



Western Michigan University  
ScholarWorks at WMU

---

Paper Engineering Senior Theses

Chemical and Paper Engineering

---

12-1978

## Variables Affecting the Drainage Test

Jeffrey S. Honour  
*Western Michigan University*

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>



Part of the Wood Science and Pulp, Paper Technology Commons

---

### Recommended Citation

Honour, Jeffrey S., "Variables Affecting the Drainage Test" (1978). *Paper Engineering Senior Theses*. 223.  
<https://scholarworks.wmich.edu/engineer-senior-theses/223>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact [wmu-scholarworks@wmich.edu](mailto:wmu-scholarworks@wmich.edu).



VARIABLES AFFECTING  
THE DRAINAGE TEST

by

Jeffrey S. Honour

A Thesis Submitted  
in partial fulfillment of  
the course requirements for  
The Bachelor of Science Degree

Western Michigan University

Kalamazoo, Michigan

December 14, 1978

## TABLE OF CONTENTS

ABSTRACT.....	I
INTRODUCTION.....	2
FLOCCULATION THEORY.....	3
EXPERIMENTAL INTRODUCTION.....	9
pH EFFECTS.....	10
PULP EFFECTS.....	11
SALTS.....	12
CONCENTRATION EFFECTS.....	14
BASIS OF CONCLUSIONS.....	15
CLOSING.....	16
EXPERIMENTAL DESIGN.....	19
EXPERIMENTAL PROCEDURE.....	21
DATA AND GRAPHS.....	22
CONCLUSIONS.....	
ZETA POTENTIAL.....	54
SCHULZE-HARDY RULE.....	56
ACID SIDE.....	57
ALKALINE SIDE.....	60
ACID-ALKALINE COMPARISONS.....	62
STATISTICAL INFERENCES.....	63
CLOSING.....	64
RECOMMENDATIONS.....	65
ACKNOWLEDGEMENTS.....	66
BIBLIOGRAPHY.....	67

## ABSTRACT

Certain variables affecting the Canadian Standard Freeness Test were investigated. Variables investigated included the zeta potential, pH, chemical type, and concentration. Chemicals used were  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  on the acid side. Chemicals used on the alkaline side included  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{K}_2\text{HPO}_4$ . pH values were 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. Concentrations used were  $1 \times 10^{-3} \text{ M}$ ,  $3 \times 10^{-3} \text{ M}$ ,  $5 \times 10^{-3} \text{ M}$ ,  $7 \times 10^{-3} \text{ M}$ ,  $9 \times 10^{-3} \text{ M}$ ,  $1.1 \times 10^{-2} \text{ M}$ ,  $1.3 \times 10^{-2} \text{ M}$ , and  $1.5 \times 10^{-2} \text{ M}$ . Zeta potential was measured using a Laser Zee Meter. Quantitative interpretation of the Schulze-Hardy rule was attempted but failed. Freeness was found to decrease as zeta potential increased or decreased and was maximized as ZP closed in on a value of zero. Freeness was found to be affected most greatly by concentration-chemical type and chemical type-pH interaction. A statistical analysis was prepared to determine this interaction with the help of the W.M.U. Stat Lab.

The standard freeness test as outlined in TAPPI Standard T227 os-58 is one of the oldest and yet universal tests in the industry. Originally this test was used to control the manufacture of groundwood pulp.<sup>1</sup> Today this test is used on virtually all pulps as a measure of the drainage of water through pulp. With this in mind an earlier paper, presented by this author, outlined an preliminary experiment which various variables and their effect on the freeness was to be measured. This paper is a combination of the former with experimental data and conclusions now included. Variables examined include the pH, zeta potential, and various simple electrolytes at different concentrations. Chemicals used on the acid side included NaCl, CaCl<sub>2</sub>, AlCl<sub>3</sub>, and SnCl<sub>4</sub>·5H<sub>2</sub>O. Chemicals used on the alkaline side included KCl, K<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>HPO<sub>4</sub>. pH was controlled with standard grade HCl and NaOH. The main objective of this experiment was to find what relationships between these variables and the freeness could be established. A majority of this work involved a statistical analysis. A secondary objective involved trying to show the relationships covered in the Schulze-Hardy rule involving flocculation.

Cellulose when dispersed in water, to form a stable suspension, generally has a net negative charge.<sup>2</sup> This electrical charge, on the surface exposed to water, is caused by ionization of polar groups, adsorption of ions from the surrounding medium (hydroxyl or hydrogen ions from water included), and partial solution of the crystal lattice.<sup>3</sup> It has also been found that maximum drainage, thus highest freeness value, is achieved when this charge is minimized. This charge, for a negative pulp, is also found to decrease when an increasing amount of an electrolyte is added.<sup>4</sup> Therefore as this charge is minimized the phenomena of flocculation takes place. (flocculation meaning "to form a floccule like a tuft of wool or loosely fibrous structure" as compared to coagulation which in essence means "to drive together"<sup>5</sup>). This flocculation is a direct function of the interactions between fibers. This may be regarded as a process of fiber entanglement in which the fiber length, flexibility, and concentration determine the geometry of entanglement and surface roughness, friction and fiber colloidal properties determine the effectiveness of these interfiber contacts and thus directly effect drainage.<sup>7</sup>

This flocculation involves bonding of fines and long fibers together in large aggregates with relatively large spaces between fibers through which water can drain easily. Hence maximum drainage is reached at the point of flocculation and this "maximum" flocculation is reached when the "particles" have their maximum affinity for each other and this occurs when their charge is minimized. This flocculation, when charge is minimized, is again accompanied by the maximum drainage, though this maximum drainage may occur at a slightly positive charge, which is believed to be caused by additional adsorption of the electrolyte on the cellulose.<sup>2</sup>

The importance of maximum freeness being attained at a charge neutralization is further backed up by studies which show maximum freeness, with no electrolytes in solution, is obtained at the isoelectric point of the pulp (isoelectric point is the pH at which minimum ionization exists).<sup>9</sup>

The charge referred to above is commonly known as zeta potential, which is sometimes confusing to understand. This zeta potential may be defined as electrical potential difference between solution far from solid-liquid interface and between solution and the stagnant layer surrounding the dispersed solid.<sup>6</sup>

In layman's terms this definition means zeta potential is the measure of the electric potential (electrokinetic potential) which occurs at the solid-liquid interface.

The following statements have better application if examined closer. In essence they state that by maximizing drainage, and correspondingly minimizing zeta potential, this can reduce water removal in the press section because the sheet is more highly compressed at the couch roll and is thereafter less porous and harder to dry; by maximizing water removal on the wire less water has to be removed in the presses thus saving money.<sup>8</sup>

Before proceeding the author again points out for the reader, as stated earlier, that this paper is entitled "Variables Affecting the Drainage Test," and little has been said of this test. It must be remembered that maximum drainage is reached at a zeta potential approximately equal to zero. Also at zeta potential equal to zero flocculation occurs thus both these principles, zeta potential and flocculation, must be investigated somewhat as they are very important in drainage and warrant some mention.. With this in mind the theory of flocculation is further discussed. Flocculation, as mentioned, occurs when zeta potential is minimized. In this study it will be assumed that zeta potential will be minimized by using simple electrolytes. Today, the theory of flocculation is believed to involve the diffuse double layer which was first proposed by Verwey and Overbeek.<sup>10</sup> More commonly this theory has



become known as the DLVO Theory for flocculation ( called this after the men who first formulated the Diffuse Double Layer Theory, Derjaguin, Landau, Verwey, and Overbeek). This theory is unique in that it varies from the older Helmholtz Double Layer Theory. In the Helmholtz Theory, the particle, namely the negatively charged cellulose is surrounded by cations in a monolayer causing charge neutralization and finally flocculation.<sup>13</sup> The DLVO Theory varies from this idea and is now the accepted theory believed to describe flocculation.<sup>11</sup> In the Helmholtz Theory it was formulated that electrostatic forces acted alone causing flocculation. If these electrostatic forces acted alone the solid, negatively charged cellulose, would have cations from the solution attracted to the solid surface in an amount equivalent to its charge and would form on the solid a film of cations similar in structure and thickness to one row of ions in a crystal lattice. This is where this theory (Helmholtz) fails; this is because the electrostatic forces which tend to produce concentration changes in solution are opposed by osmotic forces which tend to equalize the concentration of every ion everywhere in the solution. Therefore as a result of these rival forces a diffuse double layer is produced. In this double layer theory the concentration of cations is high next to the interface forming a fixed layer.

The concentration of cations next to the interface is high but not so high as to neutralize the whole charge on the solid and the remainder of the cation amount required for neutralization is extended in solution somewhat at a distance from the interface. The concentration of anions adjacent to the interface is small, but not zero, and gradually increases as distance from interface becomes greater.<sup>6</sup>

As this happens charge is neutralized and flocculation takes place. The thickness of this diffuse layer appears to be of colloidal dimensions. In very diluted electrolytic solutions the diffuse layer may be  $10^{-5}$  to  $10^{-4}$  cm. in thickness.<sup>10</sup>

This double layer is therefore a result of unequal distribution of positive and negative ions between both phases.

The beauty of this DLVO theory is that it gives quantitative formulation of the Schulze-Hardy rule.<sup>11</sup> The

Schulze-Hardy rule is a rule governing flocculation for mono-, di-, and trivalent ions; basically it relates critical concentration needed for flocculation. The Schulze-Hardy

rule, as follows, is  $c_1:c_2:c_3:1/1^6:1/2^6:1/3^6$  where  $c_1$  is concentration of monovalent ion needed for flocculation in ratio with concentration of divalent and then trivalent which would be needed to cause flocculation also. For example if 100 milimoles of a monovalent salt were needed for coagulation the corresponding amount of divalent and trivalent

salts needed for flocculation would be 1.56 milimoles and .14 milimoles respectively. The Schulze-Hardy rule further shows that the flocculation power of electrolytes is shown to depend on the electric potential of the surface of the colloidal particle, on the charge of the counterions, and the magnitude of the Van der Waals attractive forces. In a nutshell it will take more of a monovalent ion to flocculate a material than divalent and accordingly it would take more of a divalent salt to flocculate than trivalent. In dealing with nonionics I will just say they are adsorbed through steric hinderance and are bad for flocculation preventing adsorption of ionics. A monomolecular layer of non-ionic surfactant would be adsorbed in preference to an ionic; dispersion would be stable but flocculation impossible.<sup>12</sup>

The discussion of experimental interaction between variables, data, and conclusions remain as the bulk of this paper. One hundred and sixty eight freeness tests were run along with the same amount of zeta potential tests. At this point I again point out the freeness was run using the method outlined in TAPPI Standard T227 os-58. Zeta potential was measured using the Laser Zee Meter<sup>TM</sup> at Brown Paper Company. Zeta Potential was measured according to the method described in the 500 Laser Zee Meter<sup>TM</sup> Handbook.<sup>23</sup> This method is known as microelectrophoresis.<sup>23</sup> The zeta potential read was in millivolts. The experimental variables and reasons for use are outlined on the following pages.

pH of the experiment was controlled and freeness measured at pH values of 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. The reason for this is that zeta potential changes over a pH range; showing fibers are strongly negative at a high pH and zero at a pH of approximately 2.0 which is commonly referred to as the isoelectric point.<sup>9</sup> The reason a paper machine can not be run at this pH is because of the corrosive action on the machinery. Originally the reason for this was to attempt to show that with increasing pH, on the acid side, increasing amounts of salt would be needed to cause flocculation and accordingly maximum drainage. It is theorized and will be attempted to be shown as pH is further increased, on the alkaline side, that the slurry will remain dispersed and freeness will drop.<sup>18</sup> This affect should become more pronounced as increasing amounts of salts are added on the alkaline side increasing the negative charge.

Originally the same type of pulp with two different amounts of beating were to be investigated for a similar reason as pH is controlled. Time problems caused this experiment to include only one amount of refining. A passing remark, though, concerning the reason two amounts of refining originally were to be investigated is included to show why the author planned this approach. The reason beating would have been changed is twofold. First, with less refining lignin is less degraded. This causes the zeta potential to be more negative because higher lignin content pulps give a more negative zeta potential because of the presence of fatty and resin acids which cause the lignin to function as a anionic surface active agent.<sup>19</sup> The other effect, which is the more dominant of the two, is that with increased refining more surface area is exposed therefore thus increasing carboxyl and hydroxyl groups ionizable thusly making zeta potential more negative. This increased refining also increases what is commonly known as the cationic demand plateau.<sup>18</sup> Increasing this cationic demand actually means more cationic material is needed to cause flocculation.

Four different salts were investigated on the acid side while three different salts were investigated on the alkaline side. The salts on the acid side were  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . In the original paper  $\text{ThCl}_4$  was to be used but radioactive properties of this chemical caused changing to  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ .  $\text{CaCO}_3$  was also replaced because problems concerning synthetic and natural types wanted to be avoided.<sup>20</sup>  $\text{Al}(\text{NO}_3)_3$  was replaced because of greater availability of  $\text{AlCl}_3$ . Salts on the alkaline side included  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{K}_2\text{HPO}_4$ . Referring back to the original paper, again, on the acid side the effect of the cation was thought to be most pronounced. By observation it is noticable that I have chosen a mono-, di-, tri-, and quadvalent series of cations. The original purpose in this was twofold. First, the application of the Schulze-Hardy rule was investigated, but failed for reasons described in the conclusion. Secondly, the more positive the cation the more pronounced effect appeared on the zeta potential. As already stated as pH rises the cationic material will increase in amount needed to cause flocculation because charge on the cellulose becomes more negative; also at higher pH values cations that are greater in charge than the mono-valent type form unique complexes which also call for a

greater concentration to give the same actual positive charge.<sup>20,21,22</sup> For example, the  $\text{Al}^{+++}$  ion acts as a tri-valent ion at low pH values but as pH increases the  $\text{Al}^{+++}$  forms complexes with negative ions in solution thus decreasing the positive charge.<sup>++</sup> A similar effect holds for the  $\text{Ca}^{++}$  and  $\text{Sn}^{++++}$  ions. Not much has been written concerning high pH values and the effect that salts have but it is believed the anion is the dominant species. With this in mind, it was initially decided, with greater concentrations of salts being added on the alkaline side the charge would become more negative and material would remain dispersed and drain slower. As noticed anions used again are of the mono-, di-, and tri-valent types. Ions chosen were also chosen, as best could, to differ from ions present in the acid and base which controlled pH in an attempt to lower this interaction.



Concentration values differed over a wide range in an attempt to show the affect on freeness and prove the Schulze-Hardy rule. Originally , values of concentration were to be ranged from  $1 \times 10^{-5} \text{ M}$  to  $2 \times 10^{-1} \text{ M}$  (estimated in original paper). Much thought and further reading was done in an attempt to decide the concentration range. Conclusions show the final concentration range chosen was too narrow to show application of the Schulze-Hardy rule. It must be stated though, as calculations show, some of the concentrations needed (to prove Schulze-Hardy rule) were very low; an attempt to reach these would have been quantitatively very difficult. This error that followed just shows a greater concentration range should have been set-up, regardless of difficulty. This error lies in the fact that many concentration values <sup>10,26,27,4</sup> have been shown in the literature. The effect of varying concentrations had on freeness has already been discussed somewhat and is known to affect total charge on the slurry.

Data was collected in an attempt to prove and show various relations. The Schulze-Hardy rule was attempted to be proven but did not succeed. A statistical analysis was also run to find which variable had the greatest effect on the freeness. The statistical analysis was run excluding zeta potential. This was done because zeta potential was not a variable that was controlled, but was the resultant of a combination of other variables. The statistical analysis was also broken into two sections, one for the acid side and one for the basic side. With these limitations a typical three-way analysis of variance program was run and conclusions made. 24 The variables studied were then chemical type, concentration, and pH. The statistical analysis is a simplified program and again time was a very detrimental factor. I worked closely with a Stat Lab group in attempting to break this problem down. The people I worked with designed a incorrect model for analysis which complicated things greatly. With the closing of the semester close only a brief analysis was possible and basic decisions made.

In closing the limitations of the freeness test must be realized and considered. Throughout the experiment procedure must remain the same. Water temperature must remain constant and particular care must be taken in caring for the freeness tester as any small changes in the tester can cause variations in freeness readings.<sup>1</sup> Pulp agitation must remain the same prior to testing as turbulence can effect bonding and thus freeness.<sup>14</sup> This lies in the fact that with added agitation great competition takes place for bonding sights on the cellulose. This process, for example, of added agitation creates a hydrodynamic shear which disrupts the established networks. With this in mind agitation , after refining, will be kept constant at all times. At this point the author would like to say something of the validity of this experiment. It must be remembered that this thesis is a study of the variables affecting the freeness test and only that. No relation between actual paper machine operation and this test are mentioned except for a passing remark earlier in this paper concerning saving money by added drainage. Concerning the freeness test much has been written on it and the validity of it has been argued extensively.<sup>15,16</sup>

For experimental purposes deionized water will be used and again the validity of using deionized water has been argued; but one must remember here that the only reason it will be used is to decrease the variables affecting the zeta potential on the cellulose initially. One author in particular<sup>16</sup> has argued extensively that other properties should be used to evaluate a pulp such as weighted fiber length, coarseness, intrinsic fiber length, compactibility when wet, and cohesiveness. The freeness test is a static test measuring drainage while in actuality this is a dynamic process so application to actual operation has been questioned greatly. With all these shortcomings it remains that freeness is still used extensively in the mill as a way of characterizing pulps. It remains a fast test as these other tests, including the measure of zeta potential, take longer and thus are unsuitable for mill use other than in a lab. Another method used in calculating pulp characteristics could be the calculation of Drainage Time which is calculated by using the equation,  $DT_{(\text{seconds})} = 28.78 - .181Csf + .00327(Csf)^2$ .<sup>17</sup> The author, though, makes no comment on the usefulness of calculating drainage time as only one reference was found in an extensive search of literature in which this equation was used. Finally, one last thing must be said concerning freeness. People often characterize freeness as being a

measure of beating. This idea is incorrect and should be avoided. This lies in the idea that while with increased beating surface area of the pulp is increased but as shown in this paper drainage of pulp is affected by many variables, not just beating.

