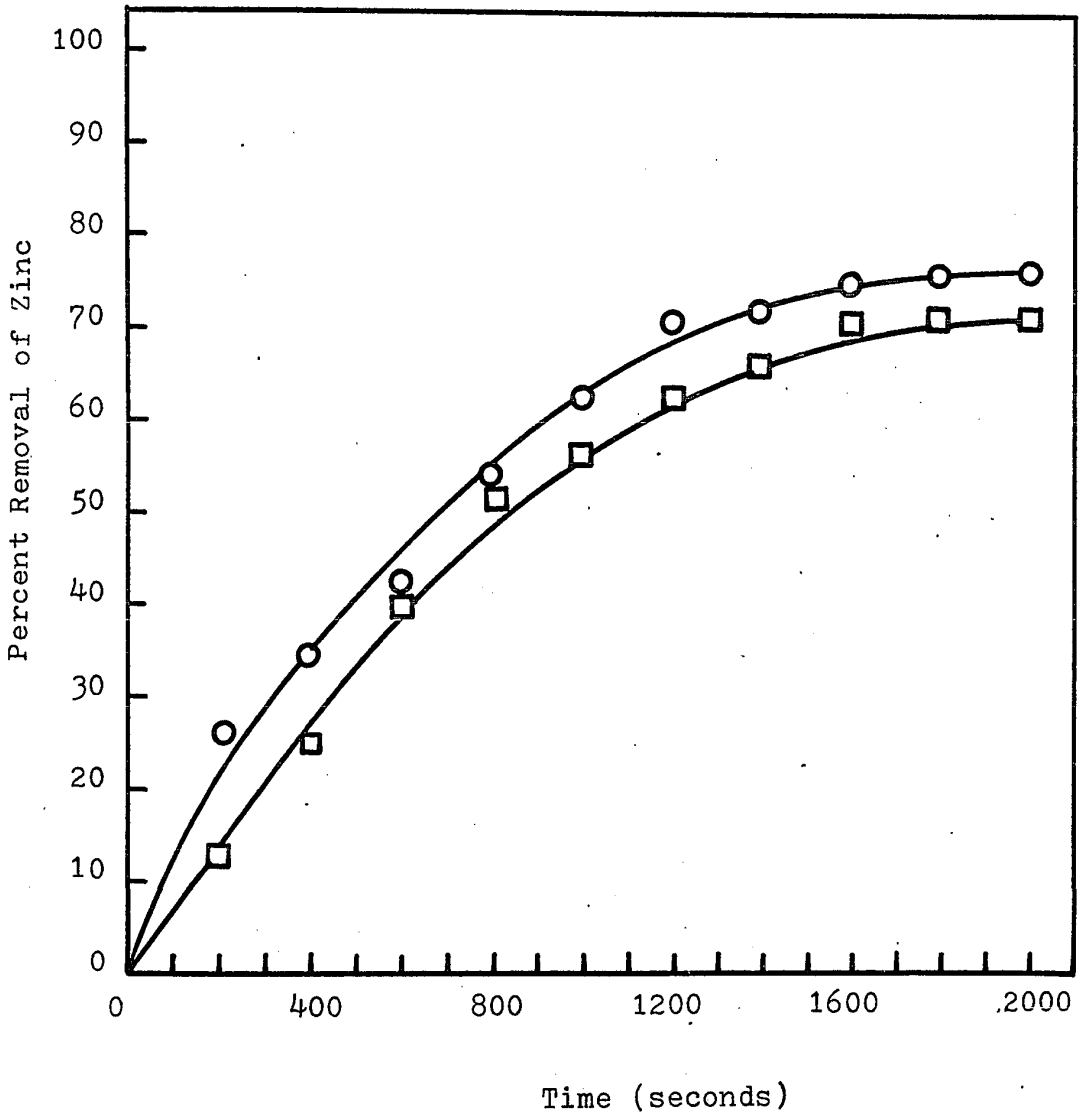
8. Effects of Ethanol on Batch Removal of Zinc

It has been reported that some researchers (13) add ethanol to batch runs as a frother. As a result of this an experiment was performed to investigate what effects, if any, are produced by addition of alcohol to a run. Two runs were performed under identical conditions, with the exception that 1 ml of 95% ethanol was added to one run. The runs are BR-7 and BR-8 and are tabulated in Tables 17 and 18, Appendix E.

A number of observations were made during the two runs. First ethanol showed evidence of surface activity because a very fine and unstable foam was formed on top of the liquid pool after the alcohol alone was injected. This foam collapsed almost instantaneously. Also the bubble size decreased instantly upon injection of the alcohol. The small bubbles formed maintained their size even though the concentration of alcohol in the bulk is negligible. This effect is similar to the observations of Zieminski and Hill (39) on the bubble aeration of water in the presence of some organic compounds.

The two runs are shown in Figure 26. The run with alcohol shows a higher removal throughout the run as compared to the run without ethanol. One can only speculate as to the cause of this phenomena. Perhaps ethanol removes some additional zinc because it is surface

Figure 26- Effect of Ethanol on a Batch Removal of Zinc



○ with Ethanol

□ without Ethanol

pH = 5.0, NaDBS = 0.5 gm/l

active and because of the polar nature of the molecule. Also ethanol could possibly increase foam stability near the end of the run thus enabling more surfactant and more zinc to be removed. Another alternative is that for the same gas rates ethanol produces a higher surface generation rate thus bringing about a higher removal. If this was the case, one would expect the ultimate removals for each run to be the same but they are not the same, one being 71.8% and the other 76.3%. As previously stated these are only speculations, and based on these preliminary findings it is recommended that a more detailed study be undertaken with regard to this effect.

VI. CONCLUSIONS

Based on the studies carried out on the equilibrium stage foam fractionating unit it is concluded that:

1. The rising bubble technique for measuring the surface excess of NaDBS bears no definite relation to the Gibbs' Adsorption Isotherm or to that for monomolecular adsorption. It is to be emphasized that in the development of his equation, Gibbs noted that the system must be in complete thermodynamic equilibrium.
2. The foam fractionation of zinc can be explained by the double layer concept as proposed by Rubin et al. (13). It is the attraction of the surface layer of collector molecules for cations in the diffuse layer. The concentration of cations in this diffuse layer is greater than in the bulk. Removal of the zinc cation is a function of the competition of zinc cations and other cations of the solution for the collector.
3. The optimum conditions for the foam fractionation of zinc in the system zinc/NaDBS/NaCl is:
    (a) pH in the range of 3 to 6
    (b) NaDBS concentration of 0.3 to 0.4 gm/liter
    (c) the efficiency decreases with increasing electrolyte concentration
    (d) the efficiency decreases with increasing bulk zinc concentration.

4. The zinc/NaDBS/NaCl system has been quantitatively described within the limits of the experimental data obtained, by equations (12) and (13) provided that the collector concentration is sufficient to produce a complete monolayer of surfactant, but not so high that it competes with the surface for the zinc cations.
5. The surface viscosity of the surfactant NaDBS was determined to be 0.55×10^{-4} dyne sec/cm. This value incorporates not only any experimental error but also any limitations in Lemlich's foam theory (38).
6. Ion flotation is seen to have a strong dependence on collector concentration. Removal of zinc was observed to reach a different limiting value for each collector ratio. The ultimate removal is some function of the collector ratio but the shape of the removal curves is not significantly affected by the collector concentration.
7. The efficiency of batch removal of zinc is not improved by maintaining a constant collector concentration throughout the batch run.
8. The distribution factor for zinc as a function of bulk zinc concentration increases with lower surfactant concentration.
9. Ethanol was demonstrated to have a definite effect on the batch removal process. Ethanol produced smaller

bubble sizes which maintain their size even though the ethanol appears to increase the removal of zinc from the batch cell but the mechanism by which this occurs is not known.

VII. RECOMMENDATIONS FOR FUTURE WORK

Since the effect of the four fundamental variables (pH, electrolyte concentration, bulk metal concentration, and surfactant concentration) have been firmly established for the zinc and the copper systems (19), it is therefore recommended that a study be made of a continuous removal system involving one or both cations. In particular a study should be made on the various parameters which affect the separation efficiency. These parameters would include, among others, such variables as column height, foam drainage and bulk liquid entrainment, feed point location and surface generation rate.

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APPENDIX A

Table 2

Surface Tension Measurements at 22°C

NaDBS Concentration x 10^4 (g-mol/l)	Surface Tension (dynes/cm)
500.0	30.4
100.0	30.6
50.0	31.4
10.0	44.3
5.0	48.5
1.0	61.4
0.50	66.8
0.10	69.0
0.05	71.7
0.01	72.5

Calculation of Maximum Adsorption:

The maximum value of $d\gamma/d \ln C$ occurs on the linear portion of the surface tension versus concentration curve,

$$\frac{d\gamma}{d \ln C} = \frac{61.5 - 44.5}{\ln (10^{-4}) - \ln (10^{-3})} = -7.383 \text{ dyne/cm.}$$

at $T = 22^{\circ}C = 295.15^{\circ}K$

and $R = 8.3143 \times 10^{7}$ erg/$^{\circ}$K mol

$$= - \frac{1}{2RT} \frac{d\gamma}{d \ln C}$$

$$= - \frac{(-7.383)}{(2)(8.3143 \times 10^{7})(295.15)}$$

$$= 1.50 \times 10^{-10} \text{ g-mol/cm.}^{2}$$

Also $$= \frac{10^{16}}{6.02 \times 10^{23}} \frac{1}{A} \left(\frac{\text{moles}}{\text{cm.}^{2}} \right)$$

or $$A = \frac{10^{16}}{6.02 \times 10^{23}} \frac{1}{1.50 \times 10^{-10}}$$

$$= 110.42 \text{ square angstroms.}$$

This corresponds to the minimum surface area per molecule.

APPENDIX B

Diffusion of DBS Anion

Equations for diffusion starting with a zero surface concentration were derived by Ward and Tordai (41). The rate of diffusion to the surface for no back diffusion or convection is:

$$\frac{d\Gamma}{dt} = (\sqrt{D/\pi})(X/\sqrt{t})$$

Integrating from $\Gamma = 0$ at $t = 0$

to $\Gamma = \Gamma$ at $t = t$

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

where D = bulk phase diffusion coefficient

X = g-mol/cm^3

The diffusivity of the dodecylbenzene sulphonate anion was determined using the Wilke-Chang empirical correlation for liquid diffusivities as given in Treybal (42). Using a molal volume of 406.5 cm^3/g-mol at the normal boiling point the diffusivity was calculated as 4.23×10^{-6} cm^2/sec. For a bulk concentration of 0.5 gm/litre of NaDBS which corresponds to 1.435×10^{-6} g-mol/cm^3

and a surface excess of 8×10^{-10} g-mol/cm^2 from experiment, this corresponds to a time of 0.0577 seconds as the time required to form a complete monolayer of surfactant.

