ADSORPTION AT LIQUID-GLASS INTERFACES AND AT FREE SURFACES

by

ELBERT CECIL TABOR

A. B., Kentucky Wesleyan College, 1929

A THESIS

submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

KANSAS STATE AGRICULTURAL COLLEGE

1930

TABLE OF CONTENTS

INTRODUCTION

Adsorption in solution may be defined as the tendency of the solute to become more or less concentrated at the surfaces or interfaces of the solution.

J. Willard Gibbs in 1876 published an article in which he expressed the relation between surface tension and surface concentration in mathematical terms. This was the first attempt to express this relation but for ordinary use it was very complicated; later it came to the hands of Ostwald who simplified the formula into its present form.

$$u = -\frac{1}{RT}\ \frac{d\gamma}{d\log c}$$

u is the excess solute in the surface. R is the gas constant 8.315 x 10^7. T is the absolute temperature.

$\frac{d\gamma}{d\log c}$ is the slope of the surface tension/ log conc. curve at the concentration c.

This equation has been used by many experimenters in calculating the concentration of the solute in surfaces and interfaces but the calculated values in many cases have shown very little agreement with the results obtained from experimental data. Since this disagreement between the observed and calculated values has arisen it is to be expected that the accuracy of the so-called Gibbs' adsorption equation when applied to adsorption at free surfaces and interfaces would be questioned. There have been a great many tests made on various substances in an effort to determine the accuracy of the equation and to attempt to explain the divergence of the observed from the calculated values. A comparison of the results of these experiments is shown in Table I. These workers have shown that the liquid-air interface of a bubble moving through a solution holds many times more solute than is predicted by the Gibbs equation.

Donnan and Barker (1911) published an account of their work on nonylic acid and saponin. They claimed that the experimental results agreed with the calculated values within the limits of experimental error. In these experiments pumping and mixing of the solution were at a maximum and as a result of these the concentration varied greatly in different parts of the apparatus. In determining the adsorption it is necessary to know the concentration of the solution with which the film is last in contact and as this was not possible with their arrangement of apparatus their results cannot be considered to be correct. Their calculations of the observed adsorption were made on the basis of a very small change in the concentration of a large volume of adsorbing solution and this in itself gave many opportunities for error in the measurements. The drop number method of measuring the surface tension was

Table I

Previous Work on Adsorption at Air-Water Interface.

Worker	Solute Studied	Comparison of Values
Milner	Sodium oleate	No comparison.
Donnan and Barker	Nonylic acid	Agreement claimed but results do not permit this assumption.
	Saponin	Agreement claimed but results show experimental values to be two times the calculated.
McBain and Davies	p-Toluidine	Observed two times calculated.
	Amyl alcohol	Observed four times calculated.
	Camphor	Observed three times calculated.
Laing, McBain, and Harrison	Sodium oleate	Observed greated than calculated and twice monomolecular adsorption.
Harkins and Gans	Nonylic acid	Approximate agreement.
	Amyl alcohol	Observed three times calculated.
McBain and DuBois	Phenol	Observed 3-8 times calculated.
	p-Toluidine	Observed 2 times calculated.
	Iso amyl alcohol	Observed 3 times calculated.
	Resorcinol	Observed 2-3 times calculated.
	Thymol	Results not consistent, observed adsorption less than calculated.
	Acetic acid	Observed 3-7 times calculated.
	Butyric acid	Observed 3-4 times calculated.
	Caproic acid	Observed 2-4 times calculated.
	Nonylic acid	Results show no agreement whatever with calculated or previous experimental results.
	Sodium chloride	Observed much less than calculated.

used and this for saponin solutions is not very accurate. The concentration changes were found by the changes in the surface tension of the solution and this would not give an accurate determination of the loss or gain in the concentration. Their results therefore cannot be taken as the values for the actual adsorption in these solutions.

McBain and Davies (1927) and McBain and DuBois (1929) obtained quite a variation in their results on adsorption in many different solutions. While their methods were a great improvement over that of Donnan and Barker, it seems that they have not obtained values for the true adsorption. In their method bubbles of gas were passed through the solutions and the films collected. If no stable films were formed, they assumed that accurate results could be obtained by collecting the liquid forced over by the bubbles when they reached the surface of the adsorbing solution and considering it to be the same as the collapsed film solution. To find the actual adsorption it is necessary to collect the well drained films and find the excess concentration of the solute in this condensed film solution, as the true adsorption can only be found where the actual surface in which the solute is concentrated and not by the use of the solution through which the bubbles are passed. On some of their solutes their results agreed with those of other workers but on other solutions they obtained no consistent values whatever.