A majority of this design was attributed to the statistical set-up. pH values varied from 4.5 to 9.5 with increments of one (six total). Concentration values were  $1 \times 10^{-3} \text{ M}$ ,  $3 \times 10^{-3} \text{ M}$ ,  $5 \times 10^{-3} \text{ M}$ ,  $7 \times 10^{-3} \text{ M}$ ,  $9 \times 10^{-3} \text{ M}$ ,  $1.1 \times 10^{-2} \text{ M}$ ,  $1.3 \times 10^{-2} \text{ M}$ , and  $1.5 \times 10^{-2} \text{ M}$ . Chemicals used on the acid side were  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ , and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . Materials used on the alkaline side were  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{HPO}_4$ . pH was adjusted with standard 1N  $\text{HCl}$  and  $\text{NaOH}$ . Deionized water was used in all samples to minimize the effect of ions in the water. Pulp slurries were made according to the basic method using a soft wood pulp (pulp dispersed in deionized water also).

The data recorded, in this paper, are only the final corrected values. All corrections were initially made in a separate workbook and recorded. Temperatures used in corrections were read utilizing the thermistor on the Laser Zee giving a very accurate temperature reading. A static zeta potential was read and subtracted from the dynamic zeta potential reading to give the measured zeta potential (ZP<sub>m</sub>). This measured zeta potential was then corrected for temperature by using the equation:  $\text{ZP}_c = \text{ZP}_m (1 - .02t)$  where  $\text{ZP}_c$  is the corrected zeta potential and  $t$  is the temperature output.

read upon depressing the temperature button.

A final say on the method of addition, which remained constant, seems appropriate. The method of addition was fiber dispersion, pH adjustment, salt addition, and final pH adjustment, if needed. The reason for this was to give the same conditions for complex formation stated earlier.

1. Weigh out appropriate chemical at desired concentration for dispersion in 1100 ml. of deionized water and pulp soln. <sup>25</sup>
2. Get correct amount of stock soln. (according to standard) to have a 3% final dispersion
3. Dilute stock sample to 1000 ml. with deionized water
4. Adjust pH
5. Add and mix chemical into the slurry
6. Re-adjust pH
7. Dilute sample to 1100 ml. with deionized water (#2 corrected for 1100 ml. in original calculation)
8. Remove 100 ml. sample for ZP
9. Screen 100 ml. sample through 100 mesh screen
10. Run Csf on remaining 1000 ml. sample
11. Make handsheet
12. Go through Laser Zee set-up (Automatic Transfer Module procedure)
13. Measure temperature of sample (100ml.)
14. Stop particles and read ZP<sub>static</sub>
15. Depress H.V. button and read ZP<sub>dynamic</sub>
16. Dry handsheet and correct Csf for weight and temperature
17. Record corrected Csf
18. Correct ZP and record



# Acid Side Data Set #1

6

CHEMICAL	REFINING TIME	pH	(MOLARITY) CONCENTRATION	(mv) $\phi_p$	Csf	
-	7 min	4.5	-	-9.04	693	
NaCl	"	"	$1 \times 10^{-3}$	-19.22	691	691.23 = avg Csf @ $1 \times 10^{-3} M$
NaCl	"	"	$3 \times 10^{-3}$	-17.30	687	687.25 = avg Csf @ $3 \times 10^{-3} M$
NaCl	"	"	$5 \times 10^{-3}$	-19.92	693	680.58 = avg Csf @ $5 \times 10^{-3} M$
NaCl	"	"	$7 \times 10^{-3}$	-2.26	704	681.83 = avg Csf @ $7 \times 10^{-3} M$
NaCl	"	"	$9 \times 10^{-3}$	+2.46	687	663.67 = avg Csf @ $9 \times 10^{-3} M$
NaCl	"	"	$1.1 \times 10^{-2}$	-1.02	700	660.92 = avg Csf @ $1.1 \times 10^{-2} M$
NaCl	"	"	$1.3 \times 10^{-2}$	0	712	660.58 = avg Csf @ $1.3 \times 10^{-2} M$
NaCl	"	"	$1.5 \times 10^{-2}$	-1.48	710	640.58 = avg Csf @ $1.5 \times 10^{-2} M$
CaCl <sub>2</sub>	"	"	$1 \times 10^{-3}$	0	716	
CaCl <sub>2</sub>	"	"	$3 \times 10^{-3}$	-4.01	697	
CaCl <sub>2</sub>	"	"	$5 \times 10^{-3}$	-2.45	694	
CaCl <sub>2</sub>	"	"	$7 \times 10^{-3}$	-7.62	709	
CaCl <sub>2</sub>	"	"	$9 \times 10^{-3}$	+2.82	694	
CaCl <sub>2</sub>	"	"	$1.1 \times 10^{-2}$	+3.02	704	697.24 = avg Csf for NaCl
CaCl <sub>2</sub>	"	"	$1.3 \times 10^{-2}$	-.64	690	667.54 = avg Csf for CaCl <sub>2</sub>
CaCl <sub>2</sub>	"	"	$1.5 \times 10^{-2}$	-.28	710	688.75 = avg Csf for AlCl <sub>3</sub>
AlCl <sub>3</sub>	"	"	$1 \times 10^{-3}$	+1.47	712	608.79 = avg Csf for SnCl <sub>4</sub>
AlCl <sub>3</sub>	"	"	$3 \times 10^{-3}$	0	706	
AlCl <sub>3</sub>	"	"	$5 \times 10^{-3}$	-1.03	693	
AlCl <sub>3</sub>	"	"	$7 \times 10^{-3}$	+1.92	685	
AlCl <sub>3</sub>	"	"	$9 \times 10^{-3}$	+2.6	707	
AlCl <sub>3</sub>	"	"	$1.1 \times 10^{-2}$	+1.61	695	
AlCl <sub>3</sub>	"	"	$1.3 \times 10^{-2}$	+3.09	693	
AlCl <sub>3</sub>	"	"	$1.5 \times 10^{-2}$	+1.97	686	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$1 \times 10^{-3}$	-11.0	688	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$3 \times 10^{-3}$	-.10	674	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$5 \times 10^{-3}$	+4.26	645	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$7 \times 10^{-3}$	+4.92	650	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$9 \times 10^{-3}$	+10.27	570	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$1.1 \times 10^{-2}$	+12.87	559	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$1.3 \times 10^{-2}$	+12.35	491	
SnCl <sub>4</sub> · 5H <sub>2</sub> O	"	"	$1.5 \times 10^{-2}$	+13.89	352	

(22)

668.88 = avg Csf @ pH = 4.5

# Acid Side Data Set #2

7

CHEMICAL	REFINING TIME	pH	(MOLARITY) CONCENTRATION	(mv) $\beta$ P	Csf
-	7 min.	5.5	-	-5.04	692
NaCl	"	"	$1 \times 10^{-3}$	-4.99	691
NaCl	"	"	$3 \times 10^{-3}$	-4.07	677
NaCl	"	"	$5 \times 10^{-3}$	-2.91	673
NaCl	"	"	$7 \times 10^{-3}$	0	684
NaCl	"	"	$9 \times 10^{-3}$	+2.13	679
NaCl	"	"	$1.1 \times 10^{-2}$	+4.40	673
NaCl	"	"	$1.3 \times 10^{-2}$	+7.31	695
NaCl	"	"	$1.5 \times 10^{-2}$	+4.87	691
CaCl <sub>2</sub>	"	"	$1 \times 10^{-3}$	-5.28	685
CaCl <sub>2</sub>	"	"	$3 \times 10^{-3}$	-3.30	706
CaCl <sub>2</sub>	"	"	$5 \times 10^{-3}$	+2.62	686
CaCl <sub>2</sub>	"	"	$7 \times 10^{-3}$	+2.84	692
CaCl <sub>2</sub>	"	"	$9 \times 10^{-3}$	+4.89	697
CaCl <sub>2</sub>	"	"	$1.1 \times 10^{-2}$	+2.90	693
CaCl <sub>2</sub>	"	"	$1.3 \times 10^{-2}$	+1.63	688
CaCl <sub>2</sub>	"	"	$1.5 \times 10^{-2}$	+1.24	671
AlCl <sub>3</sub>	"	"	$1 \times 10^{-3}$	-7.09	693
AlCl <sub>3</sub>	"	"	$3 \times 10^{-3}$	-8.20	667
AlCl <sub>3</sub>	"	"	$5 \times 10^{-3}$	-3.34	713
AlCl <sub>3</sub>	"	"	$7 \times 10^{-3}$	-2.03	683
AlCl <sub>3</sub>	"	"	$9 \times 10^{-3}$	-5.53	673
AlCl <sub>3</sub>	"	"	$1.1 \times 10^{-2}$	+2.93	765
AlCl <sub>3</sub>	"	"	$1.3 \times 10^{-2}$	+1.11	747
AlCl <sub>3</sub>	"	"	$1.5 \times 10^{-2}$	+3.53	749
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1 \times 10^{-3}$	-6.36	750
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$3 \times 10^{-3}$	-3.94	716
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$5 \times 10^{-3}$	+2.16	700
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$7 \times 10^{-3}$	+10.82	668
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$9 \times 10^{-3}$	+9.06	608
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.1 \times 10^{-2}$	+7.89	552
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.3 \times 10^{-2}$	+9.8	597
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.5 \times 10^{-2}$	+9.34	503

(23)

680-16 avg Csf for pH of 5.5

# Acid Side Data Set #3

8

CHEMICAL	REFINING TIME	pH	EMOLARITY) CONCENTRATION	(mV) β P	Csf
—	7 min	6.5	—	-2.79	714
NaCl	"	"	$1 \times 10^{-3}$	-4.95	716
NaCl	"	"	$3 \times 10^{-3}$	-2.6	732
NaCl	"	"	$5 \times 10^{-3}$	-4.87	716
NaCl	"	"	$7 \times 10^{-3}$	+3.50	735
NaCl	"	"	$9 \times 10^{-3}$	-3.89	694
NaCl	"	"	$1.1 \times 10^{-2}$	+2.07	702
NaCl	"	"	$1.3 \times 10^{-2}$	+2.23	704
NaCl	"	"	$1.5 \times 10^{-2}$	+3.04	689
CaCl <sub>2</sub>	"	"	$1 \times 10^{-3}$	-8.38	683
CaCl <sub>2</sub>	"	"	$3 \times 10^{-3}$	-4.15	671
CaCl <sub>2</sub>	"	"	$5 \times 10^{-3}$	-2.73	667
CaCl <sub>2</sub>	"	"	$7 \times 10^{-3}$	-6.20	664
CaCl <sub>2</sub>	"	"	$9 \times 10^{-3}$	-3.97	691
CaCl <sub>2</sub>	"	"	$1.1 \times 10^{-2}$	-2.44	639
CaCl <sub>2</sub>	"	"	$1.3 \times 10^{-2}$	+3.34	683
CaCl <sub>2</sub>	"	"	$1.5 \times 10^{-2}$	-1.25	671
AlCl <sub>3</sub>	"	"	$1 \times 10^{-3}$	-5.56	663
AlCl <sub>3</sub>	"	"	$3 \times 10^{-3}$	-2.34	665
AlCl <sub>3</sub>	"	"	$5 \times 10^{-3}$	-2.41	656
AlCl <sub>3</sub>	"	"	$7 \times 10^{-3}$	+2.36	681
AlCl <sub>3</sub>	"	"	$9 \times 10^{-3}$	+1.79	649
AlCl <sub>3</sub>	"	"	$1.1 \times 10^{-2}$	+2.04	652
AlCl <sub>3</sub>	"	"	$1.3 \times 10^{-2}$	+6.61	637
AlCl <sub>3</sub>	"	"	$1.5 \times 10^{-2}$	+7.40	660
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1 \times 10^{-3}$	-1.93	614
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$3 \times 10^{-3}$	-2.41	619
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$5 \times 10^{-3}$	+1.78	631
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$7 \times 10^{-3}$	+2.11	627
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$9 \times 10^{-3}$	+5.11	615
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.1 \times 10^{-2}$	+7.35	597
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.3 \times 10^{-2}$	+8.91	590
SnCl <sub>4</sub> ·5H <sub>2</sub> O	"	"	$1.5 \times 10^{-2}$	+7.69	595

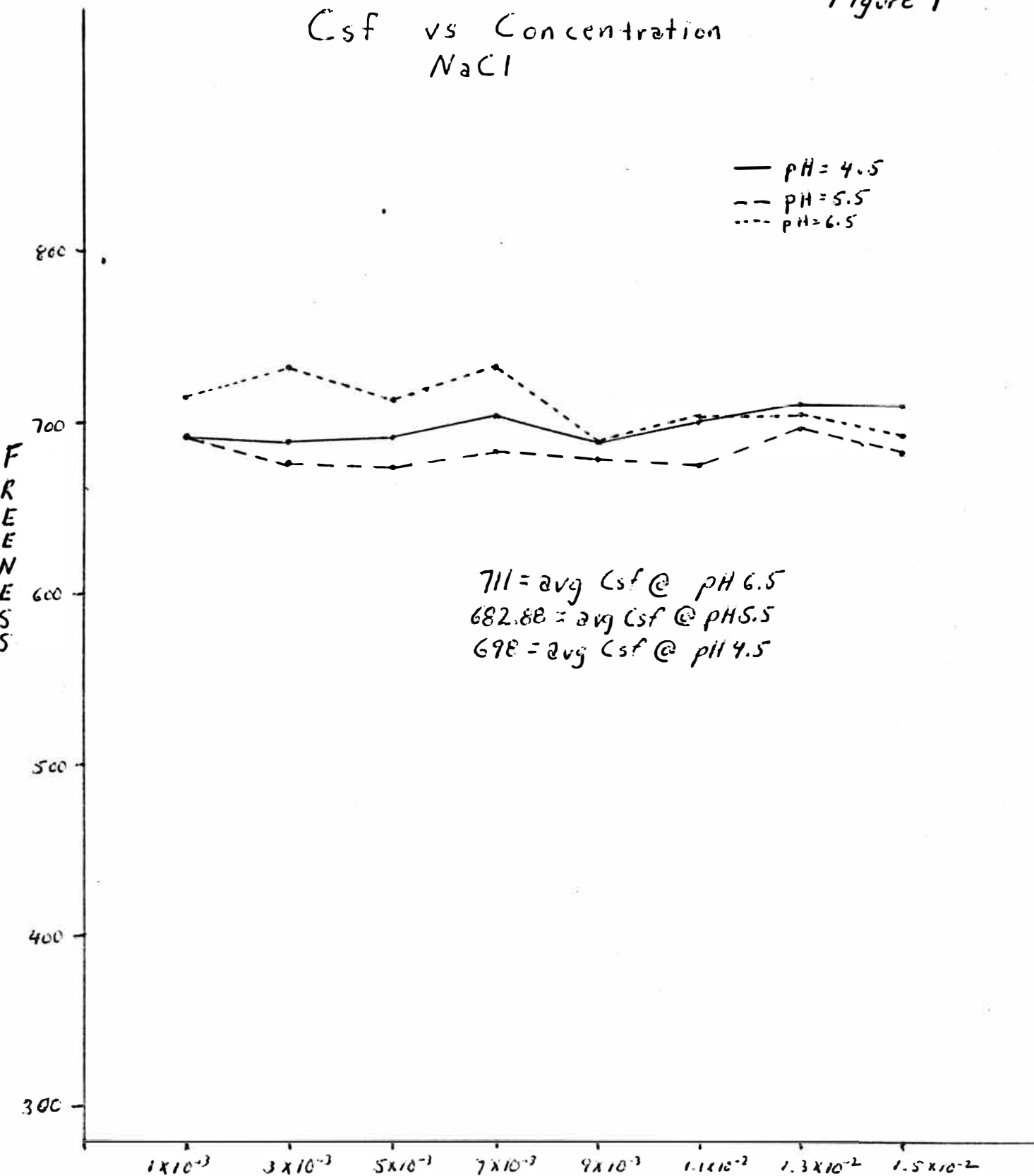
670.5938 = avg Csf for Acid Side

(24)

662.75 = avg Csf @ pH = 6.5

Figure 1

$C_{sf}$  vs Concentration  
NaCl



(25)