The residence time of bubbles in the column varied between 0.6 and 1.0 seconds. There is sufficient time for a monolayer of surfactant to be formed.

Ward and Tordai also developed a diffusion equation allowing for the back diffusion of surfactant but they found that the back diffusion of surfactant was negligible and that the above equation was adequate.

APPENDIX C

Error Analysis

The surface excess is calculated from the following equation:

$$\Gamma = \frac{V_F\,(Y_F - X_B)}{6G}\,\sqrt[3]{6G/n\,N} \qquad (1)$$

where X_B = bulk concentration

Y_F = foam concentration

G = gas flowrate

N = bubble frequency

V_F = foam flowrate

n = 5

The error equation for gamma becomes:

$$\frac{\Delta\Gamma}{\Gamma} = \frac{\Delta V_F}{V_F} + \frac{\Delta Y_F + \Delta X_B}{Y_F - X_B} + \frac{\Delta G}{G} + \frac{1}{3}\left(\frac{\Delta G}{G} + \frac{\Delta N}{N}\right) \qquad (2)$$

For a typical run

X_B = 9.895 ppm $\pm$ 0.4 ppm

Y_F = 31.006 ppm $\pm$ 0.4 ppm

N = 2432 $\pm$ 40 bubbles per minute

G = 25 ± 0.5 ml of gas in 12.1 ± 0.2 seconds

V_F = 9.1580 gm. in 9.050 ± 0.008 minutes

therefore evaluation each term in (2) and substituting yields :

$$\frac{\Delta\Gamma}{\Gamma} = 0.0928 \text{ or } 9.28\%$$

The corresponding error in the distribution factor $D = \Gamma/X_B$ is:

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

$$= 0.0928 + 0.4/9.895$$

$$= 0.1332 \text{ or } 13.32\%.$$

These are the maximum errors to be expected in the surface excess and distribution factor. The error may be greater or lesser depending upon individual values of Y_F and X_B.

APPENDIX D

Solubility Products of $Zn(OH)_2$

$$K_{sp} = (Zn^{++})(OH^-)^2$$

10 ppm Zn = 1.5295×10^{-4} mol/litre

Table 3

Solubility Products of $Zn(OH)_2$

	K_{sp}	pH of Initial pptn
(1)	4.5×10^{-17}	7.73
(2)	7×10^{-18}	7.33

The solubility product varies from 7×10^{-18} (aged) to 1×10^{-16} (fresh). $Zn(OH)_2$ is more soluble than would be expected from these solubility products because of the equilibrium:

$$Zn(OH)_2\ (s) = Zn(OH)_2\ (aq)$$

Further $Zn(OH)_2$ readily dissolves in excess alkalai bases to give zincate ions, probably $Zn(OH)_4^{=}$.

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APPENDIX E

Table 4

Surface Excess and Distribution Factor of NaDBS vs. Bulk Concentration

Run	Bulk Conc. (ppm)	Surface Excess x 10^{10} (g-mol/cm^2)	Distribution Factor x 10^3 (cm)
1	1113.45	9.22	0.289
2	1125.41	5.87	0.182
3	1046.20	7.98	0.266
4	1040.15	9.14	0.306
5	1721.47	8.12	0.164
6	418.08	6.90	0.576
7	734.05	6.75	0.321
8	148.46	6.40	1.500
9	333.09	5.65	0.591
10	682.92	7.17	0.366
11	1023.03	10.40	0.354
12	1440.88	9.34	0.226
13	2101.67	11.80	0.196
14	1644.95	11.40	0.241
15	1006.87	7.78	0.269
16	1950.05	9.51	0.170
17	3027.96	8.46	0.097
18	4168.75	7.51	0.063
19	116.97	4.65	1.380
20	235.10	6.12	0.907
21	340.11	7.81	0.800
22	458.24	11.00	0.836
23	597.38	11.90	0.695
24	733.88	12.10	0.574
*25	132.96	5.91	1.550
*26	217.84	6.79	1.090
*27	298.36	7.18	0.838
*28	407.18	8.16	0.698
*29	513.82	8.53	0.578
*30	594.34	9.39	0.550

*Runs 25 to 30 contain 0.01 g-mol/l NaCl

Table 5

Surface Excess and Distribution Factor of Zinc vs. Bulk Zinc Concentration

Run	Bulk Conc. (ppm)	Surface Excess x 10^{10} ($g\text{-}mol/cm^2$)	Distribution Factor x 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	4.990	1.250	1.630
36	6.440	1.320	1.340
37	8.850	1.350	0.995
38	15.100	1.380	0.597
39	23.420	1.410	0.393
40	30.530	1.440	0.309
	Feed Composition:	0.5 gm/liter NaDBS pH = 5.0 ± 0.1 no NaCl	
41	0.703	0.160	1.490
42	1.140	0.237	1.350
43	2.290	0.522	1.490
44	4.670	0.848	1.190
45	9.470	1.030	0.710
46	13.300	1.070	0.524
47	22.760	1.110	0.320
48	23.740	1.080	0.298
49	31.460	1.130	0.236
50	34.150	1.140	0.219
51	41.400	1.180	0.186
	Feed Composition:	0.5 gm/l NaDBS pH = 5.0 ± 0.1 0.01 g-mol/liter NaCl	
95	0.104	0.128	8.010
96	0.320	0.353	7.220
97	0.525	0.393	4.860
98	1.108	0.527	3.110
99	5.252	1.160	1.440
100	11.378	1.090	0.630
	Feed Composition:	0.05 gm/liter NaDBS pH = 5.0 ± 0.1 no NaCl	

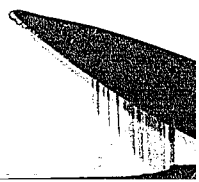

Table 6

Surface Excess and Distribution Factor of Zinc vs. NaCl Concentration

Run	NaCl Conc. (g-mol/l)	Surface Excess x 10^{10} (g-mol/cm^2)	Distribution Factor x 10^3 (cm)
52	0	1.350	0.995
53	0	1.290	0.912
54	0.010	0.979	0.676
55	0.010	1.130	0.814
56	0.010	1.030	0.710
57	0.025	0.664	0.459
58	0.030	0.548	0.374
59	0.050	0.289	0.197
60	0.100	0.189	0.132
61	0.100	0.112	0.077
62	0.200	0.092	0.063
63	0.250	0.025	0.017
64	0.500	0.014	0.009

Feed Composition: 10 ppm Zinc
0.5 gm/liter NaDBS
pH = 5.0 $\pm$ 0.1

Table 7

Surface Excess and Distribution Factor of Zinc vs. pH

Run	pH	Surface Excess x 10^{10} ($g\text{-}mol/cm^2$)	Distribution Factor x 10^3 (cm)
65	1.600	0.369	0.232
66	1.860	0.774	0.481
67	2.000	0.816	0.563
68	2.380	0.959	0.602
69	2.540	1.020	0.636
70	2.460	0.924	0.666
71	3.100	1.110	0.746
72	3.480	1.090	0.692
73	3.850	1.170	0.739
74	4.050	1.090	0.783
75	5.000	1.130	0.814
76	5.150	1.170	0.752
77	6.120	0.995	0.736
78	6.130	1.050	0.769
79	7.050	0.929	0.655
80	7.490	0.635	0.017

Feed Composition: 10 ppm zinc
0.5 gm/liter NaDBS
0.01 g-mol/liter NaCl

Table 8

Surface Excess and Distribution Factor of Zinc vs. NaDBS Concentration

Run	NaDBS Conc. (gm/liter)	Surface Excess x 10^{10} ($g\text{-}mol/cm^2$)	Distribution Factor x 10^3 (cm)
81	0.030	0.560	0.462
82	0.075	0.878	0.724
83	0.100	1.010	0.754
84	0.100	1.060	0.824
85	0.200	1.170	0.856
86	0.250	1.120	0.872
87	0.300	1.160	0.853
88	0.400	1.170	0.856
89	0.500	1.030	0.710
90	0.500	1.130	0.814
91	0.600	1.050	0.783
92	0.700	0.883	0.635
93	0.800	0.785	0.586
94	0.900	0.666	0.479

Feed Composition: 10 ppm zinc
0.01 g-mol/liter NaCl
pH = 5.0 $\pm$ 0.1

Table 9

Experimental and Calculated Data for Each Run

Run	X_B	Y_F	pH	S(cm^2/min)	Foam wt.	G(ml/min)	N(min^{-1})	t(min)
1	1113.45	1723.93	5.08	3201.3	10.824	176.89	1854	6.42
2	1125.41	1570.95	5.01	3231.5	10.979	166.67	2148	7.40
3	1046.20	11339.93	5.00	3045.4	0.750	165.93	1814	9.12
4	1040.15	9966.37	5.08	3394.2	0.764	194.81	1822	6.27
5	1721.47	10697.73	5.00	3830.1	0.767	211.27	2226	6.35
6	418.08	6599.29	5.05	2192.6	1.707	88.76	2366	20.00
7	734.05	8475.38	5.02	2700.8	1.301	110.29	2864	15.85
8	148.46	663.48	4.99	2433.4	14.910	106.84	2232	14.15
9	333.09	964.72	5.05	2458.5	11.548	106.84	2302	15.07
10	682.92	1470.03	5.00	2646.7	8.975	106.84	2872	10.68
11	1023.03	1839.30	4.99	2524.4	11.573	106.84	2492	10.32
12	1440.88	2723.60	5.02	1459.6	6.103	65.29	1290	16.48
13	2101.67	3530.14	5.06	1497.1	7.670	65.29	1392	17.78
14	1644.95	3102.57	5.05	1547.1	7.624	65.29	1536	18.10
15	1006.87	1500.92	5.08	2804.1	13.727	131.58	2252	8.92
16	1950.05	2533.91	5.06	2748.2	13.680	131.58	2120	8.77
17	3027.96	3674.70	5.02	2764.6	12.497	131.58	2158	9.92
18	4168.75	4662.79	5.04	2786.6	15.122	131.58	2210	10.25
19	116.97	300.73	4.88	1963.9	23.668	80.56	2064	13.67
20	235.10	542.25	4.85	1975.3	21.433	80.56	2100	15.63
21	340.11	754.89	4.70	2036.1	22.318	80.56	2300	16.70
22	458.24	878.27	4.95	2070.9	28.374	80.56	2420	15.03
23	597.38	1035.78	4.78	2042.6	27.138	80.56	2322	14.03
24	733.88	1316.67	4.98	2009.2	19.738	80.56	2210	13.80
25	132.96	448.53	4.85	1975.3	29.627	80.56	2100	23.00
26	217.84	714.04	4.65	2011.6	15.032	80.56	2218	15.67