CONCENTRATION

Figure 2

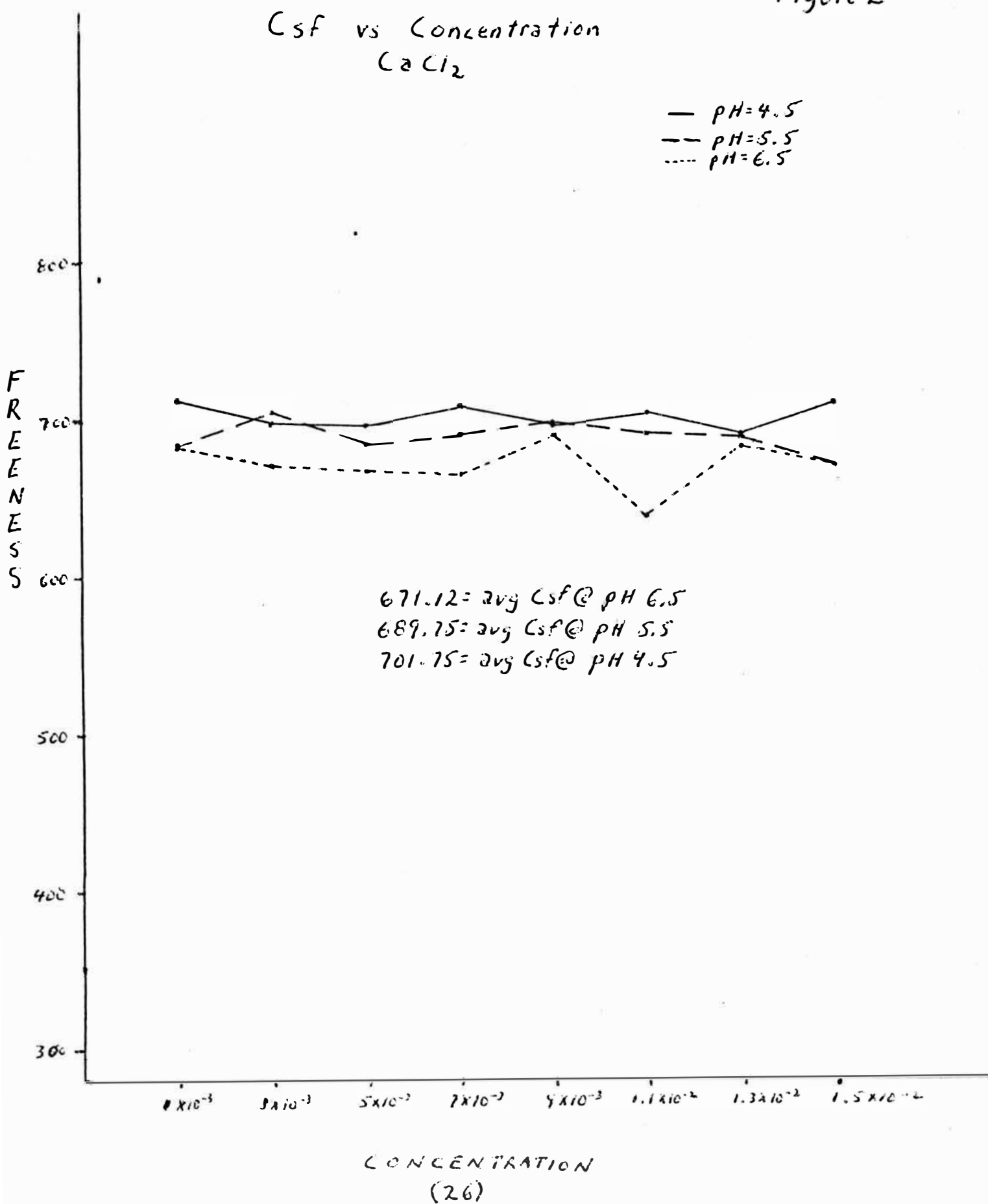
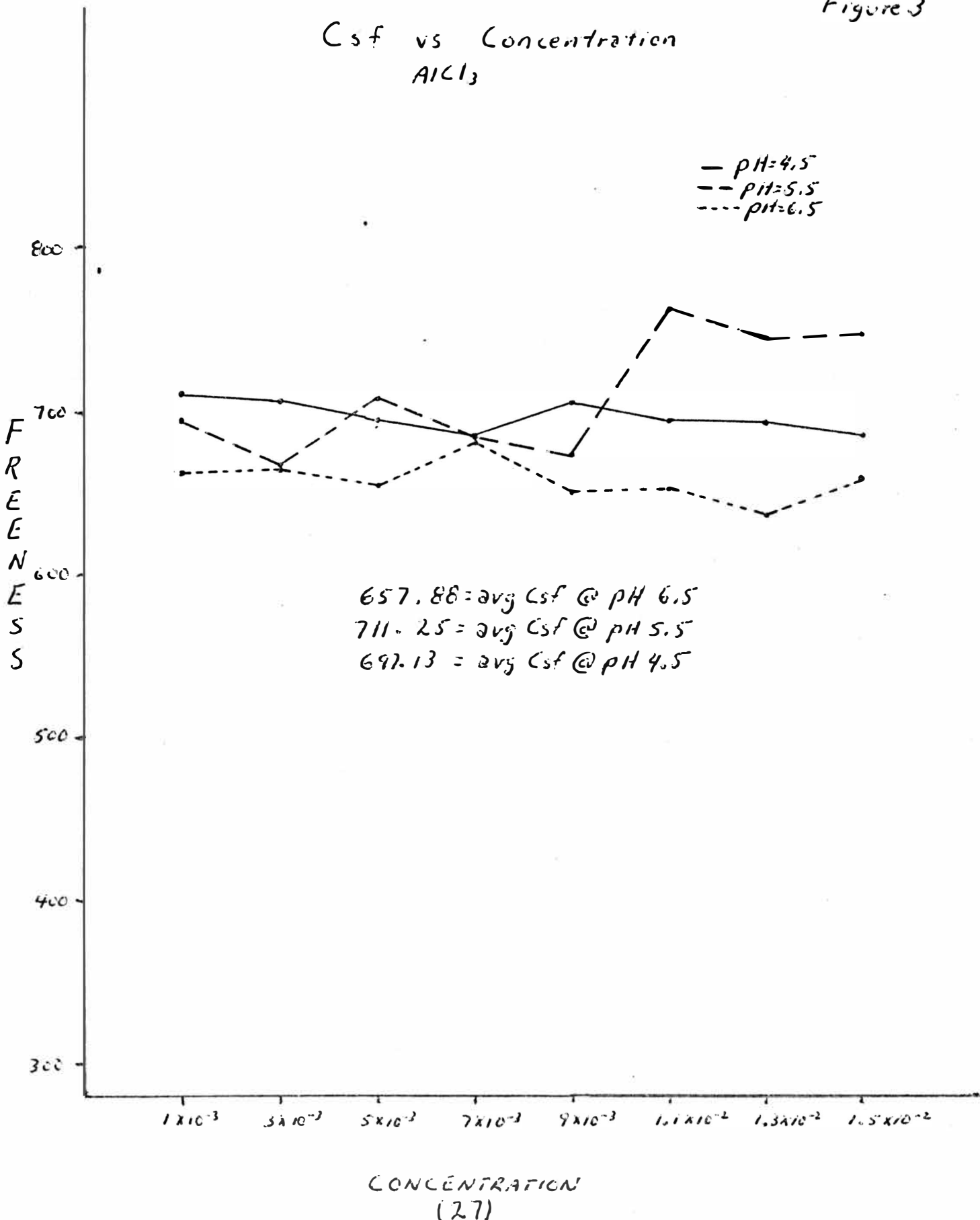
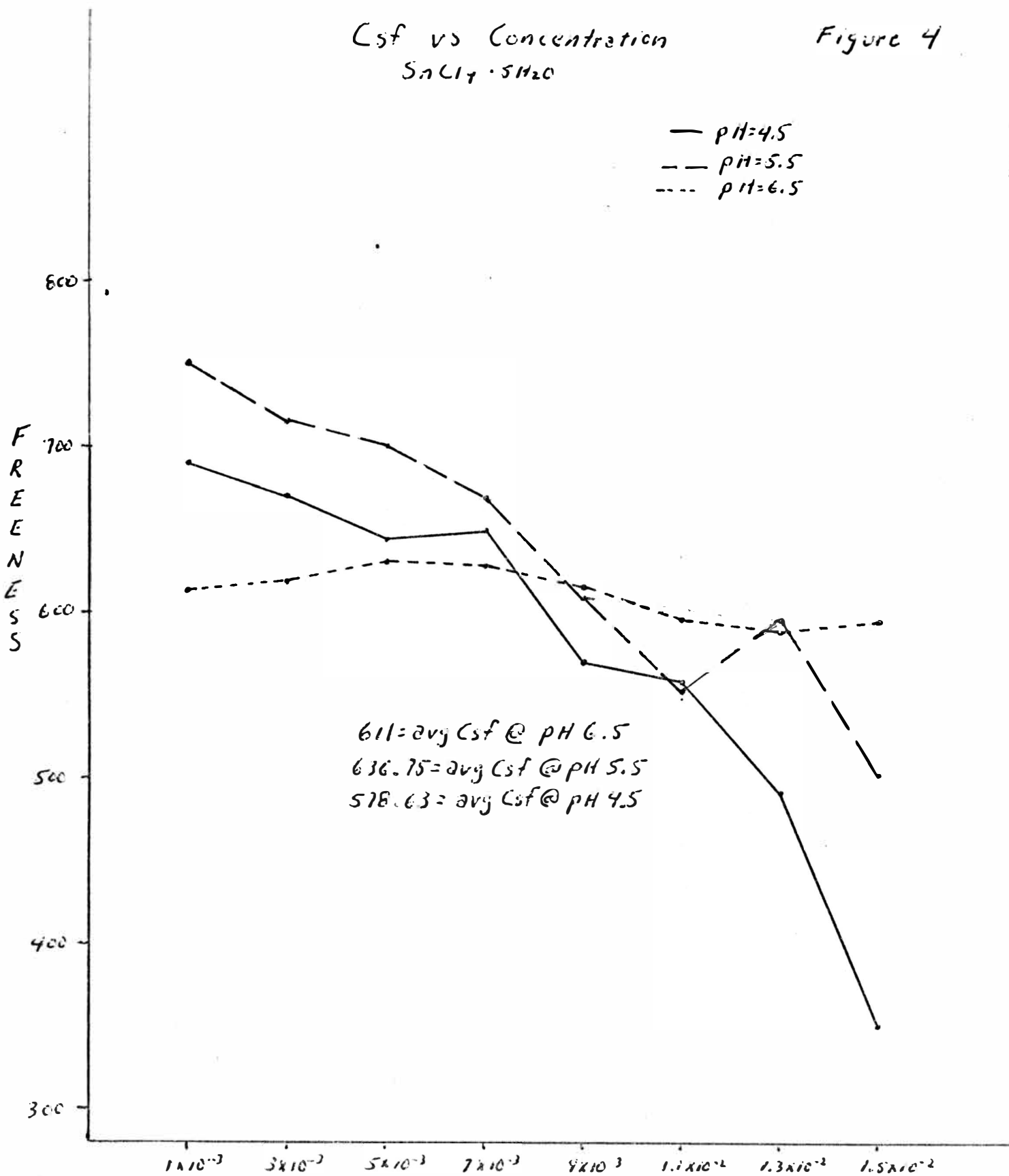


Figure 3



Csf vs Concentration  
 $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$

Figure 4



CONCENTRATION

(28)

Csf vs pH  
NaCl

Figure 5

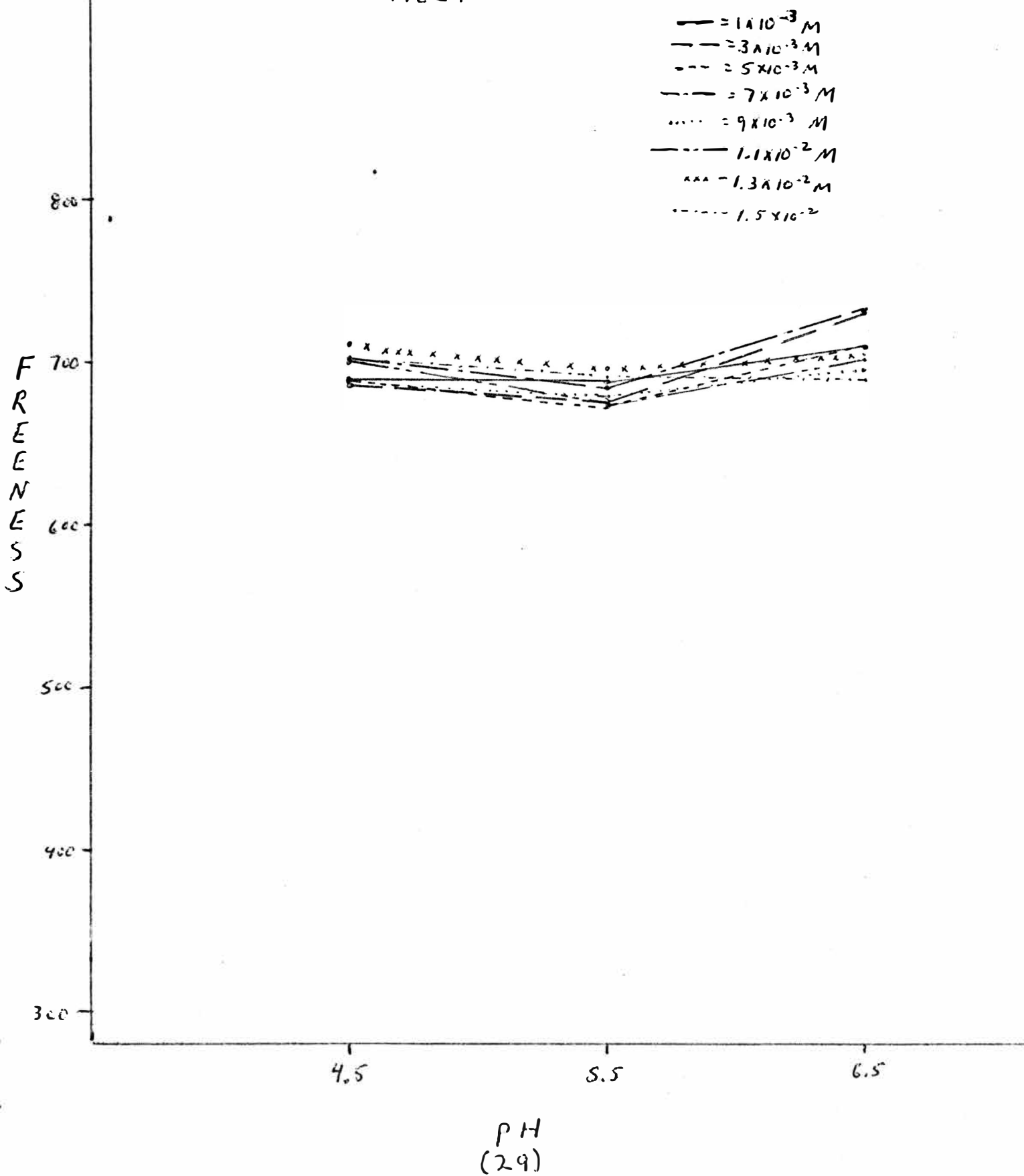




Figure 5A Csf Averages, Averaged over pH Ranges

NaCl

699.33 = avg Csf @  $1 \times 10^{-3} M$   
 698.67 = avg Csf @  $3 \times 10^{-3} M$   
 694.00 = avg Csf @  $5 \times 10^{-3} M$   
 701.67 = avg Csf @  $7 \times 10^{-3} M$   
 686.67 = avg Csf @  $9 \times 10^{-3} M$   
 691.67 = avg Csf @  $1.1 \times 10^{-2} M$   
 703.67 = avg Csf @  $1.3 \times 10^{-2} M$   
 696.67 = avg Csf @  $1.5 \times 10^{-2} M$

CaCl<sub>2</sub>

694.67 = avg Csf @  $1 \times 10^{-3} M$   
 691.33 = avg Csf @  $3 \times 10^{-3} M$   
 682.33 = avg Csf @  $5 \times 10^{-3} M$   
 688.33 = avg Csf @  $7 \times 10^{-3} M$   
 694.00 = avg Csf @  $9 \times 10^{-3} M$   
 678.67 = avg Csf @  $1.1 \times 10^{-2} M$   
 687.00 = avg Csf @  $1.3 \times 10^{-2} M$   
 689.00 = avg Csf @  $1.5 \times 10^{-2} M$

AlCl<sub>3</sub>

689.33 = avg Csf @  $1 \times 10^{-3} M$   
 679.33 = avg Csf @  $3 \times 10^{-3} M$   
 687.33 = avg Csf @  $5 \times 10^{-3} M$   
 683.00 = avg Csf @  $7 \times 10^{-3} M$   
 676.33 = avg Csf @  $9 \times 10^{-3} M$   
 704.00 = avg Csf @  $1.1 \times 10^{-2} M$   
 692.33 = avg Csf @  $1.3 \times 10^{-2} M$   
 678.33 = avg Csf @  $1.5 \times 10^{-2} M$