Run	X_B	Y_F	pH	S(cm^2/min)	Foam wt.	G(ml/min)	N(min^{-1})	t(min)
27	298.36	622.63	4.80	2021.3	23.808	80.56	2250	15.27
28	407.18	687.92	4.85	2083.4	30.871	80.56	2464	14.63
29	513.82	764.09	4.90	2032.0	32.325	80.56	2286	13.40
30	594.34	855.50	5.00	2001.3	33.522	80.56	2184	13.37
31	0.354	3.101	4.91	2712.2	13.303	120.00	2450	10.80
32	0.584	5.009	5.03	2764.6	12.859	124.31	2418	10.82
33	0.906	6.983	4.94	2773.0	13.972	124.31	2440	11.94
34	2.194	20.505	5.01	2649.3	9.699	118.34	2348	11.07
35	4.993	32.797	5.02	2673.9	7.868	118.34	2414	10.05
36	6.435	33.291	5.09	2667.3	8.564	118.34	2396	10.02
37	8.850	35.355	5.00	2678.4	9.046	118.34	2426	10.17
38	15.104	46.467	5.00	2677.6	7.718	118.34	2424	10.03
39	23.416	50.028	5.00	2684.9	9.321	118.34	2444	10.05
40	30.529	64.302	5.03	2684.2	7.568	118.34	2442	10.10
41	0.703	3.405	4.96	2766.9	10.351	122.95	2478	9.67
42	1.144	6.532	5.08	2772.2	7.320	124.31	2438	9.20
43	2.289	11.613	5.00	2776.8	12.859	124.31	2418	10.82
44	4.665	22.458	5.07	2557.9	8.570	101.90	2850	10.75
45	9.466	29.394	4.94	2542.8	9.091	101.90	2800	10.60
46	13.296	33.569	4.98	2559.1	9.411	101.90	2854	10.70
47	22.762	46.325	5.08	2531.9	8.407	101.90	2764	10.75
48	23.743	45.331	5.00	2665.8	8.822	118.34	2392	10.11
49	31.456	53.174	5.07	2493.5	9.091	101.90	2640	10.68
50	34.149	60.293	5.07	2672.4	7.715	118.34	2410	10.11
51	41.400	63.350	5.01	2484.6	9.491	101.90	2612	10.90
52	8.850	35.355	5.00	2678.4	9.046	118.34	2426	10.17
53	9.265	30.607	5.01	2536.9	11.402	101.69	2792	11.35
54	9.466	28.799	4.98	2577.5	9.386	101.69	2928	11.00
55	9.079	31.806	5.00	2611.8	8.580	106.76	2764	10.10
56	9.466	29.394	4.94	2542.8	8.570	101.90	2800	10.75
57	9.466	21.265	4.98	2597.8	10.397	101.69	2998	10.88
58	9.584	17.029	5.01	2004.4	12.017	75.83	2476	12.45

Run	X_B	Y_F	pH	S(cm^2/min)	Foam wt.	G(ml/min)	N(min^{-1})	t(min)
59	9.601	15.592	5.10	2582.7	8.909	101.69	2946	10.95
60	9.375	12.158	5.00	1929.8	10.721	75.83	2210	12.50
61	9.466	11.345	5.02	2467.2	9.993	101.69	2568	10.42
62	9.445	10.836	5.08	1942.6	10.642	75.83	2254	12.73
63	9.466	9.942	4.96	2445.8	8.827	101.69	2502	10.70
64	9.265	9.601	5.11	2454.9	6.886	101.69	2530	10.60
65	10.419	17.845	1.60	2576.0	8.824	106.76	2652	10.53
66	10.536	23.069	1.86	1992.4	12.136	75.83	2432	15.08
67	9.472	25.014	2.00	2739.3	9.254	121.95	2444	9.84
68	10.419	25.414	2.38	2573.4	11.273	106.76	2644	10.48
69	10.536	27.866	2.54	1989.7	10.513	75.83	2422	13.67
70	9.066	21.754	2.46	2024.1	13.352	75.83	2550	13.86
71	9.744	31.806	3.10	2575.4	8.826	106.76	2650	10.40
72	10.303	24.152	3.48	2000.6	13.952	75.83	2462	13.55
73	10.381	27.866	3.85	1986.4	12.057	75.83	2410	13.83
74	9.079	30.005	4.05	2581.2	8.838	106.76	2668	10.08
75	9.079	31.806	5.00	2611.8	8.580	106.76	2764	10.10
76	10.149	25.003	5.15	1986.9	13.737	75.83	2412	13.45
77	8.833	20.361	6.12	2013.5	15.112	75.83	2510	13.30
78	8.948	29.772	6.13	2596.6	8.677	106.76	2716	10.12
79	9.278	26.452	7.05	2585.7	9.487	106.76	2682	10.37
80	2.444	12.530	7.49	2733.3	8.677	106.76	2716	10.12
81	7.930	13.961	4.92	2668.0	16.422	120.00	2332	10.13
82	7.930	19.484	5.02	2678.6	15.191	120.00	2360	11.42
83	8.751	23.142	5.05	2731.2	13.905	121.46	2442	11.10
84	8.447	20.361	4.75	1876.6	17.322	75.83	2032	15.80
85	8.948	32.805	4.98	2420.1	8.545	101.35	2422	11.00
86	8.369	20.593	4.75	2002.7	16.469	75.83	2470	13.78
87	8.927	26.924	5.02	2725.0	11.617	121.95	2406	10.08
88	9.278	29.772	5.00	2414.1	9.901	101.35	2422	11.00
89	9.466	29.394	4.94	2542.8	9.091	101.90	2800	10.60
90	9.079	31.806	5.00	2611.7	8.580	106.76	2764	10.10

Run	X_B	Y_F	pH	S(cm^2/min)	Foam wt.	G(ml/min)	N(min^{-1})	t(min)
91	8.751	28.294	5.00	2631.2	10.144	101.35	3136	11.00
92	9.083	27.592	5.08	2853.9	9.665	121.95	2764	9.50
93	8.751	18.257	5.00	2414.1	14.337	101.35	2422	11.00
94	9.083	22.109	4.98	3044.1	9.665	121.95	3354	9.50
95	0.104	2.011	4.97	1952.7	8.688	78.81	2120	10.14
96	0.320	5.043	5.10	1940.4	9.591	78.81	2080	10.12
97	0.525	6.519	5.00	1952.2	8.449	78.81	2118	10.16
98	1.108	7.006	5.00	1953.9	11.560	78.81	2124	10.13
99	5.252	19.923	5.07	1946.6	10.129	78.81	2100	10.09
100	11.378	25.217	5.10	1949.1	10.083	78.81	2108	10.04

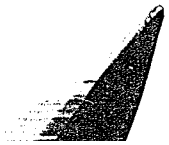

Table 10

Percent Ultimate Removal vs. Collector Ratio

Collector Ratio	% Removal
1	21.23
3	60.18
6	95.40
8	96.08
10	97.89
14	96.44
18	96.68

Feed: 10 ppm Zn
no NaCl
initial pH = 5.0 ± 0.1
gas flowrate = 365 ml/min

Collector Ratio	% Removal
1	13.92
3	51.62
3	46.97
6	68.14
6	70.01
6	72.04
8	82.53
10	87.60
14	88.38
18	92.42

Feed: 10 ppm Zn
0.01 g-mol/liter NaCl
initial pH = 5.0 ± 0.1
gas flowrate = 365 ml/min

Table 11

Run BR-1

Collector Ratio = 3

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
9.175	0.000	0.000
8.912	130.000	2.861
7.349	260.000	19.896
6.671	400.000	27.292
6.103	540.000	33.481
5.592	680.000	39.048
4.969	810.000	45.846
4.561	900.000	50.293
4.439	965.000	51.616

Feed Compositiion: 9.175 ppm zinc
0.01 g-mol/l NaCl
pH = 5.0
gas flowrate = 365 ml/min

Table 12

Run BR-2

Collector Ratio = 6

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
8.404	0.000	0.000
7.442	200.000	11.443
6.103	380.000	27.377
5.383	600.000	35.948
4.561	730.000	45.732
4.158	860.000	50.522
3.642	970.000	56.657
2.867	1150.000	65.883
2.791	1280.000	66.790
2.677	1430.000	68.144
2.117	1560.000	74.804

Feed Composition: 8.404 ppm zinc
0.01 g-mol/l NaCl
pH = 5.0
gas flowrate = 365 ml/min

Table 13

Run BR-3

Collector Ratio = 10

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
8.554	0.000	0.000
7.676	295.000	10.261
6.760	500.000	20.976
6.451	700.000	24.592
6.233	935.000	27.139
4.238	1060.000	50.456
3.175	1300.000	62.889
1.935	1650.000	77.381
1.577	1880.000	81.566
1.162	2080.000	86.420
1.061	2150.000	87.601

Feed Composition: 8.554 ppm zinc

0.01 g-mol/l NaCl

pH = 5.0

gas flowrate = 365 ml/min

Table 14

Run BR-4

Collector Ratio = 3

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
8.656	0.000	0.000
7.915	120.000	8.560
6.984	260.000	19.310
6.320	370.000	26.988
5.175	530.000	40.212
4.846	635.000	44.017
4.270	760.000	50.665
3.642	880.000	57.918
3.447	1000.000	60.181

Feed Composition: 8.656 ppm zinc

pH = 5.0

gas flowrate = 365 ml/min

Table 15

Run BR-5

Collector Ratio = 6

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
9.175	0.000	0.000
6.984	210.000	23.878
5.677	400.000	38.129
4.038	600.000	55.986
2.982	830.000	67.499
1.577	1020.000	82.813
0.994	1180.000	89.167
0.895	1360.000	90.245
0.513	1520.000	94.406
0.422	1600.000	95.404

Feed Composition: 9.175 ppm zinc

pH = 5.0

gas flowrate = 365 ml/min

Table 16

Run BR-6

Collector Ratio = 10

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
8.809	0.000	0.000
6.451	280.000	26.773
5.051	500.000	42.661
3.059	790.000	65.276
1.755	1000.000	80.081
0.895	1260.000	89.840
0.575	1500.000	93.470
0.361	1760.000	95.896
0.215	1920.000	97.565
0.186	2160.000	97.892

Feed Composition: 8.809 ppm zinc

pH = 5.0

gas flowrate = 365 ml/min

Table 17

Run BR-7

Collector Ratio = 6

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
11.447	0.000	0.000
8.394	200.000	26.667
7.515	400.000	34.347
6.559	600.000	42.695
5.270	800.000	53.960
4.297	1000.000	62.457
3.326	1200.000	70.947
3.100	1400.000	72.922
2.777	1600.000	75.737
2.713	1800.000	76.299
2.713	2000.000	76.299

Feed Composition: 11.447 ppm zinc

pH = 5.0

1 ml. 95% ethanol

gas flowrate = 365 ml/min

Table 18

Run BR-8

Collector Ratio = 6

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
10.636	0.000	0.000
9.227	200.000	13.245
7.988	400.000	24.898
6.399	600.000	39.834
5.043	800.000	52.582
4.622	1000.000	56.545
3.973	1200.000	62.644
3.649	1400.000	65.690
3.003	1600.000	71.768
3.003	1800.000	71.768
3.003	2000.000	71.768

Feed Composition: 10.636 ppm zinc

pH = 5.0

gas flowrate = 365 ml/min

Table 19

Run BR-9

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
11.127	0.000	0.000
9.730	200.000	12.555
8.122	400.000	27.008
7.182	600.000	35.449
6.401	800.000	42.472
5.467	1000.000	50.864
5.106	1200.000	54.109
3.726	1400.000	66.513
3.395	1600.000	69.486
2.908	1800.000	73.863
2.431	2000.000	78.151

Feed Composition: 11.127 ppm zinc

pH = 5.0

0.10 gm/l NaDBS

gas flowrate = 365 ml/min

NaDBS injected at a rate of 2.33 ml/min

at a concentration of 1.1910 gm/l

Table 20

Run BR-10

PPM-ZINC	TIME-SEC.	PERCENT-REMOVAL
10.775	0.000	0.000
9.461	200.000	12.190
8.324	400.000	22.747
7.859	600.000	27.059
7.481	800.000	30.564
6.822	1000.000	36.687
6.643	1200.000	38.348
5.436	1400.000	49.550
5.269	1600.000	51.095
5.104	1800.000	52.628
4.552	2000.000	57.755

Feed Composition: 10.775 ppm zinc

pH = 5.0

0.05 gm/l NaDBS

gas flowrate = 365 ml/min

NaDBS injected at a rate of 2.33 ml/min

at a concentration of 0.5955 gm/l

Appendix F

COMPUTER PROGRAMS

Nomenclature for Computer Programs 1 and 2

ABSORB	the absorbance of a standard
STDCDN	the concentration of the standard of ABSORB
NDATA	an integer counter for the number of points on the calibration curve
BESFIT	subroutine for a linear line of best fit using the least squares method
KURVE	subroutine for a fourth degree polynomial line of best fit using the least squares method
YINT	the y intercept of the linear line of best fit
BUBRAT	bubble emission frequency
GASRAT	gas flowrate under laboratory conditions
XSUBB	bulk phase concentration
FEEDXB	feed concentration
YABS	absorbance of a sample
TIME	time of a run in minutes
FOAMWT	weight of foam collected in time TIME
PH	pH of feed solution
USUBF	volumetric flowrate of foam on a gas free basis
BUBDIA	bubble diameter
GAMMAC	surface excess
SURFRT	surface generation rate
D	distribution factor

COMPUTER PROGRAM#1

The following computer program was used to calculate the surface excess and distribution factor for the surfactant, NaDBS.

```
$JOB $W681180  R. J. ST.ELOI                                    WATFIV JOB CARD
C     THE FIRST PART OF THE PROGRAM CALCULATES THE BEST STRAIGHT LINE      00000010
C     BETWEEN ABSORBANCE AND STANDARDS CONCENTRATION FOR THE SYSTEM        00000020
C     ZINC AND SODIUM DODECYLBENZENESULFONATE                              00000030
C                                                                          00000040
C                                                                          00000050
      REAL NEWXB                                                           00000060
      INTEGER RUN,NDATA                                                    00000070
      DIMENSION ABSORB(10),STDCON(10)                                      00000080
    3 READ (1,12) NDATA                                                    00000090
      DO 7 I=1,NDATA                                                       00000100
    7 READ(1,11) STDCON (I),ABSORB(I)                                      00000110
    9 CALL BESFIT (STDCON,ABSORB,NDATA,1,YINT,SLOPE)                       00000120
C                                                                          00000130
C     THIS NEXT PART OF THE PROGRAM CALCULATES THE SURFACE-EXCESS          00000140
C     AND THE DISTRIBUTION FACTOR.                                         00000150
      WRITE (3,30)                                                         00000160
      WRITE (3,31)                                                         00000170
      WRITE (3,32)                                                         00000180
    1 READ(1,10) RUN,BUBRAT,GASRAT,FEEDXB,YABS,TIME,FOAMWT,PH              00000190
      IF (RUN) 2,2,4                                                       00000200
    4 XSUBB=1000.*(FEEDXB-YINT)/SLOPE                                      00000210
      G=GASRAT                                                             00000220
      VSUBF=FOAMWT/TIME                                                    00000230
      YSUBF=1000. *(YABS-YINT)/SLOPE                                       00000240
      BUBDIA=(G*0.38197/BUBRAT)**0.33333                                   00000250
      SURFRT=15.70795*BUBRAT*BUBDIA*BUBDIA                                 00000260
    5 GAMMAC=VSUBF*(YSUBF-XSUBB)*2.8696E-9/SURFRT                          00000270
    6 D=GAMMAC/(XSUBB*2.8696E-9)                                           00000280
      WRITE (3,20) RUN,XSUBB,YSUBF,BUBDIA,SURFRT,GAMMAC,D,PH               00000290
      GO TO 1                                                              00000300
   10 FORMAT(I10,7F10.6)                                                   00000310
   11 FORMAT (2F10.4)                                                      00000320
   12 FORMAT (I3)                                                          00000330
   20 FORMAT (1X,I3,8X,F9.3,11X,F9.3,9X,F8.5,7X,F7.2,6X,E10.3,7X,E10.3,    00000340
     15X,F5.2,/)                                                           00000350
   30 FORMAT (1X,/,'                    BULK              FOAMATE          BUBBLE  00000360
     1    SURFACE      SURFACE          DISTRIBUTION ')                   00000370
   31 FORMAT (1X,' RUN    CONCENTRATION     CONCENTRATION     DIAMETER     00000380
     1AREA RATE    EXCESS                FACTOR              PH',/)       00000390
   32 FORMAT (1X,/,'                    (PPM)             (PPM)              (CM)  00000400
     1  (SQ.CM/MIN)  (G.MOL/SQ.CM)          (CM.)  ',///)                 00000410
    2 RETURN                                                               00000420
      END                                                                  00000430
      SUBROUTINE BESFIT (X,Y,NDATA,NSIX,YINT,SLOPE)                        00000440
C     SUBROUTINE FOR A LINEAR LINE OF BEST FIT Y=A*X+B USING THE LEAST
```

```
      C     SQUARE METHOD.  LIMIT OF 100 DATA POINTS.                          00000450
   33         DIMENSION X(10),Y(10)                                            00000460
   34         A=0.0                                                            00000470
   35         B=0.0                                                            00000480
   36         C=0.0                                                            00000490
   37         D=0.0                                                            00000500
   38         DO 100 I=1,NDATA                                                 00000510
   39         A=A+X(I)                                                         00000520
   40         B=B+Y(I)                                                         00000530
   41         C=C+X(I)*X(I)                                                    00000540
   42     100 D=D+X(I)*Y(I)                                                    00000550
   43         IF (NSIX) 102,102,103                                            00000560
      C       IF NSIX=0 ORIGIN IS INCLUDED                                     00000570
      C       IF NSIX=1 ORIGIN IS NOT INCLUDED                                 00000580
   44     102 E=NDATA+1                                                        00000590
   45         GO TO 101                                                        00000600
   46     103 E=NDATA                                                          00000610
   47     101 AA=(E*D-A*B)                                                     00000620
   48         BB=(C*B-A*D)                                                     00000630
   49         CC=(E*C-A*A)                                                     00000640
   50         SLOPE=AA/CC                                                      00000650
   51         YINT=BB/CC                                                       00000660
   52         WRITE (3,104) SLOPE,YINT                                         00000670
   53     104 FORMAT (1H1,/,'  THE LINE OF BEST FIT IS Y=',F14.7,'*X +',F14.7,/ 00000680
              1///)                                                           00000690
   54         RETURN                                                           00000700
   55         END                                                              00000710

        $ENTRY
***ERROR***  IMPROPER CHARACTER SEQUENCE OR INVALID CHARACTER IN INPUT DATA

FIRST 80 CHARACTERS OF INPUT RECORD ARE=>'//

       PROGRAM WAS EXECUTING LINE      4 IN ROUTINE M/PROG WHEN TERMINATION OCCURRED

CORE USAGE        OBJECT CODE=     2880 BYTES,ARRAY AREA=       80 BYTES,TOTAL AREA AVAILABLE=    34912  BYTES

COMPILE TIME=      1.49 SEC,EXECUTION TIME=      0.03 SEC,  WATFIV - VERSION 1 LEVEL 2 AUGUST  1970      DATE=  7
```