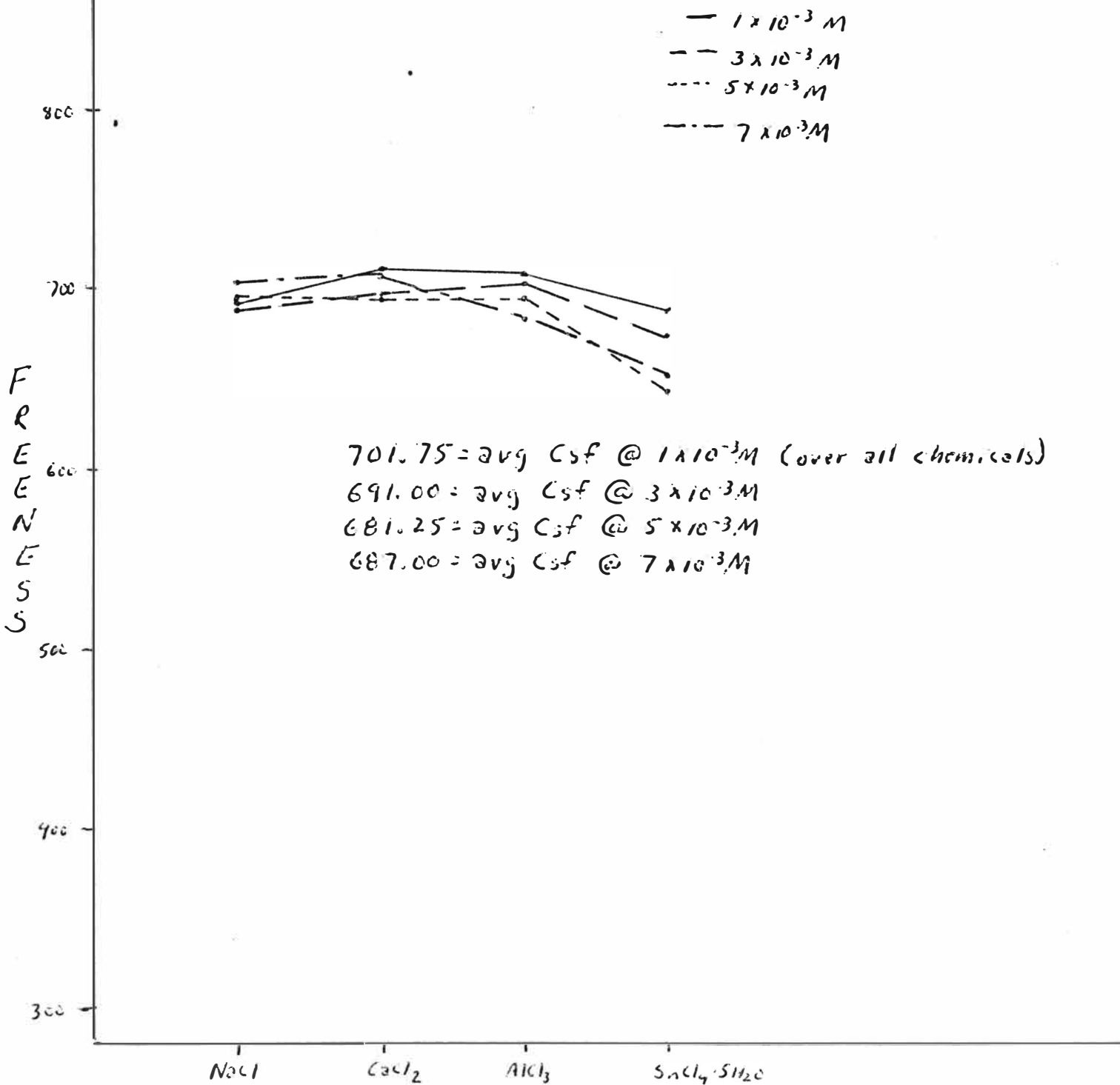
SnCl<sub>4</sub> · 5H<sub>2</sub>O

684.00 = avg Csf @  $1 \times 10^{-3} M$   
 669.67 = avg Csf @  $3 \times 10^{-3} M$   
 656.67 = avg Csf @  $5 \times 10^{-3} M$   
 648.33 = avg Csf @  $7 \times 10^{-3} M$   
 597.67 = avg Csf @  $9 \times 10^{-3} M$   
 569.33 = avg Csf @  $1.1 \times 10^{-2} M$   
 557.33 = avg Csf @  $1.3 \times 10^{-2} M$   
 483.33 = avg Csf @  $1.5 \times 10^{-2} M$

Csf vs chemical Type

Figure 6A

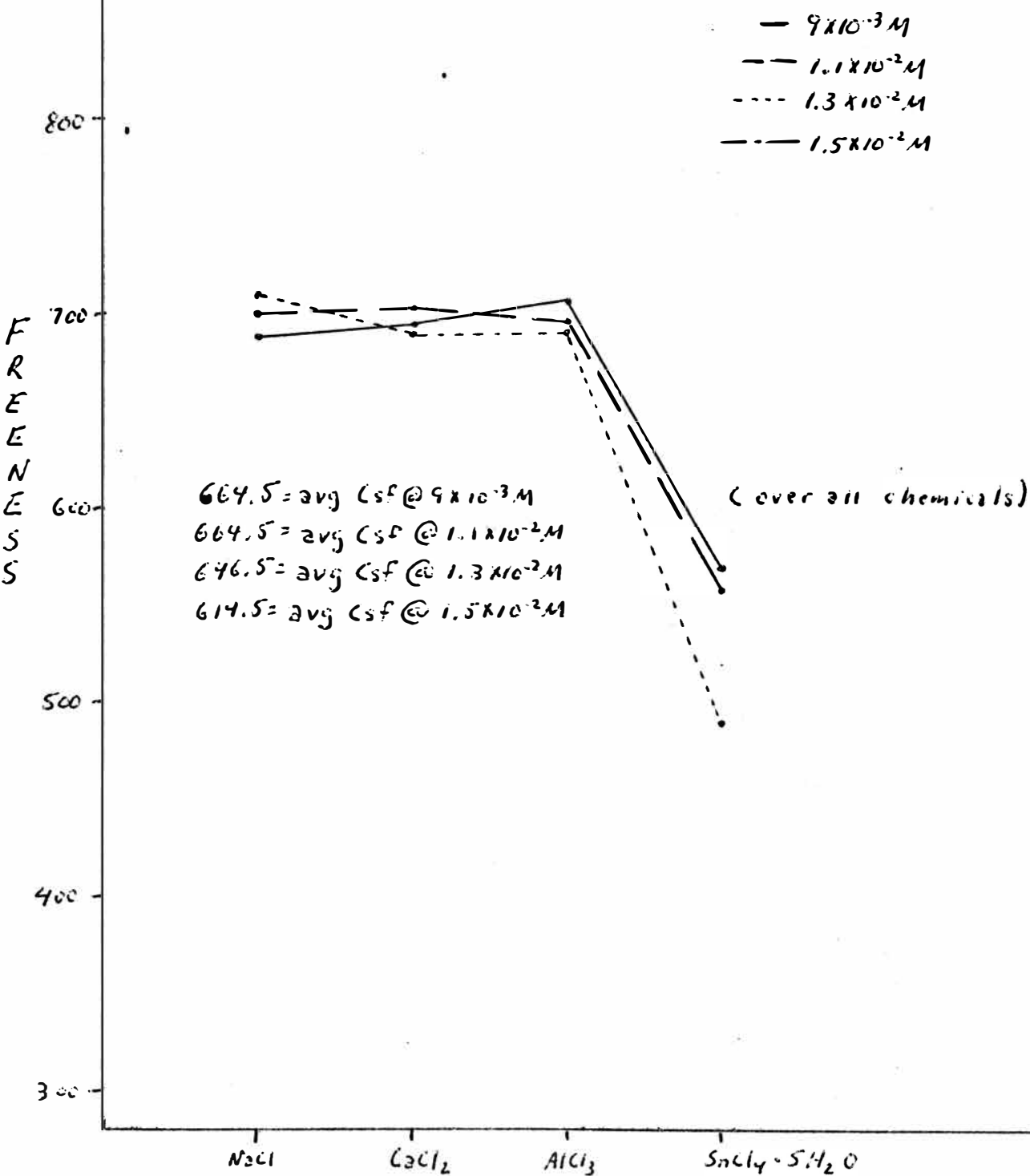
for conc.  $1 \times 10^{-3} M$  through  $7 \times 10^{-3} M$   
 $pH = 4.5$



CHEMICAL  
(21)

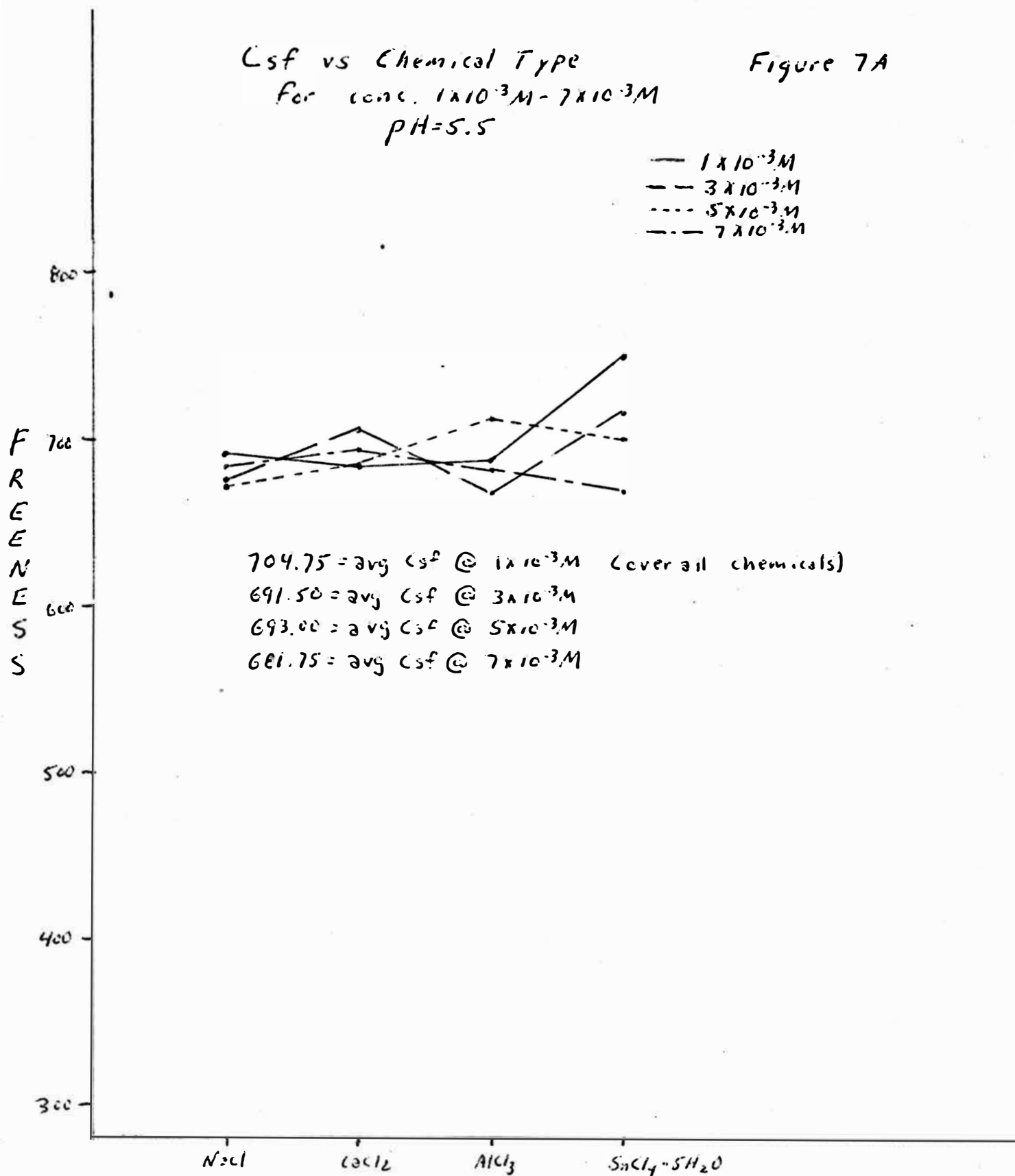
Csf vs Chemical Type  
for conc.  $9 \times 10^{-3} - 1.5 \times 10^{-2} M$   
pH = 4.5

Figure 6B

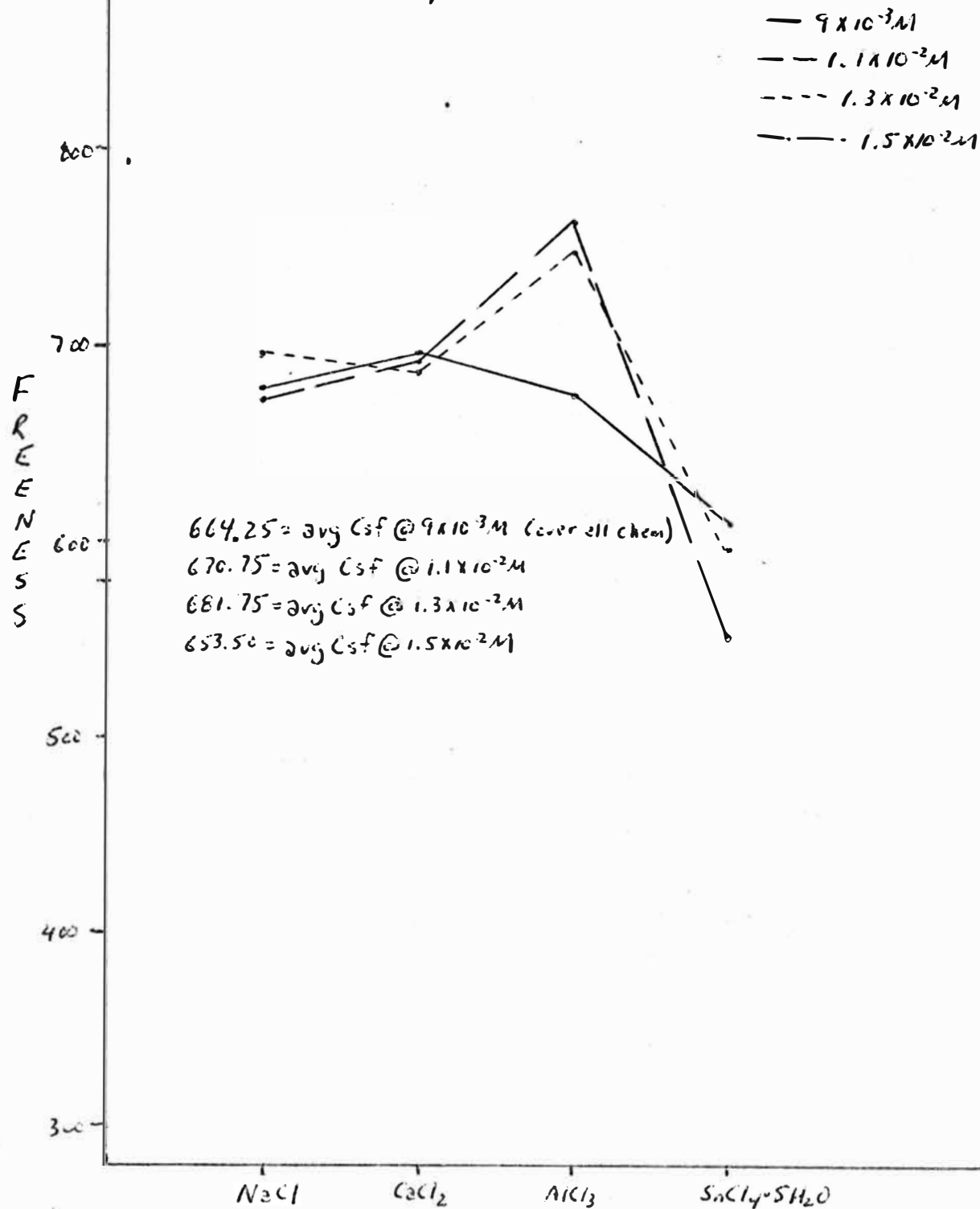


Csf vs Chemical Type  
For conc.  $1 \times 10^{-3} M - 7 \times 10^{-3} M$   
pH=5.5

Figure 7A

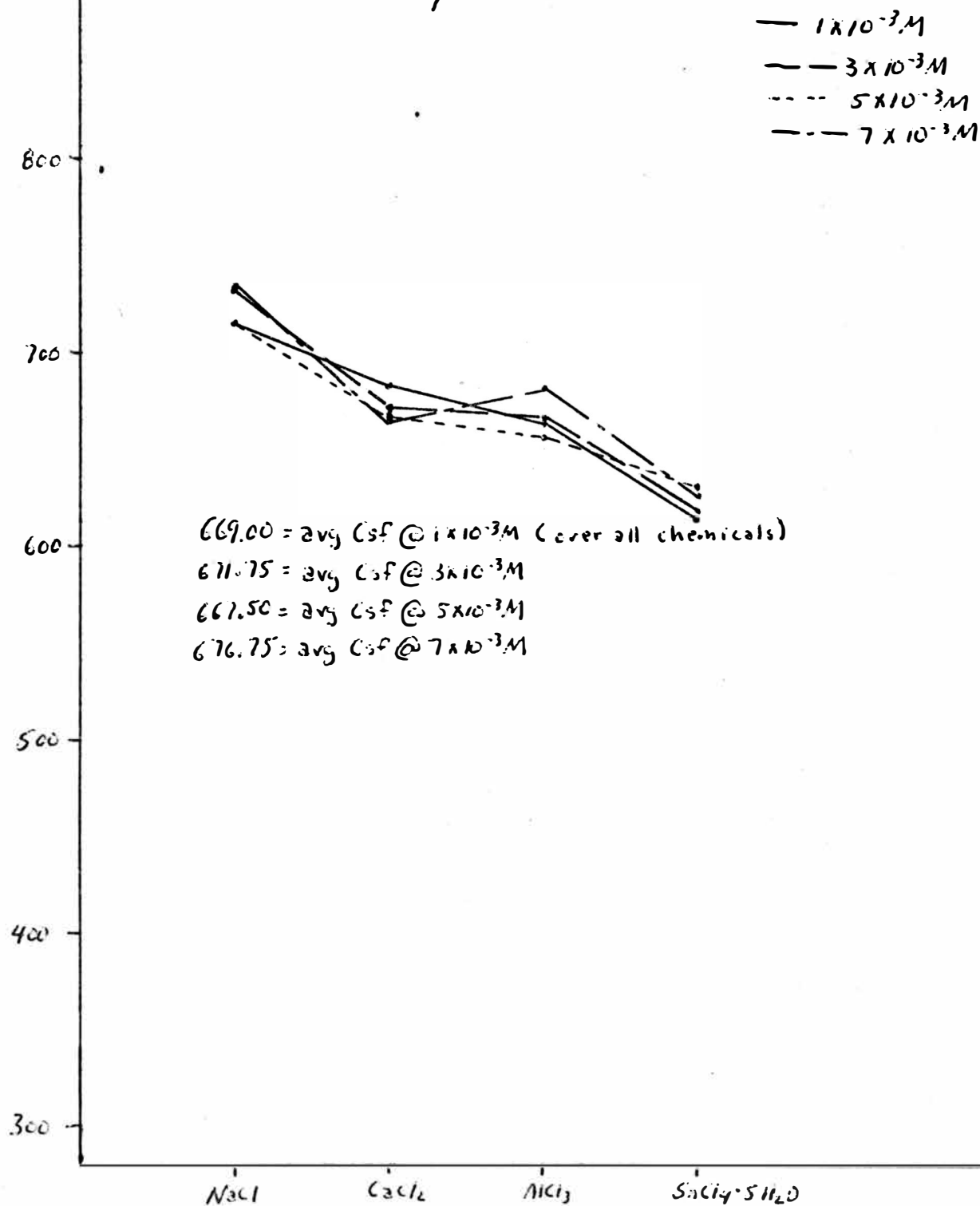


CSF vs Chemical Type Figure 7B  
 for conc.  $9 \times 10^{-3} M - 1.5 \times 10^{-2} M$   
 $pH = 5.5$