COMPUTER PROGRAM #2

The following computer program was used to calculate the surface excess and the distribution factor of zinc.

```
$JOB  SW6811B0  ST.ELDI
C     THE FIRST PART OF THIS PROGRAM CALCULATES THE FOURTH DEGREE
C     POLYNOMIAL WHICH WILL FIT THE CALIBRATION CURVE DATA
C     LEAST SQUARES METHOD
C     X= SPECTROPHOTOMETER READING
C     Y= ZINC CONCENTRATION IN PPM
C     M= NUMBER OF DATA POINTS
C     N= DEGREE OF POLYNOMIAL
C                                                                    00000040
C
      REAL NEWXB                                                     00000050
      INTEGER RUN,NDATA                                              00000060
      DIMENSION X(30),Y(30),B(30),H(10)
    3 READ (1,12) NDATA                                              00000080
      M=NDATA
      N=4
      DO 7 I=1,NDATA                                                 00000090
    7 READ (1,11)X(I),Y(I)
    9 CALL KURVE(X,Y,N,M,H)
C                                                                    00000120
C     THIS NEXT PART OF THE PROGRAM CALCULATES THE SURFACE-EXCESS     00000130
C     AND THE DISTRIBUTION FACTOR.                                   00000140
C
      WRITE (3,30)                                                   00000150
      WRITE (3,31)                                                   00000160
      WRITE (3,32)                                                   00000170
    1 READ(1,10) RUN,BUBRAT,GASRAT,FEEDXB,YABS,TIME,FOAMWT,PH        00000180
      IF (RUN) 2,2,4                                                 00000190
    4 XSUBB= 10*(H(1)+H(2)*FEEDXB+H(3)*FEEDXB**2+H(4)*FEEDXB**3+H(5)*FEE
     1DXB**4)
      G=GASRAT                                                       00000210
      VSUBF=FOAMWT/TIME                                              00000220
      YSUBF= 10*(H(1)+H(2)*YABS+H(3)*YABS**2+H(4)*YABS**3+H(5)*YABS**4)
      BUBDIA=(G*0.38197/BUBRAT)**0.33333                             00000240
      SURFRT=15.70795*BUBRAT*BUBDIA*BUBDIA                           00000250
    5 GAMMAC=VSUBF*(YSUBF-XSUBB)*1.529519E-8/SURFRT                  00000260
    6 D=GAMMAC/(XSUBB*1.529519E-8)                                   00000270
      WRITE (3,20) RUN,XSUBB,YSUBF,BUBDIA,SURFRT,GAMMAC,D,PH         00000280
      GO TO 1                                                        00000290
   10 FORMAT(I10,7F10.6)                                             00000300
   11 FORMAT (2F10.4)                                                00000310
   12 FORMAT (I3)                                                    00000320
   20 FORMAT (1X,I3,8X,F6.3,11X,F6.3,9X,F7.5,7X,F7.2,6X,E10.3,7X,E10.3,
     15X,F5.2,/)                                                     00000340
   30 FORMAT (1X,/,'                  BULK            FOAMATE          BUBBLE
     1    SURFACE     SURFACE          DISTRIBUTION ')               00000360
```

```
      31 FORMAT (1X,' RUN    CONCENTRATION    CONCENTRATION    DIAMETER    00000370
     1AREA RATE    EXCESS              FACTOR           PH',/)           00000380
   32 FORMAT (1X,/,'                (PPM)            (PPM)          (CM)  00000390
     1  (SQ.CM/MIN)   (G.MOL/SQ.CM)        (CM.)   ',///)               00000400
    2 CONTINUE
C
C
C     THE NEXT PART OF THE PROGRAM CALCULATES  Y=DATA FOR THE GIVEN
C     X=DATA AND PRINTS OUT THE VALUES OF  X,Y CALCULATED AND
C     Y EXPERIMENTAL
C
      WRITE (3,60)
   60 FORMAT(//,5X,'READING',8X,'YCALC',10X,'YEXPT')
      DO 40 I=1,M
      B(I)=H(1)+H(2)*X(I)+H(3)*X(I)**2+H(4)*X(I)**3+H(5)*X(I)**4
      WRITE (3,50) X(I),B(I),Y(I)
   50 FORMAT(//,5X,F10.6,5X,F10.6,5X,F10.6)
   40 CONTINUE
      RETURN
      END                                                               00000420

      SUBROUTINE KURVE (X,Y,N,M,HH)                                     00000010
C     LEAST SQUARE METHOD                                               00000020
C     CASE OF Y=SIGMA(A(I)*X**I),(I=0,N)                                00000030
C     N=DEGREE OF THE FUNCTION FOR CURVE FITTING                        00000040
C     M=NUMBER OF DATA                                                  00000050
      DIMENSION X(30),Y(30),A(30),B(30),S(30),T(30),H(10,11),HH(10)     00000060
      N1=2*N+1                                                          00000070
      DO 20 I=1,M                                                       00000080
      A(I)=X(I)                                                         00000090
   20 B(I)=Y(I)                                                         00000100
      S(1)=M                                                            00000110
      DO 10 K=2,N1                                                      00000120
      S(K)=0.                                                           00000130
      DO 10 I=1,M                                                       00000140
      S(K)=S(K)+A(I)                                                    00000150
   10 A(I)=X(I)*A(I)                                                    00000160
      N2=N+1                                                            00000170
      DO 30 K=1,N2                                                      00000180
      T(K)=0.0                                                          00000190
      DO 30 I=1,M                                                       00000200
      T(K)=T(K)+B(I)                                                    00000210
   30 B(I)=X(I)*B(I)                                                    00000220
      N3=N+2                                                            00000230
      DO 50 I=1,N2                                                      00000240
      DO 40 J=1,N2                                                      00000250
```

```
63            K=I+J-1                                                    00000260
64         40 H(I,J)=S(K)                                                00000270
65         50 H(I,N3)=T(I)                                               00000280
66            DO 60 K=1,N2                                               00000290
67            K1=K+1                                                     00000300
68            DO 60 J=K1,N3                                              00000310
69            H(K,J)=H(K,J)/H(K,K)                                       00000320
70            DO 60 I=1,N2                                               00000330
71            IF(I-K) 17,60,17                                           00000340
72         17 H(I,J)=H(I,J)-H(I,K)*H(K,J)                                00000350
73         60 CONTINUE                                                   00000360
74            DO 70 I=1,N2                                               00000370
75         70 HH(I)=H(I,N3)                                              00000380
76            DO 91 K=1,M                                                00000390
77            S(K)=H(1,N3)                                               00000400
78            DO 90 I=2,N2                                               00000410
79         90 S(K)=S(K)+H(I,N3)*X(K)**(I-1)                              00000420
80         91 T(K)=Y(K)-S(K)                                             00000430
81            DEV=0.0                                                    00000440
82            DO 92 I=1,M                                                00000450
83         92 DEV=DEV+ABS(T(I))                                          00000460
84            W=M                                                        00000470
85            Z=DEV/W                                                    00000480
86            WRITE(3,100) Z,(HH(I),I=1,N2)                              00000490
87        100 FORMAT(1H1,5X,E12.5,7(5X,E12.5))                           00000500
88            RETURN                                                     00000510
89            END                                                        00000520

      $ENTRY
***ERROR***  IMPROPER CHARACTER SEQUENCE OR INVALID CHARACTER IN INPUT DATA

FIRST 80 CHARACTERS OF INPUT RECORD ARE=>!//

      PROGRAM WAS EXECUTING LINE      4 IN ROUTINE M/PROG WHEN TERMINATION OCCURRED

CORE USAGE       OBJECT CODE=     5192 BYTES,ARRAY AREA=     1320 BYTES,TOTAL AREA AVAILABLE=    34912  BYTES

COMPILE TIME=      2.57 SEC,EXECUTION TIME=      0.03 SEC,  WATFIV - VERSION 1 LEVEL 2 AUGUST  1970      DATE=  7
```