CHEMICAL

$\text{Csf}$  vs Chemical Type      Figure 8A  
 for conc.  $1 \times 10^{-3} \text{M} - 7 \times 10^{-3} \text{M}$   
 $\text{pH} = 6.5$



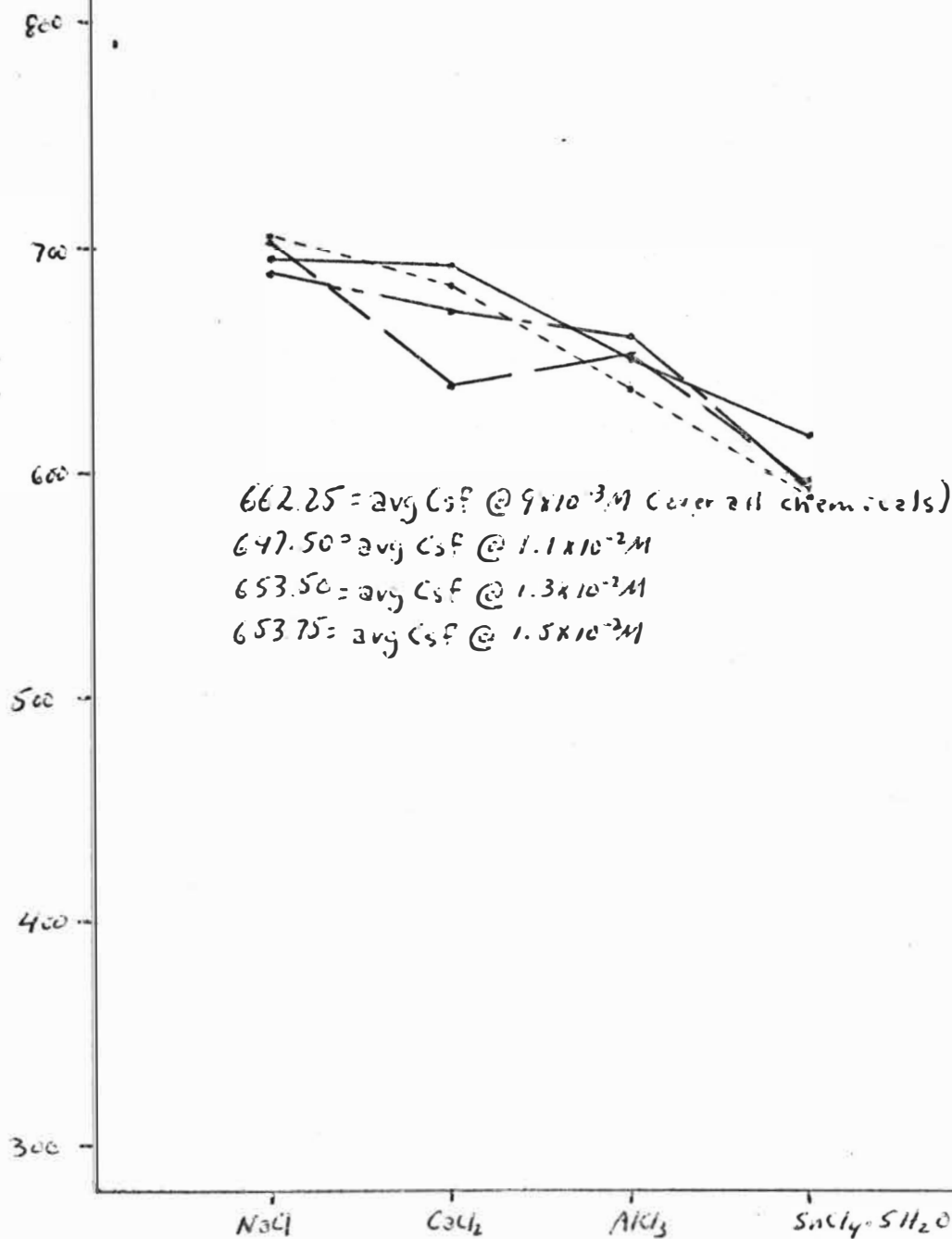
CHEMICAL

## Csf vs Chemical Type

Figure 8B

For conc  $9 \times 10^{-3} M - 1.5 \times 10^{-2} M$ 

pH=6.5

— =  $9 \times 10^{-3} M$ — — =  $1.1 \times 10^{-2} M$ - - - =  $1.3 \times 10^{-2} M$ - · - =  $1.5 \times 10^{-2} M$ FRE  
N  
SCHEMICAL  
(36)

## ANALYSIS OF VARIANCE

Figure 9

R.M., CELL SIZE = 1.000000

SOURCE	SUM OF SQUARES	DF	MEAN SQUARE	F	PROB
SUBCLASSES	517949.00	95	3346.63	2.836	0.0000
A	26241.00	7	3463.00	2.935	0.014
B	123579.50	3	41193.17	34.909	0.0000
F	4989.50	2	2494.75	2.114	0.133
AB	79054.00	21	3764.48	3.190	0.001
AP	6724.00	14	623.14	0.528	0.902
BP	27800.50	6	4633.42	3.927	0.003
ABP	49500.50	42	1180.91		

2.114	0.133
3.190	0.001
0.528	0.902
3.927	0.003

 $A = \text{concentration}$ 

$$F_{.05, 21, 42} \approx 1.84$$

 $B = \text{chemical}$ 

$$F_{AB} = 3.190 \quad 3.190 > 1.84; .001 < .05$$

 $P = \text{pH}$ 

$$F_{.05, 14, 42} \approx 1.95$$

$$F_{AP} = .528 \quad .528 < 1.95; .902 > .05$$

$$F_{BP} = 3.927$$

$$F_{.05, 6, 42} \approx 2.34 \quad 3.927 > 2.34; .003 < .05$$

(37)



## Basic Side Data Set #1

12

CHEMICAL	REFINING TIME	PH	(MOLARITY) CONCENTRATION	(mV) $\beta$ p	Csf	
—	7 min	7.5	—	-3.21	691	
KCl	"	"	$1 \times 10^{-3}$	-3.07	703	648.89 = avg Csf @ $1 \times 10^{-3} M$
KCl	"	"	$3 \times 10^{-3}$	-2.15	710	650.56 = avg Csf @ $3 \times 10^{-3} M$
KCl	"	"	$5 \times 10^{-3}$	+1.17	714	643.56 = avg Csf @ $5 \times 10^{-3} M$
KCl	"	"	$7 \times 10^{-3}$	+3.01	709	638.11 = avg Csf @ $7 \times 10^{-3} M$
KCl	"	"	$9 \times 10^{-3}$	+3.05	689	625.67 = avg Csf @ $9 \times 10^{-3} M$
KCl	"	"	$1.1 \times 10^{-2}$	+2.68	692	617.11 = avg Csf @ $1.1 \times 10^{-2} M$
KCl	"	"	$1.3 \times 10^{-2}$	+2.47	697	602.33 = avg Csf @ $1.3 \times 10^{-2} M$
KCl	"	"	$1.5 \times 10^{-2}$	+3.11	706	581.33 = avg Csf @ $1.5 \times 10^{-2} M$
K <sub>2</sub> SO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-6.10	680	
K <sub>2</sub> SO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-5.93	672	
K <sub>2</sub> SO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-1.27	684	
K <sub>2</sub> SO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-1.41	679	
K <sub>2</sub> SO <sub>4</sub>	"	"	$9 \times 10^{-3}$	-2.05	666	
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-2.00	666	
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-3.15	659	
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-4.11	642	
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-6.21	641	
K <sub>2</sub> HPO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-6.08	639	
K <sub>2</sub> HPO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-5.11	616	673.58 = avg Csf for KCl
K <sub>2</sub> HPO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-5.31	623	634.42 = avg Csf for K <sub>2</sub> SO <sub>4</sub>
K <sub>2</sub> HPO <sub>4</sub>	"	"	$9 \times 10^{-3}$	+1.71	625	569.83 = avg Csf for K <sub>2</sub> HPO <sub>4</sub>
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-6.12	590	
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-6.84	567	
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-7.01	543	

659.67 = avg Csf @ pH = 7.5

# Basic Side Data Set #2

13

CHEMICAL	REFINING TIME	PH	(MOLARITY) CONCENTRATION	(mv) E <sub>sp</sub>	Csf
-	7 min	8.5	-	-4.10	685
KCl	"	"	$1 \times 10^{-3}$	-3.98	682
KCl	"	"	$3 \times 10^{-3}$	-3.71	681
KCl	"	"	$5 \times 10^{-3}$	-2.15	690
KCl	"	"	$7 \times 10^{-3}$	-2.41	674
KCl	"	"	$9 \times 10^{-3}$	-3.01	666
KCl	"	"	$1.1 \times 10^{-2}$	-3.37	671
KCl	"	"	$1.3 \times 10^{-2}$	-1.04	647
KCl	"	"	$1.5 \times 10^{-2}$	-5.14	619
K <sub>2</sub> SO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-3.02	623
K <sub>2</sub> SO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-2.91	641
K <sub>2</sub> SO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-4.00	638
K <sub>2</sub> SO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-4.15	630
K <sub>2</sub> SO <sub>4</sub>	"	"	$9 \times 10^{-3}$	-5.07	614
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-7.11	628
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-6.77	618
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-5.38	597
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-4.01	626
K <sub>2</sub> HPO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-4.99	618
K <sub>2</sub> HPO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-3.07	618
K <sub>2</sub> HPO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-5.11	617
K <sub>2</sub> HPO <sub>4</sub>	"	"	$9 \times 10^{-3}$	-5.73	587
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-5.84	545
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-5.11	519
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-7.11	497

622.75 = avg Csf @ pH=8.5

(39)

## Basic Side Data Set #3

14

CHEMICAL	REFINING TIME	pH	(MOLARITY) CONCENTRATION	(mV) $\gamma \cdot p$	Csf
-	7 min.	9.5	-	-6.10	662
KCl	"	"	$1 \times 10^{-3}$	-7.11	671
KCl	"	"	$3 \times 10^{-3}$	-5.40	686
KCl	"	"	$5 \times 10^{-3}$	-7.33	666
KCl	"	"	$7 \times 10^{-3}$	-4.12	664
KCl	"	"	$9 \times 10^{-3}$	-3.91	657
KCl	"	"	$1.1 \times 10^{-2}$	-1.07	657
KCl	"	"	$1.3 \times 10^{-2}$	-8.04	619
KCl	"	"	$1.5 \times 10^{-2}$	-9.11	596
K <sub>2</sub> SO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-7.04	604
K <sub>2</sub> SO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-7.11	618
K <sub>2</sub> SO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-11.04	621
K <sub>2</sub> SO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-9.12	627
K <sub>2</sub> SO <sub>4</sub>	"	"	$9 \times 10^{-3}$	-5.31	617
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-12.01	605
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-10.11	600
K <sub>2</sub> SO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-11.11	597
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1 \times 10^{-3}$	-4.42	610
K <sub>2</sub> HPO <sub>4</sub>	"	"	$3 \times 10^{-3}$	-6.01	590
K <sub>2</sub> HPO <sub>4</sub>	"	"	$5 \times 10^{-3}$	-11.71	545
K <sub>2</sub> HPO <sub>4</sub>	"	"	$7 \times 10^{-3}$	-12.00	520
K <sub>2</sub> HPO <sub>4</sub>	"	"	$9 \times 10^{-3}$	-11.85	510
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.1 \times 10^{-2}$	-14.01	500
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.3 \times 10^{-2}$	-19.31	475
K <sub>2</sub> HPO <sub>4</sub>	"	"	$1.5 \times 10^{-2}$	-19.05	435

625.9444 = avg Csf for Basic Side

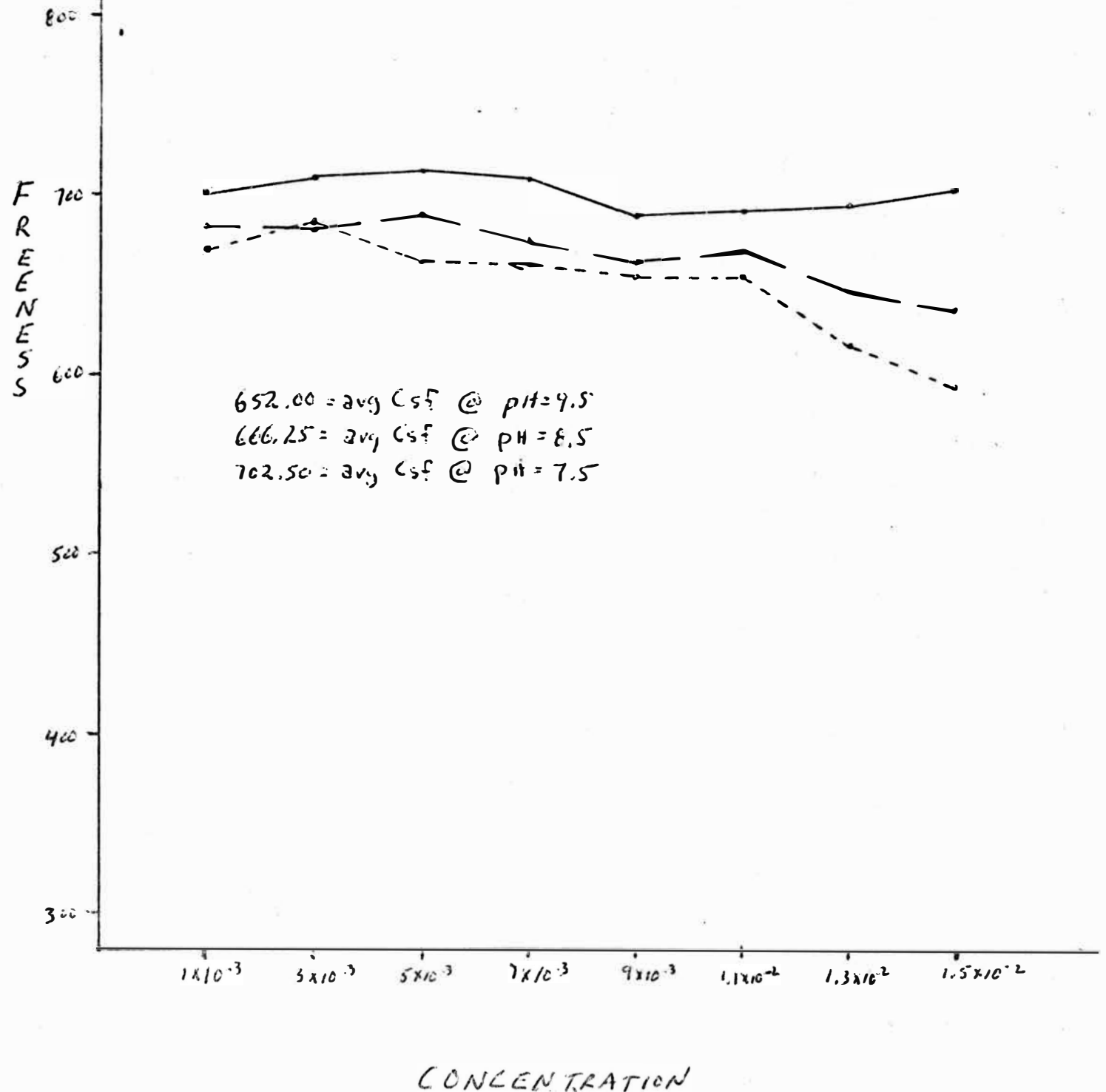
595.42 = avg Csf @ pH = 9.5

(40)