COMPUTER PROGRAM #3

The following computer programs were used to simulate the batch fractionation of a dilute aqueous zinc solution. Two complete programs with print outs are included; one with electrolyte and one without electrolyte, both for collector ratios of six.

```
$JOB $W681180  R. J. ST.ELOI                    WATFIV JOB CARD
C
C                    FOAM SEPARATION OF ZINC
C
C     THIS IS A PROGRAM TO SIMULATE THE REMOVAL OF ZINC++ FROM DILUTE
C     AQUEOUS SOLUTION . THE SURFACE EXCESS OF ZINC IS CALCULATED AS A
C     FUNCTION OF (1) BULK ZINC CONCENTRATION (2) HYDRONIUM ION
C      CONCENTRATION  (3) SODIUM CHLORIDE CONCENTRATION AND (4) SODIUM
C     DODECYLBENZENESULPHONATE CONCENTRATION
C     THE SURFACE EXCESS OF COLLECTOR IS ALSO CALCULATED AS A FUNCTION
C     BULK COLLECTOR CONCENTRATION,
C     THIS PROGRAM ALSO TAKES INTO ACCOUNT THE OVERFLOW OF FOAM
C
C
C
C     .........COLLECTOR RATIO = 6
C
C
      DIMENSION D(100,1),NPNTS(1),PERCNT(100,1)
      DIMENSION ZNXS(40),ZNDF(40),DBSXS(40),DBSDF(40),ZINC(40),Y(40)
      REAL K1,K2,K3,K4,K5,K6,K7,K8,NACL,PH
      S=  15950.
      WRITE(3,99)S
   99 FORMAT('1',T44,'SURFACE GENERATION RATE=',F10.0,'SQ.CM./MIN.')
C
C  THE FOLLOWING ARE THE CONSTANTS USED TO EVALUATE THE SURFACE
C  EXCESS OF ZINC AND NADBS
C
      K1= 115. E-4
      K2= 79.5 E 6
      K3= 11.2
      K4= 24.4
      K5= 137.
      K6= 127.
      K7=  73.8 E-10
      K8= 6.52
C
C
C     YO = INITIAL NADBS CONC. IN GM./L.
C
      YO= 348.475*.9177  E-03
C
C     PH= INITIAL HYDRONIUM ION CONC. IN G-MOL/L
C
      PH=.00001
C
```

```
      C     NACL= INITIAL ELECTROLYTE CONC. IN G-MOL/L
      C
   17       NACL = 0.0
      C
      C     XO= INITIAL ZINC CONC. IN G-MOL/CC.
      C
   18       XO=0.15295 E-06
      C
   19       Q=0.0
   20       Y(1)=YO
   21       SURFAC=0.0
   22       R=0.0
   23       N=39.
   24       X=XO
   25       ALPHA=-(K3*NACL+K4*PH)
   26       CONST=S*(10**ALPHA)
   27       WRITE(3,1)
   28     1 FORMAT(//,T10,'X=ZINC CONC.',T27,'AMT REMOVED',T44,'Y=NADBS CONC.'
            1,T61,'TIME',T78,'PERCENT',T95,'LIQUID',/,T10,'G-MOL/CC.',T27,'G-MO
            1LS',T44,'GRAM/L',T61,'SECONDS',T78,'REMOVED',T95,'OVERFLOW',/,T95,
            1'CC.')
      C
      C     THIS DO LOOP CALCULATES THE REMOVAL OF ZINC AND NADBS AS A
      C     FUNCTION OF TIME
      C
   29       DO 2 I=1,N
   30       A=(CONST*K1*X)
   31       B=1.0+(K2*X)
   32       C=(K5*Y(I))/(1.+K6*Y(I))
   33       M=(I-1)*60.
   34       D(I,1)=FLOAT(M)
   35       PERCNT(I,1)=100*R/(XO*400)
   36       WRITE(3,3)X,R,Y(I),D(I,1),PERCNT(I,1),Q
   37     3 FORMAT(//,T10,E12.5,T27,E12.5,T44,E12.5,T61,E12.5,T78,E12.5,T95,E1
            12.5)
      C
      C
      C     THIS PART OF THE PROGRAM CALCULATES THE SURFACE EXCESS AND THE
      C     DISTRIBUTION FACTOR FOR ZINC AND THE COLLECTOR AS A FUNCTION OF
      C     TIME
      C
      C
      C     ZNXS= SURFACE EXCESS OF ZINC
   38       ZNXS(I)=((K1*X)/(1.+K2*X))*(10.**ALPHA)*C
      C     ZNDF= DISTRIBUTION FACTOR FOR ZINC
   39       ZNDF(I)=ZNXS(I)/X
```

```
      C
   40         ZINC(I)=X*65.38 E 06
      C
      C       DBSXS= SURFACE EXCESS OF NADBS
   41         DBSXS(I)=(K7*Y(I))/(1.+K8*Y(I))
      C       DBSDF= DISTRIBUTION FACTOR FOR NADBS
   42         DBSDF(I)=(DBSXS(I)/Y(I))*348.475*1000.
      C
      C
      C       THIS NEXT CARD ACCOUNTS FOR THE LIQUID OVERFLOW UNDER THE
      C       GIVEN EXPERIMENTAL CONDITIONS
      C
   43         Q=Q+4.58
      C
   44         R=R+ (A/B)*C+(4.58*X)
   45         SURFAC=S*((K7*Y(I))/(1.+K8*Y(I)))+SURFAC+((4.58/1000.)*(Y(I)/348.4
             175))
   46         Y(I+1)=((.4*Y0)-(SURFAC*348.475))/(.4-(Q/1000.))
   47       2 X=((400.*X0)       -R)/(400.-Q)
   48       6 NPNTS(1)=I-1
      C
   49         WRITE(3,33)
   50        33 FORMAT(//,T10,'ZINC CONC.',T27,'ZN SURFACE',T44,'ZINC',T61,'NADBS'
             1,T78,'NADBS',T95,'NADBS',/,T10,'PPM.',T27,'EXCESS',T44,'DISTRIBUTI
             10N',T61,'CONC.',T78,'SURFACE',T95,'DISTRIBUTION',/,T27,'G-MOL/SQ.C
             1M.',T44,'FACTOR',T61,'GM/L',T78,'EXCESS',T95,'FACTOR',/,T44,'CM.',
             1T78,'G-MOL/SQ.CM.',T95,'CM.')
   51         WRITE(3,44)(ZINC(I),ZNXS(I),ZNDF(I),Y(I),DBSXS(I),DBSDF(I),I=1,40)
   52        44 FORMAT(//,T10,E12.5,T27,E12.5,T44,E12.5,T61,E12.5,T78,E12.5,T95,E1
             12.5)
      C
   53         RETURN
   54         END

      $ENTRY
```

SURFACE GENERATION RATE= 15950.SQ.CM./MIN.

X=ZINC CONC. G-MOL/CC.	AMT REMOVED G-MOLS	Y=NADBS CONC. GRAM/L	TIME SECONDS	PERCENT REMOVED	LIQUID OVERFLOW CC.
0.15295E-06	0.00000E 00	0.31980E 00	0.00000E 00	0.00000E 00	0.00000E 00
0.14728E-06	0.29438E-05	0.30904E 00	0.60000E 02	0.48116E 01	0.45800E 01
0.14156E-06	0.58531E-05	0.29828E 00	0.12000E 03	0.95670E 01	0.91600E 01
0.13580E-06	0.87272E-05	0.28753E 00	0.18000E 03	0.14265E 02	0.13740E 02
0.12999E-06	0.11565E-04	0.27678E 00	0.24000E 03	0.18903E 02	0.18320E 02
0.12414E-06	0.14366E-04	0.26604E 00	0.30000E 03	0.23481E 02	0.22900E 02
0.11825E-06	0.17128E-04	0.25533E 00	0.36000E 03	0.27996E 02	0.27480E 02
0.11233E-06	0.19851E-04	0.24465E 00	0.42000E 03	0.32446E 02	0.32060E 02
0.10636E-06	0.22532E-04	0.23401E 00	0.48000E 03	0.36830E 02	0.36640E 02
0.10036E-06	0.25172E-04	0.22341E 00	0.54000E 03	0.41143E 02	0.41220E 02
0.94335E-07	0.27766E-04	0.21288E 00	0.60000E 03	0.45385E 02	0.45800E 02
0.88282E-07	0.30315E-04	0.20242E 00	0.66000E 03	0.49550E 02	0.50380E 02
0.82208E-07	0.32815E-04	0.19205E 00	0.72000E 03	0.53637E 02	0.54960E 02

0.76121E-07	0.35264E-04	0.18178E 00	0.78000E 03	0.57640E 02	0.59540E 02
0.70029E-07	0.37659E-04	0.17162E 00	0.84000E 03	0.61554E 02	0.64120E 02
0.63943E-07	0.39996E-04	0.16159E 00	0.90000E 03	0.65374E 02	0.68700E 02
0.57877E-07	0.42271E-04	0.15171E 00	0.96000E 03	0.69092E 02	0.73280E 02
0.51847E-07	0.44478E-04	0.14200E 00	0.10200E 04	0.72700E 02	0.77860E 02
0.45874E-07	0.46612E-04	0.13247E 00	0.10800E 04	0.76189E 02	0.82440E 02
0.39986E-07	0.48665E-04	0.12316E 00	0.11400E 04	0.79544E 02	0.87020E 02
0.34219E-07	0.50627E-04	0.11407E 00	0.12000E 04	0.82750E 02	0.91600E 02
0.28619E-07	0.52485E-04	0.10524E 00	0.12600E 04	0.85788E 02	0.96180E 02
0.23247E-07	0.54224E-04	0.96686E-01	0.13200E 04	0.88630E 02	0.10076E 03
0.18181E-07	0.55823E-04	0.88431E-01	0.13800E 04	0.91243E 02	0.10534E 03
0.13527E-07	0.57256E-04	0.80499E-01	0.14400E 04	0.93586E 02	0.10992E 03
0.94148E-08	0.58492E-04	0.72915E-01	0.15000E 04	0.95606E 02	0.11450E 03
0.59938E-08	0.59496E-04	0.65699E-01	0.15600E 04	0.97248E 02	0.11908E 03
0.33997E-08	0.60241E-04	0.58872E-01	0.16200E 04	0.98464E 02	0.12366E 03

0.16819E-08	0.60723E-04	0.52451E-01	0.16800E 04	0.99253E 02	0.12824E 03
0.72721E-09	0.60986E-04	0.46451E-01	0.17400E 04	0.99682E 02	0.13282E 03
0.28461E-09	0.61105E-04	0.40882E-01	0.18000E 04	0.99878E 02	0.13740E 03
0.10580E-09	0.61153E-04	0.35751E-01	0.18600E 04	0.99955E 02	0.14198E 03
0.38757E-10	0.61170E-04	0.31059E-01	0.19200E 04	0.99984E 02	0.14656E 03
0.14326E-10	0.61176E-04	0.26802E-01	0.19800E 04	0.99994E 02	0.15114E 03
0.54209E-11	0.61179E-04	0.22971E-01	0.20400E 04	0.99998E 02	0.15572E 03
0.21855E-11	0.61179E-04	0.19553E-01	0.21000E 04	0.99999E 02	0.16030E 03
0.92837E-12	0.61180E-04	0.16527E-01	0.21600E 04	0.10000E 03	0.16488E 03
0.44185E-12	0.61180E-04	0.13873E-01	0.22200E 04	0.10000E 03	0.16946E 03
0.25760E-12	0.61180E-04	0.11564E-01	0.22800E 04	0.10000E 03	0.17404E 03

ZINC CONC. PPM.	ZN SURFACE EXCESS G-MOL/SQ.CM.	ZINC DISTRIBUTION FACTOR CM.	NADBS CONC. GM/L	NADBS SURFACE EXCESS G-MOL/SQ.CM.	NADBS DISTRIBUTION FACTOR CM.
0.99999E 01	0.14064E-09	0.91953E-03	0.31980E 00	0.76500E-09	0.83361E-03
0.96290E 01	0.14011E-09	0.95137E-03	0.30904E 00	0.75647E-09	0.85300E-03
0.92551E 01	0.13955E-09	0.98578E-03	0.29828E 00	0.74753E-09	0.87331E-03

0.88784E 01	0.13893E-09	0.10231E-02	0.28753E 00	0.73815E-09	0.89462E-03
0.84988E 01	0.13826E-09	0.10636E-02	0.27678E 00	0.72831E-09	0.91698E-03
0.81165E 01	0.13754E-09	0.11079E-02	0.26604E 00	0.71798E-09	0.94045E-03
0.77314E 01	0.13675E-09	0.11564E-02	0.25533E 00	0.70713E-09	0.96509E-03
0.73439E 01	0.13588E-09	0.12097E-02	0.24465E 00	0.69573E-09	0.99100E-03
0.69539E 01	0.13492E-09	0.12685E-02	0.23401E 00	0.68375E-09	0.10182E-02
0.65618E 01	0.13387E-09	0.13338E-02	0.22341E 00	0.67115E-09	0.10468E-02
0.61676E 01	0.13270E-09	0.14067E-02	0.21288E 00	0.65790E-09	0.10769E-02
0.57719E 01	0.13140E-09	0.14884E-02	0.20242E 00	0.64397E-09	0.11086E-02
0.53747E 01	0.12993E-09	0.15805E-02	0.19205E 00	0.62932E-09	0.11419E-02
0.49768E 01	0.12828E-09	0.16853E-02	0.18178E 00	0.61391E-09	0.11769E-02
0.45785E 01	0.12641E-09	0.18051E-02	0.17162E 00	0.59772E-09	0.12137E-02
0.41806E 01	0.12427E-09	0.19434E-02	0.16159E 00	0.58071E-09	0.12523E-02
0.37840E 01	0.12179E-09	0.21043E-02	0.15171E 00	0.56286E-09	0.12929E-02
0.33897E 01	0.11891E-09	0.22936E-02	0.14200E 00	0.54415E-09	0.13354E-02

0.29992E 01	0.11553E-09	0.25184E-02	0.13247E 00	0.52457E-09	0.13799E-02
0.26143E 01	0.11151E-09	0.27886E-02	0.12316E 00	0.50411E-09	0.14264E-02
0.22373E 01	0.10667E-09	0.31174E-02	0.11407E 00	0.48279E-09	0.14748E-02
0.18711E 01	0.10080E-09	0.35220E-02	0.10524E 00	0.46062E-09	0.15252E-02
0.15199E 01	0.93578E-10	0.40254E-02	0.96686E-01	0.43765E-09	0.15774E-02
0.11887E 01	0.84645E-10	0.46556E-02	0.88431E-01	0.41395E-09	0.16312E-02
0.88441E 00	0.73611E-10	0.54417E-02	0.80499E-01	0.38960E-09	0.16865E-02
0.61554E 00	0.60254E-10	0.63999E-02	0.72915E-01	0.36472E-09	0.17431E-02
0.39187E 00	0.44944E-10	0.74985E-02	0.65699E-01	0.33945E-09	0.18005E-02
0.22227E 00	0.29268E-10	0.86091E-02	0.58872E-01	0.31396E-09	0.18584E-02
0.10996E 00	0.15993E-10	0.95088E-02	0.52451E-01	0.28844E-09	0.19164E-02
0.47545E-01	0.72882E-11	0.10022E-01	0.46451E-01	0.26312E-09	0.19739E-02
0.18608E-01	0.28934E-11	0.10166E-01	0.40882E-01	0.23821E-09	0.20305E-02
0.69174E-02	0.10661E-11	0.10076E-01	0.35751E-01	0.21397E-09	0.20856E-02
0.25339E-02	0.38217E-12	0.98606E-02	0.31059E-01	0.19061E-09	0.21387E-02

0.93665E-03	0.13713E-12	0.95722E-02	0.26802E-01	0.16837E-09	0.21892E-02
0.35442E-03	0.50032E-13	0.92295E-02	0.22971E-01	0.14744E-09	0.22367E-02
0.14289E-03	0.19314E-13	0.88375E-02	0.19553E-01	0.12798E-09	0.22810E-02
0.60697E-04	0.77956E-14	0.83971E-02	0.16527E-01	0.11011E-09	0.23216E-02
0.28888E-04	0.34946E-14	0.79092E-02	0.13873E-01	0.93893E-10	0.23584E-02
0.16842E-04	0.19001E-14	0.73759E-02	0.11564E-01	0.79359E-10	0.23914E-02
UUUUUUUUUUUU	UUUUUUUUUUUU	UUUUUUUUUUUU	0.95720E-02	UUUUUUUUUUUU	UUUUUUUUUUUU

CORE USAGE OBJECT CODE= 3368 BYTES,ARRAY AREA= 1764 BYTES,TOTAL AREA AVAILABLE= 34912 BYTES

COMPILE TIME= 2.36 SEC,EXECUTION TIME= 2.95 SEC, WATFIV - VERSION 1 LEVEL 2 AUGUST 1970 DATE=

```
$JOB $W681180  R. J. ST.ELOI                                  WATFIV JOB CARD
C
C                    FOAM SEPARATION OF ZINC
C
C      THIS IS A PROGRAM TO SIMULATE THE REMOVAL OF ZINC++ FROM DILUTE
C      AQUEOUS SOLUTION . THE SURFACE EXCESS OF ZINC IS CALCULATED AS A
C      FUNCTION OF (1) BULK ZINC CONCENTRATION (2) HYDRONIUM ION
C       CONCENTRATION  (3) SODIUM CHLORIDE CONCENTRATION AND (4) SODIUM
C      DODECYLBENZENESULPHONATE CONCENTRATION
C      THE SURFACE EXCESS OF COLLECTOR IS ALSO CALCULATED AS A FUNCTION
C      BULK COLLECTOR CONCENTRATION.
C      THIS PROGRAM ALSO TAKES INTO ACCOUNT THE OVERFLOW OF FOAM
C
C
C
C      ..........COLLECTOR RATIO = 6
C
C
C
      1        DIMENSION D(100,1),NPNTS(1),PERCNT(100,1)
      2        DIMENSION ZNXS(40),ZNDF(40),DBSXS(40),DBSDF(40),ZINC(40),Y(40)
      3        REAL K1,K2,K3,K4,K5,K6,K7,K8,NACL,PH
      4        S=  15950.
      5        WRITE(3,99)S
      6     99 FORMAT('1',T44,'SURFACE GENERATION RATE=',F10.0,'SQ.CM./MIN.')
C
C  THE FOLLOWING ARE THE CONSTANTS USED TO EVALUATE THE SURFACE
C  EXCESS OF ZINC AND NADBS
C
      7        K1= 115. E-4
      8        K2= 79.5 E 6
      9        K3= 11.2
     10        K4= 24.4
     11        K5= 137.
     12        K6= 127.
     13        K7=  73.8 E-10
     14        K8= 6.52
C
C
C      YO = INITIAL NADBS CONC. IN GM./L.
C
     15        YO= 348.475*.9177  E-03
C
C      PH= INITIAL HYDRONIUM ION CONC. IN G-MOL/L
C
     16        PH=.00001
C
```

```
      C     NACL= INITIAL ELECTROLYTE CONC. IN G-MOL/L
      C
   17       NACL=0.01
      C
      C     XO= INITIAL ZINC CONC. IN G-MOL/CC.
      C
   18       XO=0.15295 E-06
      C
   19       Q=0.0
   20       Y(1)=YO
   21       SURFAC=0.0
   22       R=0.0
   23       N=39.
   24       X=XO
   25       ALPHA=-(K3*NACL+K4*PH)
   26       CONST=S*(10**ALPHA)
   27       WRITE(3,1)
   28     1 FORMAT(//,T10,'X=ZINC CONC.',T27,'AMT REMOVED',T44,'Y=NADBS CONC.'
            1,T61,'TIME',T78,'PERCENT',T95,'LIQUID',/,T10,'G-MOL/CC.',T27,'G-MO
            1LS',T44,'GRAM/L',T61,'SECONDS',T78,'REMOVED',T95,'OVERFLOW',/,T95,
            1'CC.')
      C
      C     THIS DO LOOP CALCULATES THE REMOVAL OF ZINC AND NADBS AS A
      C     FUNCTION OF TIME
      C
   29       DO 2 I=1,N
   30       A=(CONST*K1*X)
   31       B=1.0+(K2*X)
   32       C=(K5*Y(I))/(1.+K6*Y(I))
   33       M=(I-1)*60.
   34       D(I,1)=FLOAT(M)
   35       PERCNT(I,1)=100*R/(XO*400)
   36       WRITE(3,3)X,R,Y(I),D(I,1),PERCNT(I,1),Q
   37     3 FORMAT(//,T10,E12.5,T27,E12.5,T44,E12.5,T61,E12.5,T78,E12.5,T95,E1
            12.5)
      C
      C
      C     THIS PART OF THE PROGRAM CALCULATES THE SURFACE EXCESS AND THE
      C     DISTRIBUTION FACTOR FOR ZINC AND THE COLLECTOR AS A FUNCTION OF
      C     TIME
      C
      C
      C     ZNXS= SURFACE EXCESS OF ZINC
   38       ZNXS(I)=((K1*X)/(1.+K2*X))*(10.**ALPHA)*C
      C     ZNDF= DISTRIBUTION FACTOR FOR ZINC
   39       ZNDF(I)=ZNXS(I)/X
```

```
      C
   40         ZINC(I)=X*65,38 E 06
      C
      C       DBSXS= SURFACE EXCESS OF NADBS
   41         DBSXS(I)=(K7*Y(I))/(1,+K8*Y(I))
      C       DBSDF= DISTRIBUTION FACTOR FOR NADBS
   42         DBSDF(I)=(DBSXS(I)/Y(I))*348,475*1000,
      C
      C
      C       THIS NEXT CARD ACCOUNTS FOR THE LIQUID OVERFLOW UNDER THE
      C       GIVEN EXPERIMENTAL CONDITIONS
      C
   43         Q=Q+4,58
      C
   44         R=R+ (A/B)*C+(4,58*X)
   45         SURFAC=S*((K7*Y(I))/(1,+K8*Y(I)))+SURFAC+((4,58/1000,)*(Y(I)/348,4
             175))
   46         Y(I+1)=((,4*YO)-(SURFAC*348,475))/(,4-(Q/1000,))
   47       2 X=((400,*XO)       -R)/(400,-Q)
   48       6 NPNTS(1)=I-1
      C
   49         WRITE(3,33)
   50      33 FORMAT(//,T10,'ZINC CONC,',T27,'ZN SURFACE',T44,'ZINC',T61,'NADBS'
             1,T78,'NADBS',T95,'NADBS',/,T10,'PPM,',T27,'EXCESS',T44,'DISTRIBUTI
             ION',T61,'CONC,',T78,'SURFACE',T95,'DISTRIBUTION',/,T27,'G-MOL/SQ,C
             1M,',T44,'FACTOR',T61,'GM/L',T78,'EXCESS',T95,'FACTOR',/,T44,'CM,',
             1T78,'G-MOL/SQ,CM,',T95,'CM,')
   51         WRITE(3,44)(ZINC(I),ZNXS(I),ZNDF(I),Y(I),DBSXS(I),DBSDF(I),I=1,40)
   52      44 FORMAT(//,T10,E12,5,T27,E12,5,T44,E12,5,T61,E12,5,T78,E12,5,T95,E1
             12,5)
      C
   53         RETURN
   54         END

      $ENTRY
```

SURFACE GENERATION RATE= 15950.0U.CM./MIN.