Csf vs Concentration  
KCl

Figure 10

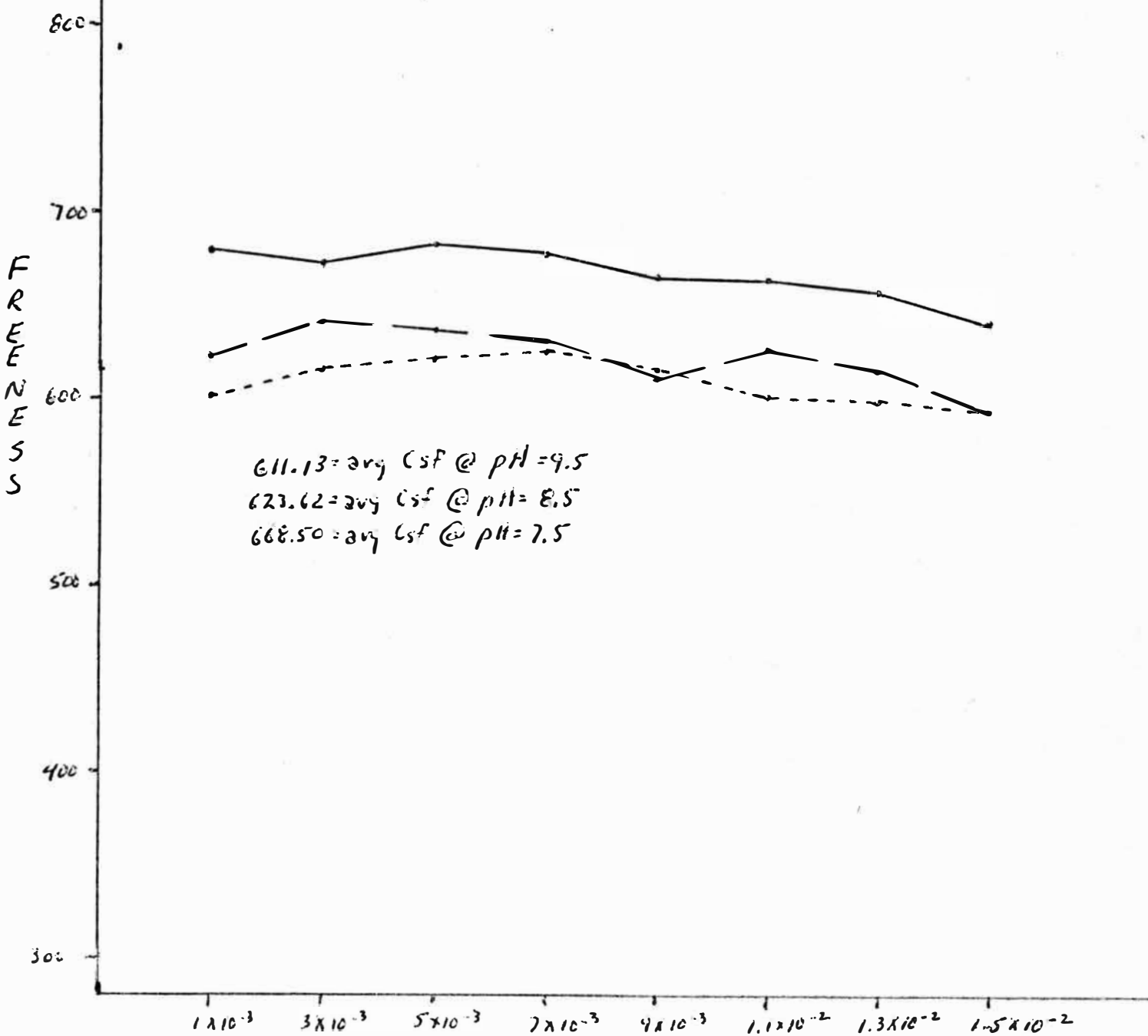
— pH=7.5  
- - pH=8.5  
- - - pH=9.5



Csf vs Concentration  
K<sub>2</sub>SO<sub>4</sub>

Figure 11

— pH 7.5  
— pH 6.5  
--- pH 4.5



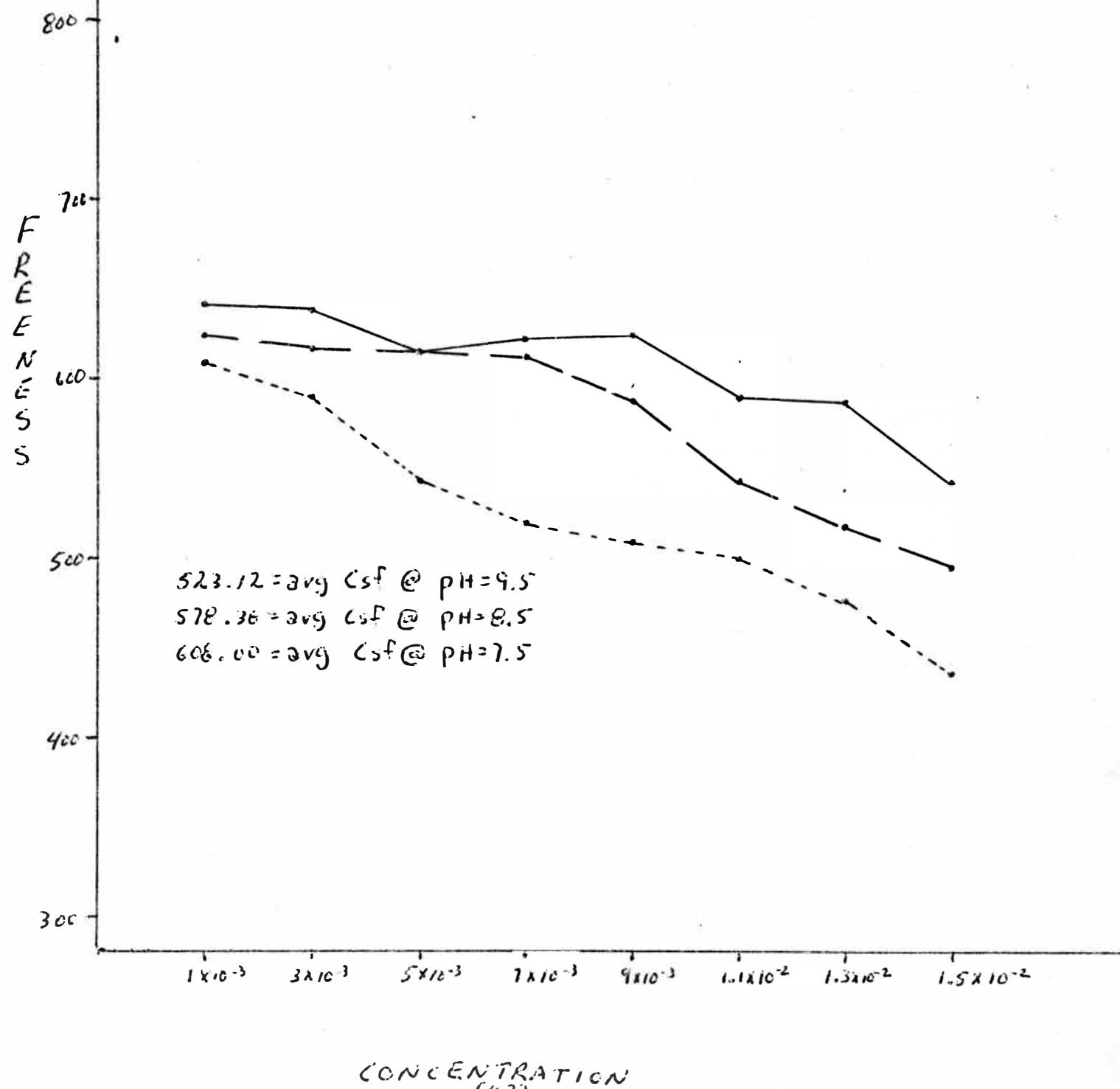
CONCENTRATION

(42)

*Csf vs Concentration*  
 $K_2HPO_4$

Figure 12

— pH=7.5  
 - - pH=8.5  
 ---- pH=9.5



Csf vs pH  
KCl

Figure 13

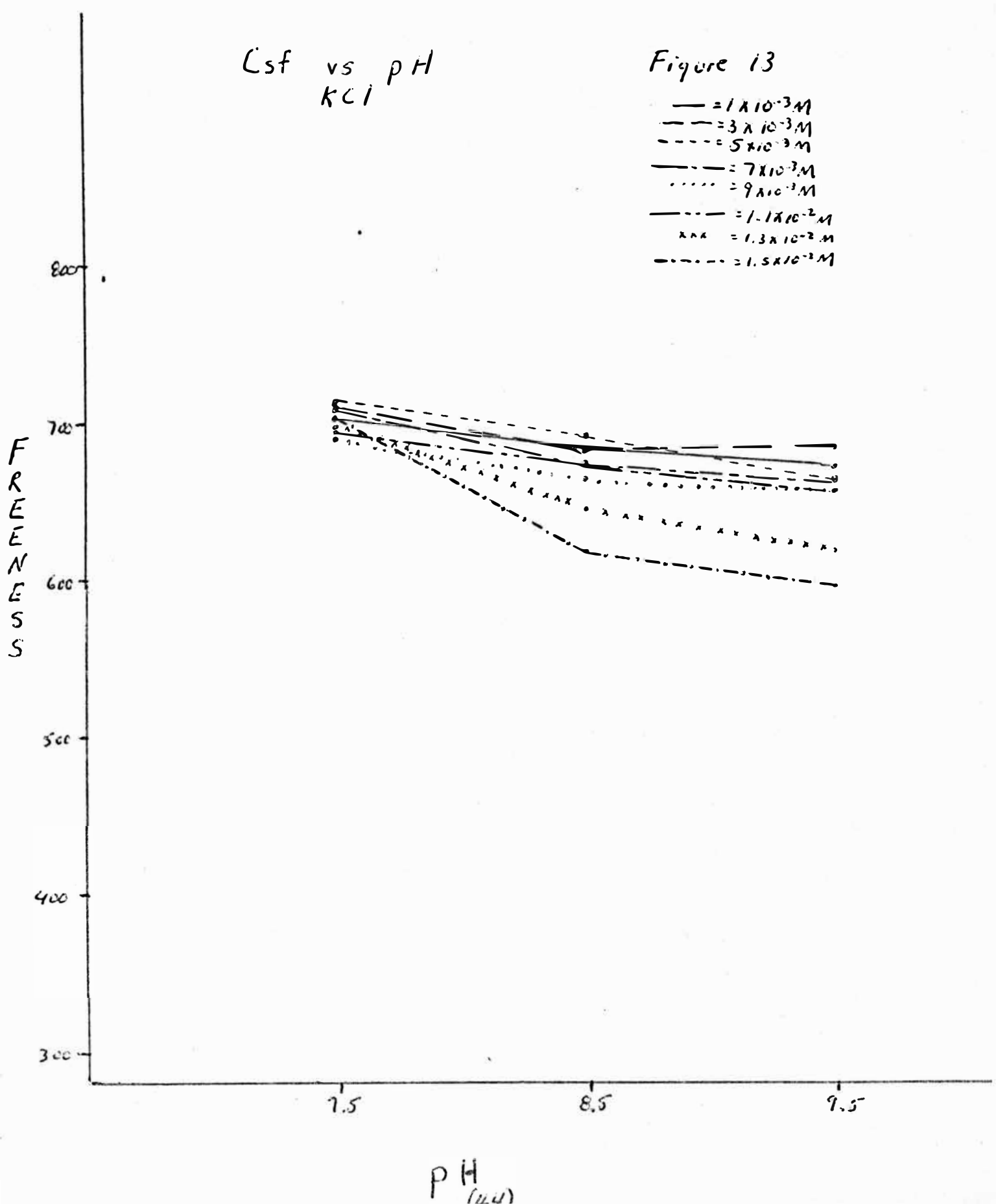


Figure 13A Csf Averages, Averaged over pH Ranges

KCl

685.33 = avg Csf @  $1 \times 10^{-3} M$   
 692.33 = avg Csf @  $3 \times 10^{-3} M$   
 690.00 = avg Csf @  $5 \times 10^{-3} M$   
 682.33 = avg Csf @  $7 \times 10^{-3} M$   
 670.67 = avg Csf @  $9 \times 10^{-3} M$   
 673.33 = avg Csf @  $1.1 \times 10^{-2} M$   
 654.33 = avg Csf @  $1.3 \times 10^{-2} M$   
 640.33 = avg Csf @  $1.5 \times 10^{-2} M$

K<sub>2</sub>SO<sub>4</sub>

635.67 = avg Csf @  $1 \times 10^{-3} M$   
 643.67 = avg Csf @  $3 \times 10^{-3} M$   
 647.67 = avg Csf @  $5 \times 10^{-3} M$   
 645.33 = avg Csf @  $7 \times 10^{-3} M$   
 632.33 = avg Csf @  $9 \times 10^{-3} M$   
 633.00 = avg Csf @  $1.1 \times 10^{-2} M$   
 625.67 = avg Csf @  $1.3 \times 10^{-2} M$   
 612.00 = avg Csf @  $1.5 \times 10^{-2} M$

K<sub>2</sub>HPO<sub>4</sub>

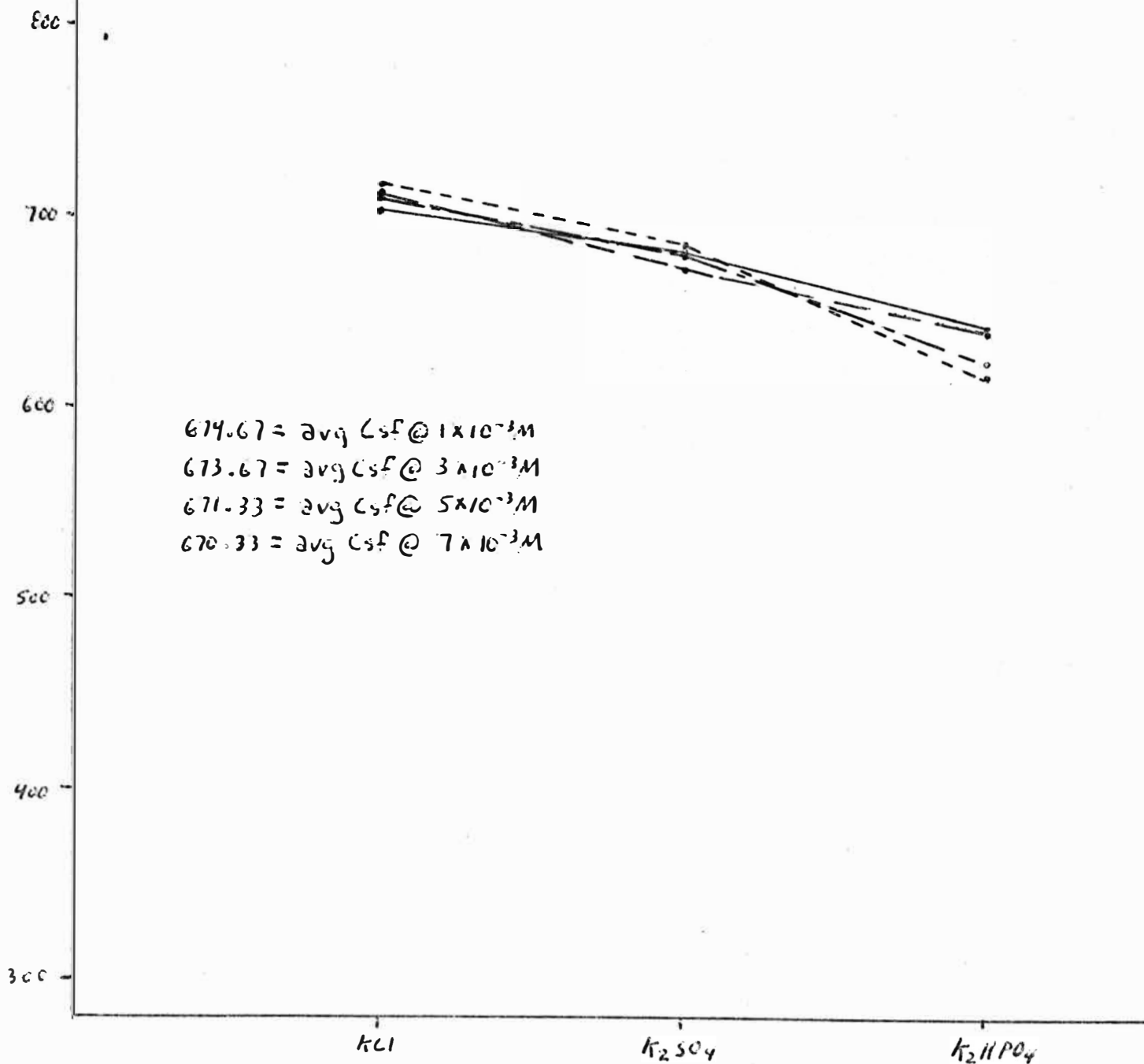
625.67 = avg Csf @  $1 \times 10^{-3} M$   
 615.67 = avg Csf @  $3 \times 10^{-3} M$   
 593.00 = avg Csf @  $5 \times 10^{-3} M$   
 586.67 = avg Csf @  $7 \times 10^{-3} M$   
 574.00 = avg Csf @  $9 \times 10^{-3} M$   
 545.00 = avg Csf @  $1.1 \times 10^{-2} M$   
 527.00 = avg Csf @  $1.3 \times 10^{-2} M$   
 491.67 = avg Csf @  $1.5 \times 10^{-2} M$



Csf vs Chemical Type  
for conc.  $1 \times 10^{-3} M - 7 \times 10^{-3} M$   
pH = 7.5