X=ZINC CONC. G-MOL/CC.	AMT REMOVED G-MOLS	Y=NADBS CONC. GRAM/L	TIME SECONDS	PERCENT REMOVED	LIQUID OVERFLOW CC.
0.15295E-06	0.00000E 00	0.31980E 00	0.00000E 00	0.00000E 00	0.00000E 00
0.14857E-06	0.24338E-05	0.30904E 00	0.60000E 02	0.39781E 01	0.45800E 01
0.14415E-06	0.48422E-05	0.29828E 00	0.12000E 03	0.79147E 01	0.91600E 01
0.13969E-06	0.72247E-05	0.28753E 00	0.18000E 03	0.11809E 02	0.13740E 02
0.13519E-06	0.95808E-05	0.27678E 00	0.24000E 03	0.15660E 02	0.18320E 02
0.13066E-06	0.11910E-04	0.26604E 00	0.30000E 03	0.19467E 02	0.22900E 02
0.12608E-06	0.14211E-04	0.25533E 00	0.36000E 03	0.23228E 02	0.27480E 02
0.12148E-06	0.16484E-04	0.24465E 00	0.42000E 03	0.26943E 02	0.32060E 02
0.11683E-06	0.18728E-04	0.23401E 00	0.48000E 03	0.30611E 02	0.36640E 02
0.11215E-06	0.20941E-04	0.22341E 00	0.54000E 03	0.34229E 02	0.41220E 02
0.10744E-06	0.23124E-04	0.21288E 00	0.60000E 03	0.37797E 02	0.45800E 02
0.10270E-06	0.25276E-04	0.20242E 00	0.66000E 03	0.41314E 02	0.50380E 02
0.97918E-07	0.27394E-04	0.19205E 00	0.72000E 03	0.44776E 02	0.54960E 02

0.93113E-07	0.29479E-04	0.18178E 00	0.78000E 03	0.48184E 02	0.59540E 02
0.88280E-07	0.31528E-04	0.17162E 00	0.84000E 03	0.51534E 02	0.64120E 02
0.83425E-07	0.33541E-04	0.16159E 00	0.90000E 03	0.54824E 02	0.68700E 02
0.78551E-07	0.35516E-04	0.15171E 00	0.96000E 03	0.58051E 02	0.73280E 02
0.73662E-07	0.37451E-04	0.14200E 00	0.10200E 04	0.61214E 02	0.77860E 02
0.68764E-07	0.39343E-04	0.13247E 00	0.10800E 04	0.64308E 02	0.82440E 02
0.63864E-07	0.41192E-04	0.12316E 00	0.11400E 04	0.67329E 02	0.87020E 02
0.58970E-07	0.42994E-04	0.11407E 00	0.12000E 04	0.70274E 02	0.91600E 02
0.54092E-07	0.44746E-04	0.10524E 00	0.12600E 04	0.73138E 02	0.96180E 02
0.49244E-07	0.46444E-04	0.96686E-01	0.13200E 04	0.75914E 02	0.10076E 03
0.44439E-07	0.48085E-04	0.88431E-01	0.13800E 04	0.78597E 02	0.10534E 03
0.39698E-07	0.49665E-04	0.80499E-01	0.14400E 04	0.81178E 02	0.10992E 03
0.35041E-07	0.51176E-04	0.72915E-01	0.15000E 04	0.83648E 02	0.11450E 03
0.30497E-07	0.52613E-04	0.65699E-01	0.15600E 04	0.85997E 02	0.11908E 03
0.26100E-07	0.53968E-04	0.58872E-01	0.16200E 04	0.88211E 02	0.12366E 03

0.21890E-07	0.55231E-04	0.52451E-01	0.16800E 04	0.90276E 02	0.12524E 03
0.17918E-07	0.56393E-04	0.46451E-01	0.17400E 04	0.92175E 02	0.13282E 03
0.14241E-07	0.57440E-04	0.40882E-01	0.18000E 04	0.93887E 02	0.13740E 03
0.10924E-07	0.58361E-04	0.35751E-01	0.18600E 04	0.95393E 02	0.14198E 03
0.80357E-08	0.59143E-04	0.31059E-01	0.19200E 04	0.96671E 02	0.14656E 03
0.56340E-08	0.59778E-04	0.26802E-01	0.19800E 04	0.97708E 02	0.15114E 03
0.37528E-08	0.60263E-04	0.22971E-01	0.20400E 04	0.98502E 02	0.15572E 03
0.23806E-08	0.60609E-04	0.19553E-01	0.21000E 04	0.99067E 02	0.16030E 03
0.14532E-08	0.60838E-04	0.16527E-01	0.21600E 04	0.99442E 02	0.16488E 03
0.86842E-09	0.60980E-04	0.13873E-01	0.22200E 04	0.99673E 02	0.16946E 03
0.51804E-09	0.61063E-04	0.11564E-01	0.22800E 04	0.99809E 02	0.17404E 03

ZINC CONC. PPM.	ZN SURFACE EXCESS G-MOL/SQ.CM.	ZINC DISTRIBUTION FACTOR CM.	NADBS CONC. GM/L	NADBS SURFACE EXCESS G-MOL/SQ.CM.	NADBS DISTRIBUTION FACTOR CM.
0.99999E 01	0.10867E-09	0.71050E-03	0.31980E 00	0.76500E-09	0.83361E-03
0.97133E 01	0.10834E-09	0.72922E-03	0.30904E 00	0.75647E-09	0.85300E-03
0.94242E 01	0.10798E-09	0.74912E-03	0.29828E 00	0.74753E-09	0.87331E-03

0.91327E 01	0.10760E-09	0.77032E-03	0.28753E 00	0.73815E-09	0.89462E-03
0.88387E 01	0.10720E-09	0.79294E-03	0.27678E 00	0.72831E-09	0.91698E-03
0.85423E 01	0.10676E-09	0.81713E-03	0.26604E 00	0.71798E-09	0.94045E-03
0.82434E 01	0.10630E-09	0.84305E-03	0.25533E 00	0.70713E-09	0.96509E-03
0.79421E 01	0.10579E-09	0.87089E-03	0.24465E 00	0.69573E-09	0.99100E-03
0.76385E 01	0.10525E-09	0.90086E-03	0.23401E 00	0.68375E-09	0.10182E-02
0.73326E 01	0.10466E-09	0.93321E-03	0.22341E 00	0.67115E-09	0.10468E-02
0.70245E 01	0.10403E-09	0.96823E-03	0.21288E 00	0.65790E-09	0.10769E-02
0.67142E 01	0.10334E-09	0.10062E-02	0.20242E 00	0.64397E-09	0.11086E-02
0.64019E 01	0.10258E-09	0.10476E-02	0.19205E 00	0.62932E-09	0.11419E-02
0.60877E 01	0.10176E-09	0.10928E-02	0.18178E 00	0.61391E-09	0.11769E-02
0.57718E 01	0.10085E-09	0.11424E-02	0.17162E 00	0.59772E-09	0.12137E-02
0.54544E 01	0.99850E-10	0.11969E-02	0.16159E 00	0.58071E-09	0.12523E-02
0.51357E 01	0.98746E-10	0.12571E-02	0.15171E 00	0.56286E-09	0.12929E-02
0.48160E 01	0.97521E-10	0.13239E-02	0.14200E 00	0.54415E-09	0.13354E-02

0.44958E 01	0.96155E-10	0.13983E-02	0.13247E 00	0.52457E-09	0.13799E-02
0.41754E 01	0.94626E-10	0.14817E-02	0.12316E 00	0.50411E-09	0.14264E-02
0.38554E 01	0.92906E-10	0.15755E-02	0.11407E 00	0.48279E-09	0.14748E-02
0.35366E 01	0.90963E-10	0.16816E-02	0.10524E 00	0.46062E-09	0.15252E-02
0.32196E 01	0.88758E-10	0.18024E-02	0.96686E-01	0.43765E-09	0.15774E-02
0.29055E 01	0.86241E-10	0.19406E-02	0.88431E-01	0.41395E-09	0.16312E-02
0.25954E 01	0.83356E-10	0.20998E-02	0.80499E-01	0.38960E-09	0.16865E-02
0.22910E 01	0.80031E-10	0.22839E-02	0.72915E-01	0.36472E-09	0.17431E-02
0.19939E 01	0.76185E-10	0.24981E-02	0.65699E-01	0.33945E-09	0.18005E-02
0.17064E 01	0.71722E-10	0.27480E-02	0.58872E-01	0.31396E-09	0.18584E-02
0.14312E 01	0.66540E-10	0.30397E-02	0.52451E-01	0.28844E-09	0.19164E-02
0.11715E 01	0.60539E-10	0.33787E-02	0.46451E-01	0.26312E-09	0.19739E-02
0.93108E 00	0.53653E-10	0.37675E-02	0.40882E-01	0.23821E-09	0.20305E-02
0.71424E 00	0.45902E-10	0.42018E-02	0.35751E-01	0.21397E-09	0.20856E-02
0.52537E 00	0.37474E-10	0.46634E-02	0.31059E-01	0.19061E-09	0.21387E-02

0.36835E 00	0.28813E-10	0.51141E-02	0.26802E-01	0.16837E-09	0.21892E-02
0.24536E 00	0.20622E-10	0.54951E-02	0.22971E-01	0.14744E-09	0.22367E-02
0.15564E 00	0.13671E-10	0.57429E-02	0.19553E-01	0.12798E-09	0.22810E-02
0.95011E-01	0.84529E-11	0.58167E-02	0.16527E-01	0.11011E-09	0.23216E-02
0.56777E-01	0.49646E-11	0.57168E-02	0.13873E-01	0.93893E-10	0.23584E-02
0.33869E-01	0.28357E-11	0.54739E-02	0.11564E-01	0.79359E-10	0.23914E-02
UUUUUUUUUUUU	UUUUUUUUUUUU	UUUUUUUUUUUU	0.95720E-02	UUUUUUUUUUUU	UUUUUUUUUUUU

CORE USAGE OBJECT CODE= 3376 BYTES,ARRAY AREA= 1764 BYTES,TOTAL AREA AVAILABLE= 34912 BYTES

COMPILE TIME= 2.59 SEC,EXECUTION TIME= 3.59 SEC, WATFIV - VERSION 1 LEVEL 2 AUGUST 1970 DATE=