Figure 14A

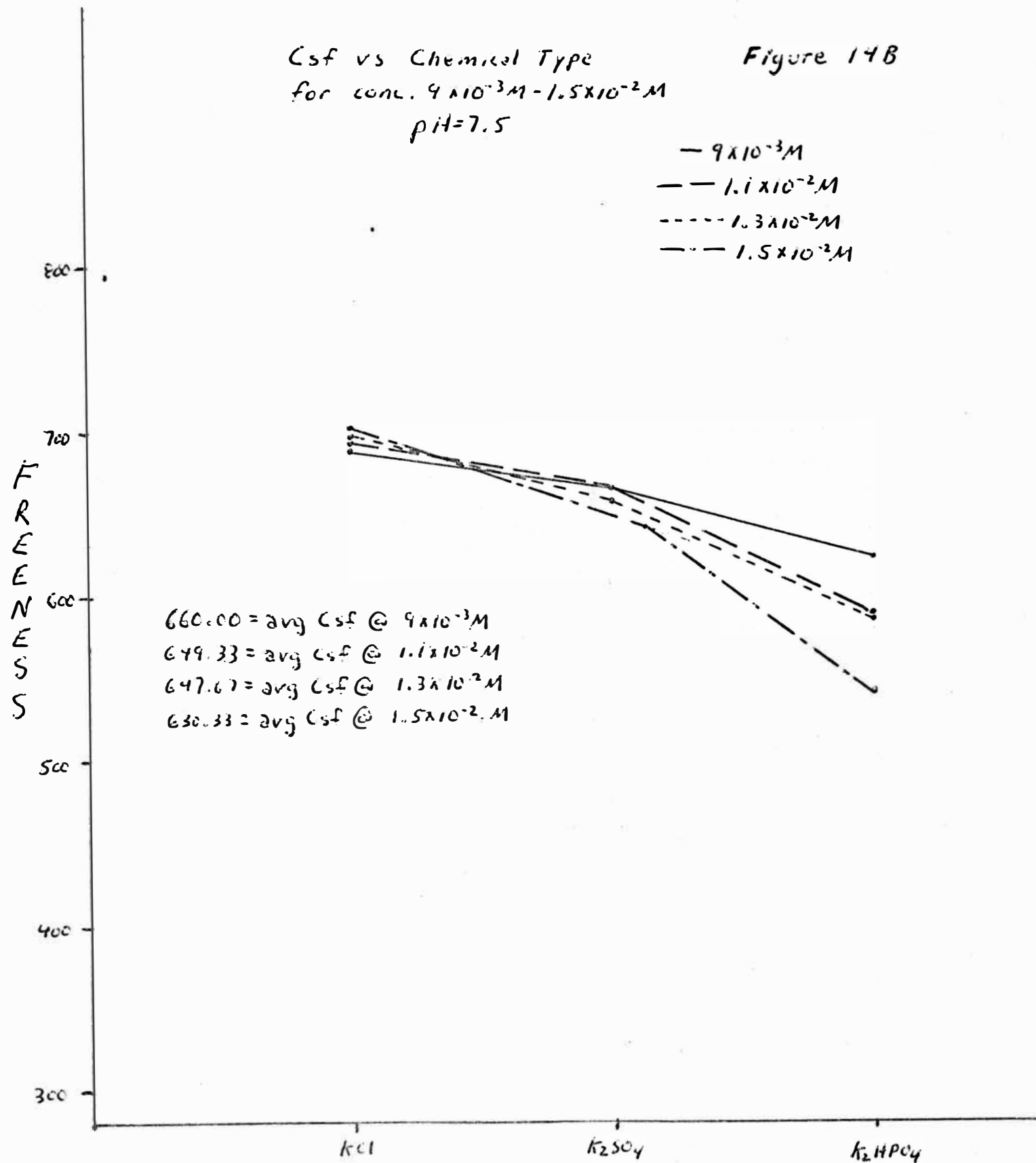
—  $1 \times 10^{-3} M$   
- -  $3 \times 10^{-3} M$   
- - -  $5 \times 10^{-3} M$   
- - -  $7 \times 10^{-3} M$



CHEMICAL

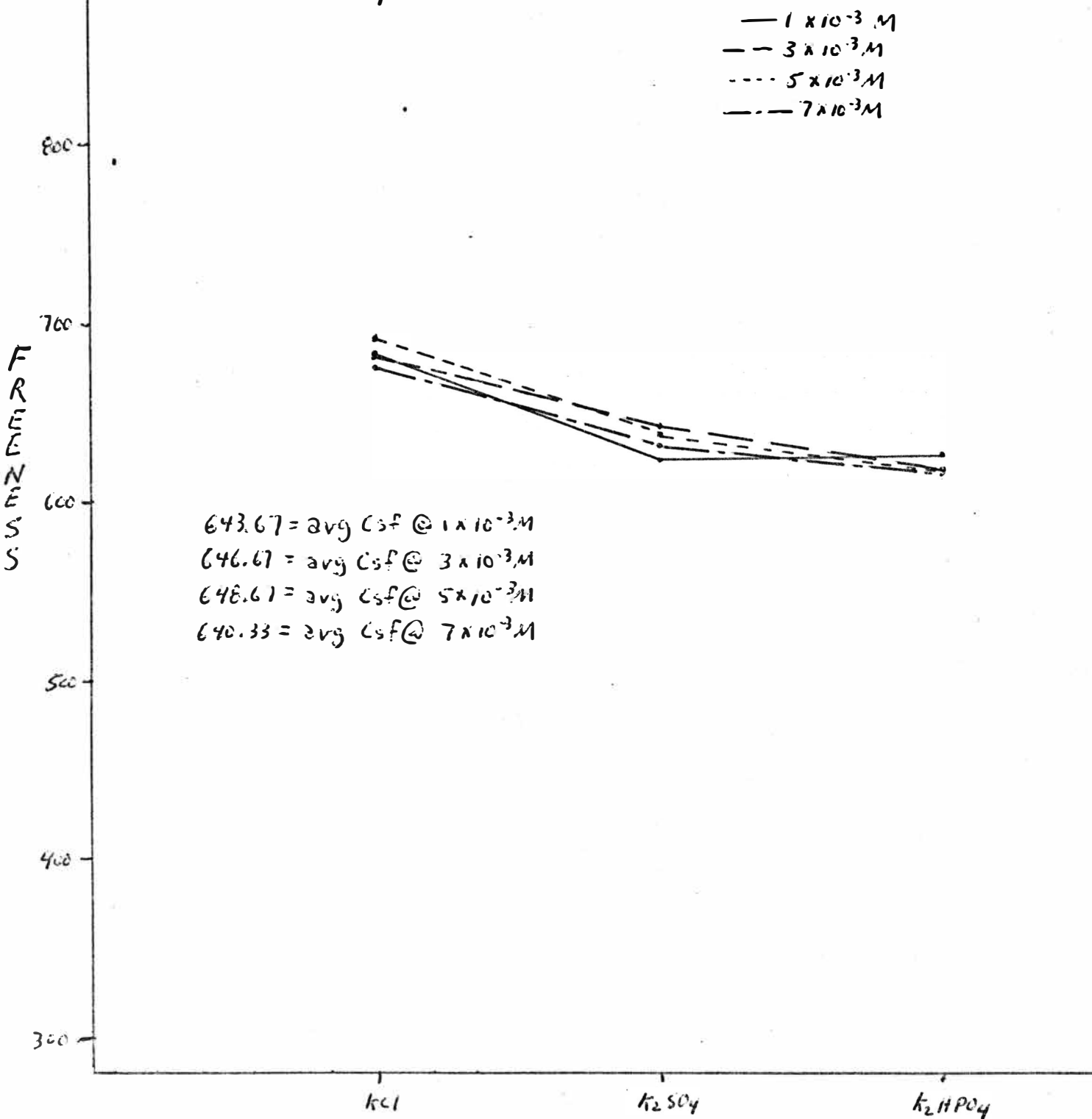
Csf vs Chemical Type  
for conc.  $9 \times 10^{-3} M - 1.5 \times 10^{-2} M$   
pH=7.5

Figure 14B



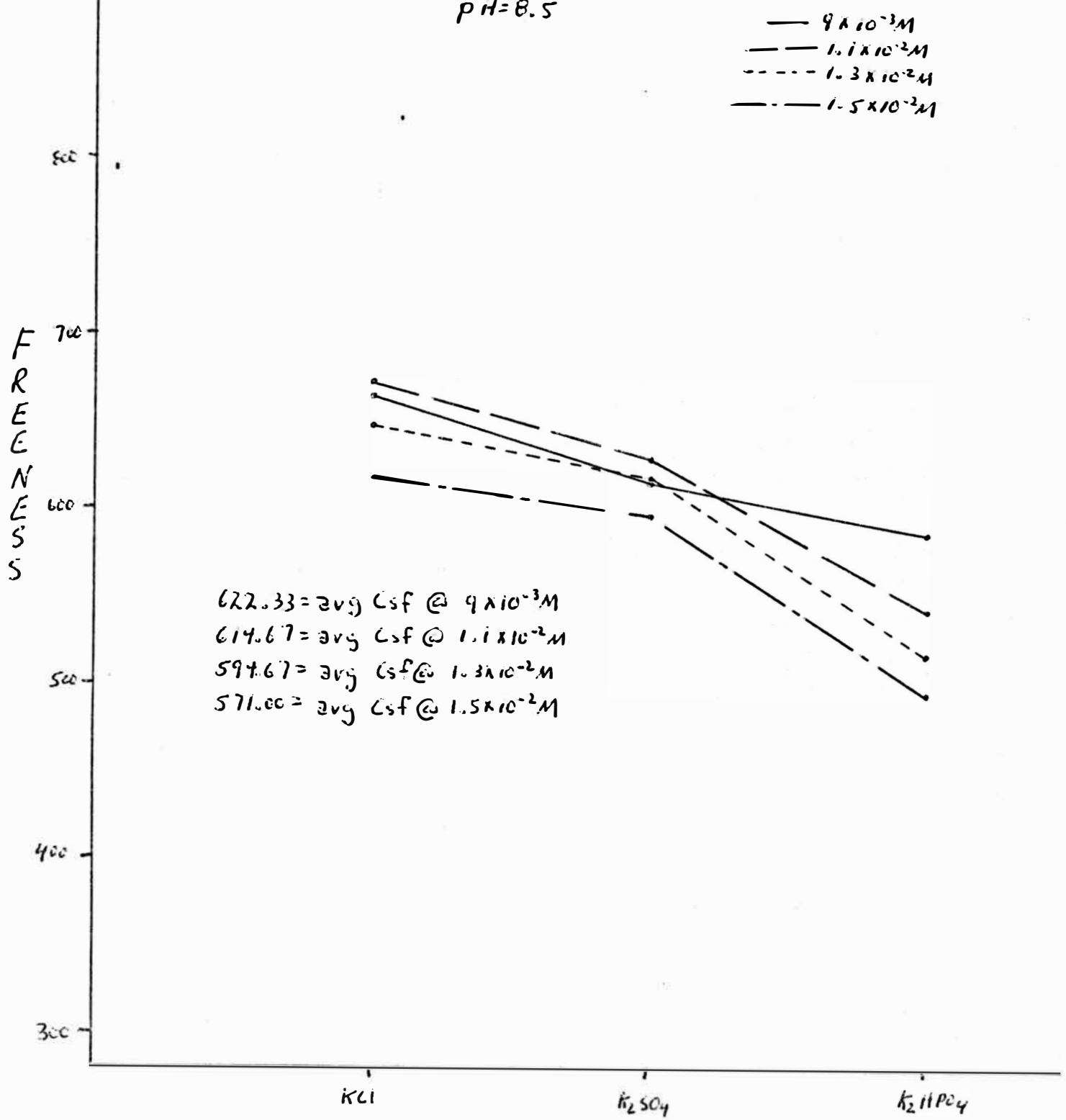
Csf vs Chemical Type  
for conc.  $1 \times 10^{-3} M$  -  $7 \times 10^{-3} M$   
pH = 8.5

Figure 15A



CHEMICAL  
(48)

Csf vs Chemical Type Figure 15B  
 for conc.  $9 \times 10^{-3} M - 1.5 \times 10^{-2} M$   
 $pH = 8.5$



672.33 = avg Csf @  $9 \times 10^{-3} M$   
 614.67 = avg Csf @  $1.1 \times 10^{-2} M$   
 594.67 = avg Csf @  $1.3 \times 10^{-2} M$   
 571.00 = avg Csf @  $1.5 \times 10^{-2} M$

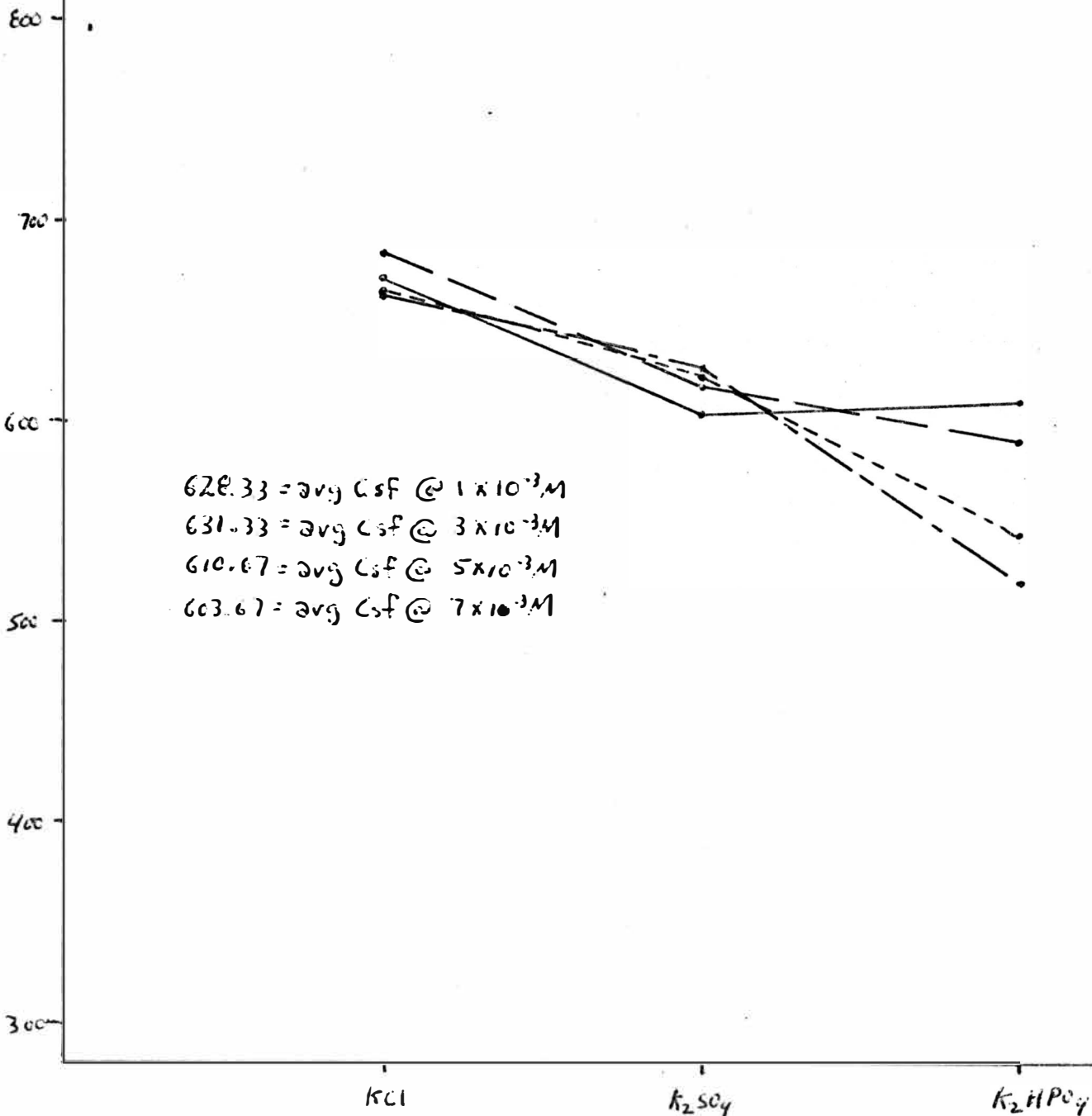
# Csf vs Chemical Type Figure 16.A

For conc.  $1 \times 10^{-3} M - 7 \times 10^{-3} M$

pH = 9.5

—  $1 \times 10^{-3} M$   
 —  $3 \times 10^{-3} M$   
 - - -  $5 \times 10^{-3} M$   
 - - -  $7 \times 10^{-3} M$

F  
R  
E  
E  
N  
E  
S  
S



628.33 = avg Csf @  $1 \times 10^{-3} M$

631.33 = avg Csf @  $3 \times 10^{-3} M$

610.67 = avg Csf @  $5 \times 10^{-3} M$

603.67 = avg Csf @  $7 \times 10^{-3} M$

CHEMICAL  
(SO)

Csf vs Chemical Type Figure 16B  
 for conc.  $9 \times 10^{-3} M - 1.5 \times 10^{-2} M$   
 $pH = 9.5$

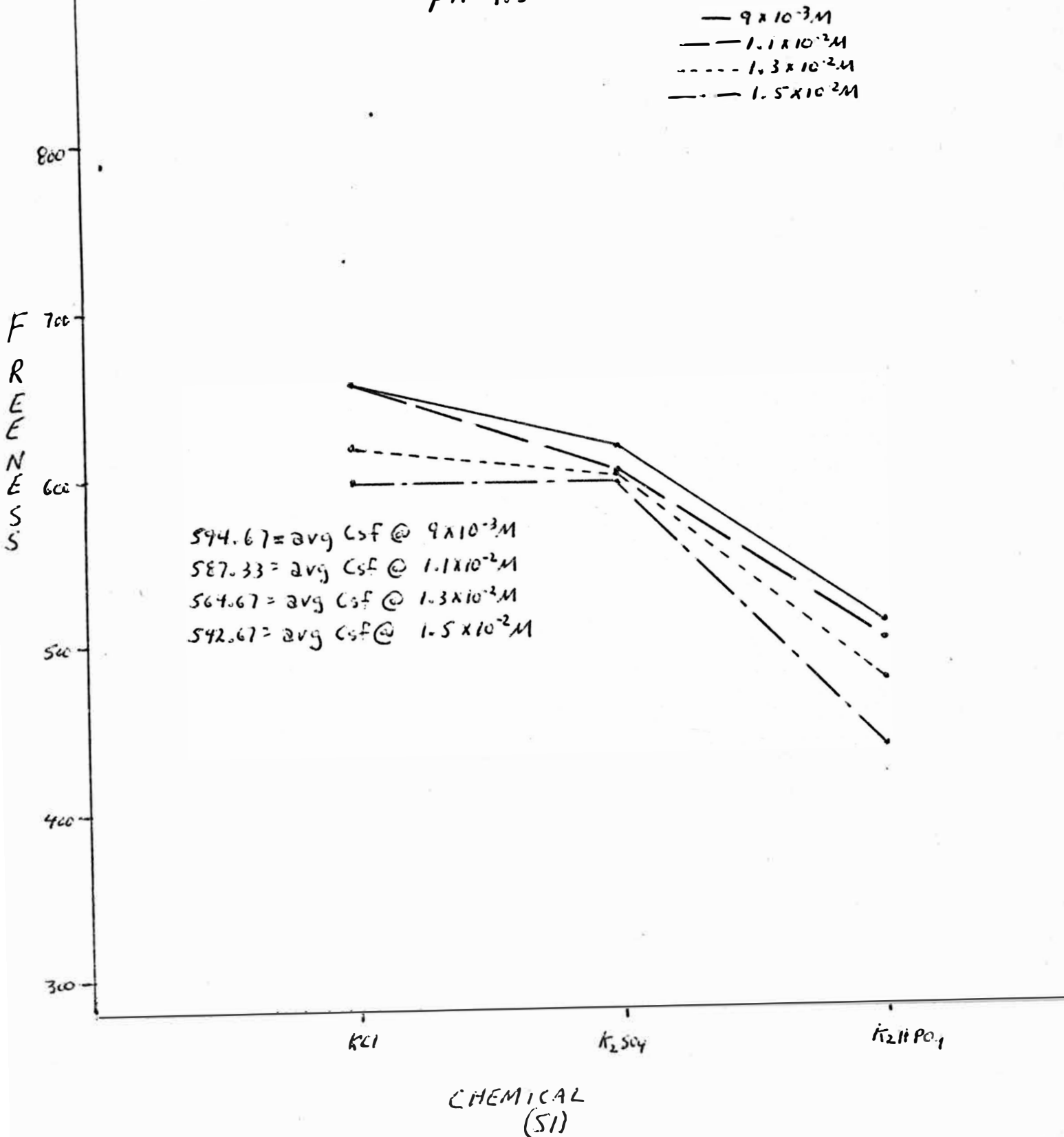


Figure 17

$$F_{.05, 14, 28} \approx 2.01$$

$$F_{AB} = 5.238 > 2.01; .000 < .05$$

$$F_{.05, 14, 28} \approx 2.01$$

$$F_{AP} = 1.21 < 2.01; .383 < .05$$

$$F_{A, 14, 28} \approx 2.69$$

$$F_{BP} = 6.04 > 2.69; .001 < .05$$

# ANALYSIS OF VARIANCE

N.O. CELL SIZE = 1.00000

SOURCE	SUM OF SQUARES	DF	MEAN SQUARE	F	PROB
BLOCK	24993.75	71	3520.22	10.374	0.000
A	37944.75	7	5420.68	25.210	0.000
B	131752.75	2	65876.38	300.370	0.000
P	8494.00	2	24952.00		
AB	15769.00	14	1125.56		
AP	3374.25	14	241.02		
BP	5196.50	4	1299.63		
REP	6670.50	28	215.02		

116.040	0.000
5.238	0.000
1.121	0.383
6.044	0.001

A = Concentration B = Chemical P = PH

Zeta Potential Calculations

$$-0.398 = \text{avg } \zeta p @ \text{ pH of } 4.5$$

$$1.045 = \text{avg } \zeta p @ \text{ pH of } 5.5$$

$$0.226 = \text{avg } \zeta p @ \text{ pH of } 6.5$$

$$-2.363 = \text{avg } \zeta p @ \text{ pH of } 7.5$$

$$-4.341 = \text{avg } \zeta p @ \text{ pH of } 8.5$$

$$-9.054 = \text{avg } \zeta p @ \text{ pH of } 9.5$$

Schulze-Hardy Rule Calculations

$$C_1 : C_2 : C_3 : \frac{1}{6} : \frac{1}{2} : \frac{1}{3}$$

for pH = 4.5

$$\text{NaCl max } C_{sf} = 1.3 \times 10^{-2} M \therefore CaCl_2 = 2.03 \times 10^{-4} M ; AlCl_3 = 1.78 \times 10^{-5} M$$

for pH = 5.5

$$\text{NaCl max } C_{sf} = 1.3 \times 10^{-2} M \therefore CaCl_2 = 2.03 \times 10^{-4} M ; AlCl_3 = 1.78 \times 10^{-5} M$$

for pH = 6.5

$$\text{NaCl max } C_{sf} = 3 \times 10^{-3} M ; CaCl_2 = 4.69 \times 10^{-5} M ; AlCl_3 = 4.12 \times 10^{-6} M$$

From Figure 5A

$$\text{NaCl : max } C_{sf} = 7 \times 10^{-3} M \therefore CaCl_2 = 1.09 \times 10^{-4} M ; AlCl_3 = 9.60 \times 10^{-6} M$$



Conclusions made about zeta potential are based on Figure 18 and the Data sets. By observation of Figure 18 it is safe to say it generally appears that the zeta potential decreases as the pH increases. The  $ZP_{avg}$  calculated @ pH=4.5 may be incorrect as some time was needed for the observer to get acquainted with the correct technique for reading zeta potential. Assuming this is true the hypothesis stated earlier in this paper is proven.

A closer examination of individual pH data is also interesting (data set). At a pH of 4.5 the maximum freeness value for  $NaCl$ ,  $CaCl_2$ , and  $SnCl_4 \cdot 5H_2O$  is reached at the minimum zeta potential which again correlates with assumptions made earlier in this paper. The maximum freeness for the  $AlCl_3$  is reached at a slightly positive charge which also may be attributed to the idea on page four of this paper and discussed in literature.

At a pH of 5.5 things are not as nice but values for  $NaCl$  and  $AlCl_3$  may be described by the cationic demand plateau described earlier. As for the  $CaCl_2$  and  $SnCl_4 \cdot 5H_2O$  complexes may be forming and thus have some effect.

The values at a pH of 6.5 seem "good" and maximum freeness values are found mainly at the minimum zeta potential

but again complex formation and adding adsorption of the cation may have some effect.

Similar results are noticable on the alkaline side and actually adhere to the proposed theory better. It can safely be said that the maximum freeness values are, for the most part, found at the minimum zeta potential.

The attempt to prove the Schulze-Hardy rule completely failed. This mainly lies in the fact that the concentration range was not big enough. Much reading was done before deciding on the concentration range and the thought that I may not reach the desired range was very apparent to me. What was done is that maximum freeness values for the monovalent cations were placed in the correct equation and values for the corresponding di- and tri- valent cations calculated for the acid side pH values. Though this rule was not shown some interesting points still do arise. At a pH of 4.5 the maximum freeness values for both  $\text{CaCl}_2$  and  $\text{AlCl}_3$  are at the smallest concentration, thus showing that it might be theorized that upon further lowering these concentrations freeness values may still rise giving further information that this rule may have been proven. At a pH of 5.5 the same assumptions may be considered with the trivalent cation differing and this may lie in the fact that a  $\text{Al}^{+++}$  complex may have formed. At a pH of 6.5 all of these previous statements seem to fail but again I can only state the idea that complexes may be forming.

Acid side conclusions follow closely to ideas discussed earlier in this paper. In first looking at the data output it is noticed that when comparing average freeness values for each pH that a pH of 5.5 has the maximum average followed by a pH of 4.5 and then 6.5. I seriously believe this does show that as pH values do stray farther and farther from acid values the zeta potential becomes more negative thus causing less flocculation as as pH increases, therefore lowering freeness. The reason the pH of 4.5 value differs may again be attributed to the thought that these were my first freeness tests performed. The zeta potential values at this pH may also be in error for the same reason. This may be further substantiated by observing these first few zeta potentials, at this pH. These are very negative and for the whole acid side no values are lower than these and they are also completely against what literature has stated and therefore may be in error.

Observing freeness values averaged over concentration ranges inferences concerning the Schulze-Hardy rule seem most applicable. As stated earlier my concentration values did not go low enough to give quantitative information concerning this rule. Maximum freeness is observed at a average concentration of  $1 \times 10^{-3}$  M and this further backs up my idea

that these values relate to the idea that this low concentration is as close as the di- and trivalent cations could get to the optimum value stated by the Schulze-Hardy rule.

No real relations can be said concerning Csf vs concentration in Figures 1, 2, and 3 as these plots seem fairly linear. Figure 4, though, shows that as concentration is increased Csf drops. I believe this idea can be attributed to an idea similar as the one stated in the previous paragraph. As more chemical is added a point is reached at where ions in solution have a detrimental effect by affecting the zeta potential. At low concentrations the zeta potential for the  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  are lower and become more positive with greater addition, therefore again showing this Csf-zeta potential interaction described earlier.

For simplicity Figure 5 is illustrative of how the Csf vs pH curves would look. By examination of data this relationship seems quite linear. Figure 5A backs this up for the most part with the exception of the  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , which has a wide freeness variation which is believed to be caused by the idea described above.

Figures 6A-8B sort of capsule what I have been trying to state; as chemical type moves from monovalent to quadvalent Csf values seem to drop. I believe this is directly resultant from the idea that these values differ farther from the

"Schulze-Hardy rule" idea stated above. This is further backed up by the averages shown on each of these Figures; the higher averages, for the most part, belong to the lower concentrations.

Basic side conclusions seem to agree readily with previous assumptions. Csf averaged over pH ranges have a maximum value at a pH of 7.5 followed by pH of 8.5 and finally 9.5. This follows with the idea that as pH is increased the solution develops a greater negative charge and concurrently a lower freeness.

Observing freeness values averaged over concentration ranges it seems as though freeness values decrease as concentration increases. This is believed to result in the idea as concentration increases anionic material increases, thusly affecting zeta potential and freeness in a way that zeta potential decreases therefore decreasing freeness.

Figures 10,11, and 12 seem to show not much of a relationship between Csf and concentration. Further investigation shows, though, that as pH increases zeta potential drops thus substantiating the idea that as pH increases zeta potential decreases and so does freeness.

As in the examination of the acid side Figure 13 is representative of the Csf vs pH relations for all the chemicals. It appears that as pH increases Csf decreases and again I relate this to the idea that zeta potential is also

decreasing. Upon examination of Figure 13A the freeness ranges for KCl and  $K_2SO_4$  seem narrow while  $K_2HPO_4$  has a wider range. I believe this lies in the fact that as concentration is increased so is anionic material, again effecting zeta potential and therefore freeness as stated earlier.

Figures 14A-16B show a relationship very similar to that shown on the acid side and believe this is again caused by the fact that the monovalent anion affects freeness to a lesser extent than the di- and trivalent and also, of course, has a lesser effect on zeta potential.



Basic comparisons between the acid-base data just reinforces the ideas I have already stated. The average acid freeness exceeds the basic and as concentration increases freeness decreases, thus further showing the effect that zeta potential has on freeness.

The statistical outputs on Figures 9&17 are for the Acid and Basic data respectively.

By first observing the acid data it is shown that interaction between concentration-chemical type and chemical type-pH have the greatest effect on the freeness; while concentration-pH effects have little effect. Basically the Csf is not affected the greatest by the concentration, chemical, or pH but by a combination of these variables. If time had permitted further testing and conclusions would have been made.

The basic side data shows the same conclusions seen on the acid side. Again time stalled further testing. With the analysis at my disposal all that can be said is that the Canadian Standard Freeness Test is affected mostly by concentration-chemical type and chemical type-pH interaction. The combination of these variables affect the test the most not the individual variables.

In closing I have tried to stress the importance of zeta potential on freeness. This property has a great effect on the freeness and it appears as zeta potential decreases so does freeness. It also appears that zeta potential also affects the pH and thus as pH becomes greater, zeta potential decreases thus affecting freeness detrimentally. The freeness test also seemed to be affected on the most part by a combination of concentration-chemical type and chemical type-pH interaction not by individual variables.

This experiment is a scaled down version of the one outlined in an earlier paper. The main downfall was time. I believe, first, I planned on doing too much originally. Secondly, I had alot of trouble locating an instrument to measure zeta potential. By the time I started I could not complete all of the experimenting I originally planned. Problems of time also showed in the statistical analysis as more time would have been needed to carry out amore complete analysis.

The only recommendations I make are to eliminate the problems that befell me. Closer interaction must be stressed , between all persons involved, to get equipment ready for use. I believe the Stat Lab holds a good future for analyzing thesis problems but, again, interaction between experimenter and statisticians must be strong. I ran into many problems with this and believe design of the experiment, for statistical purposes, must be worked at closely with the students and advisors. Any complications arising, or not understanding of what is being asked should be brought to an advisor's attention immediately. I was not aware of Stat Lab procedure and deadlines and believe this hurt in the long run. Basically, I am saying Faculty-Student interaction must remain throughout the entire scope of a project such as this.

At this point I would like to offer my gratitude to various people in which this paper could not be completed without their help. I wish to offer my sincere thanks to Mr. Bob Nitz, Mr. Al Larson, Mr. Howard Hunter, Mr. Omi Sharma, and Brown Paper Company for letting me use equipment and supplies pertinent to this experiment and also for acquainting me with the operation of this equipment.

I would also like to offer gratitude to Dr. Gerald Sievers for help on the statistical analysis and gathering of data.

In closing I would like to thank Dr. Raymond Jaynes, Dr. Stephen Kukulich, and Mr. John Fisher for helping me throughout my stay at W.M.U. A final thanks goes to Dr. Richard Valley, for assistance on the design of this experiment, and The Western Michigan University Paper Technology Foundation.

## BIBLIOGRAPHY

1. TAPPI Standard T227 os-58
2. Davison, Robert W., Tappi 57,(12):pp. 85-89 (December 1974)
3. Britt, K.W. and Unbehend, J.E., Tappi 57, (12) pp. 81-85 (December 1974)
4. Bull, Henry B. and Gortner, Ross, The Journal of Physical Chemistry vol. 35: pp. 309-330 (January-June 1931)
5. LaMer, V.K. and Healy, T.W., Review of Pure and Applied Chemistry no. 13: pp. 112-133 (1963)
6. Bickerman, J.J., "Surface Chemistry and Applications" New York, Academic Press, pp. 425-430
7. Chang, M.Y. and Robertson, A.A., Pulp and Paper Magazine of Canada 68(9): pp. T-438-T-445 (September 1967)
8. Paper Trade Journal 162(2) (January 15, 1978)
9. Strazdins, E., Tappi 55(12): pp. 1691-1697
10. Verwey, E.J.W. and Overbeek, J.Th.G., "Theory of Stability of Lyophobic Colloids" Elsevier Publishing Company, Amsterdam-New York 1948
11. Matijevic' E., Journal of Colloid and Interface Science vol. 43, no. 2: pp. 217-245 (May 1973)
12. Penniman Jr., J.G., Pulp and Paper vol. 49, no. 2 pp. 134-139
13. Castellan, Gilbert W., "Physical Chemistry" Second Edition, Addison-Wesley Publishing Company: pp. 435-442 (1971)
14. Strazdins, E., Tappi 53(1): pp. 80-83 (January 1970)
15. Penniman Jr., J.G., Tappi 58(8): pp. 189-190 (August 1975)
16. d'A Clark, J., Tappi 53(1): pp. 108-114 (January 1970)
17. Venkatesh, V. and Edwards, L.L., Norsk Skogindustri 30(9): p.258 & pp. 260-263 (September 1976)
18. Penniman Jr., J.G., Paper Trade Journal 162(5): pp. 52-55 (March 1,

19. Penniman Jr., J.G., Paper Trade Journal 162(1): pp. 29-30 (January 1, 1978)
20. Greene, B.W. and Reder, A.S., Tappi 57(5): pp. 101-106 (May 1974)
21. Tappi 48(3): pp. 157-164 (March 1965)
22. Penniman Jr., J.G., Paper Trade Journal 158(22): pp. 35-37 (June 3, 1974)
23. Goetz, P.J. and Penniman Jr., J.G., American Laboratory October 1976, "A New Technique for Microelectrophoretic Measurements"
24. Dunn, O.J. and Clark, V.A., "Applied Statistics: Analysis of Variance and Regression" John Wiley & Sons, Inc. (1974)
25. TAPPI Standard T200 os-70
26. Bickerman, J.J., "Surface Chemistry and Applications" Second Edition, N.Y. Academic Press, pp. 425-430
27. Lindstrom, T. and Soremark, C., Journal of Colloid and Interface Science vol.55, no. 1: pp. 69-72 (April 1976)