The main purpose of this investigation has been to determine if there is either positive or negative adsorption at the liquid-glass interface which would cause an increase or decrease in the concentration of the adsorbed solute in the bubble film as it passed through the adsorbing apparatus.

Originally sodium oleate was to be used as the solute but experimental difficulties prevented its use. The surface tension of sodium oleate solutions has been found by many workers but there is no agreement shown between the different methods and no satisfactory curve could be obtained for the determination of $\frac{d\gamma}{d \log c}$. Different methods for measuring the surface tension were tried but none was found to be satisfactory. The solutions were cloudy and this prevented the use of the interferometer in determining the concentration of the solutions.

Saponin was used as it has all the qualities necessary for an experiment of this type. Its molecular weight was used as 1260. This value was found to be correct in dilute solutions by Donnan and Barker by the freezing point method.

Several other solutes were used in attempts to get stable bubbles, but none could be found that were capable of forming films of the necessary stability. Phenol, caproic acid, nonylic acid, aniline, acetic acid, butyric acid, capryl alcohol, sulphonal, and sodium chloride were tried, but in either dilute or concentrated solutions no stable films would form contrary to the statements of McBain and others. At the rate that McBain and DuBois sent bubbles through their solutions it seems impossible for the bubbles to remain in their original size,for the films are not stable and the bubbles unite to form larger ones. They stated that the coalescing of the bubbles made no difference, but it obviously altered the area of the adsorbing surface. It could only have been possible to obtain film solution in such things as sodium chloride, phenol, acetic acid, butyric acid, etc. at the concentration used by continuously overflowing the solution through the bubble tube. It would be somewhat a matter of doubt whether all adsorbed material was carried over unless analyses were made on the solution in the top of the tube at the end of the run.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. H. H. King for his interest and suggestions throughout the experiment. To Dr. J. Lowe Hall the writer wishes also to acknowledge his indebtedness for the assistance and

cooperation he has given in the construction of apparatus and for the many helpful suggestions concerning the work.

EXPERIMENTAL PROCEDURE

Air bubbles were passed through an aqueous solution of the substance under observation which was contained in a system of pyrex tubes of large diameter and at a small angle from the horizontal. After passing through the saturating and adsorbing tubes the bubbles were directed through a smaller vertical tube in which a trap was constructed to collect the liquid that drained from the films, then the films were collected in a receiver and condensed to a liquid. Due to the stability of the saponin film considerable difficulty was experienced before a satisfactory method of condensation was discovered. The concentrations of the various solutions were measured on a Zeiss interferometer that had been standardized with solutions of accurately known concentrations.

With the exception of the trap in the vertical tube the apparatus was practically a duplicate of that of McBain and DuBois. It consisted mainly of a reservoir generating pressure to force the bubbles through the solution which was contained in the saturating and adsorbing tubes.

The adsorption tube was filled with the original solution which was kept at a constant height throughout each test run. This is accomplished by means of a separatory funnel which is connected to the lower end of the saturating tube which is connected to the lower end of the adsorbing tube.

Before starting a run the large funnel connected to the air reservoir was filled with water, and the air in the reservoir brought to atmospheric pressure by means of a gas burette attached to it. The reading of the burette was recorded. The temperature reading was also recorded before starting. After these preliminary adjustments the water is allowed to run into the reservoir and this causes an increase in the pressure. The clamp is then opened and the air allowed to flow through a bubbling tip where bubbles were formed at the rate of about 75 a minute. The bubbles remain in contact with the solution for approximately 30 seconds before they are collected. The level of the solution in the tubes was carefully adjusted to allow the films to enter the vertical tube evenly. The bubbles were counted visually as they passed a reference point and the number recorded on a counting machine. The vertical tube and the trap were rinsed out with the solution immediately before starting the run and the first bubble always continued through the tube into the receiver. The bubbles were allowed to run until the water had almost run out of the funnel and then the stopcock was closed. After the pressure in the reservoir had decreased until no more bubbles were formed the clamp was closed and the total number of bubbles recorded, making allowance for the number remaining in the vertical tube. The burette was again used to bring the reservoir to atmospheric pressure and the reading recorded. The temperature was again recorded to enable the mean temperature to be found. The water funnel was filled with a measured volume of water to find the volume of air that passed through the solution. The volume of the water less the change in the burette readings gives the volume of the air in the bubbles.

The solution in the adsorbing tube was kept stationary at the point where the bubbles entered the vertical tube, thus allowing them to drain partly before entering the trap. On continuing through the trap the drainage of the films was completed and liquid that drained from the films was collected in the trap and reserved for analysis.

In the case of saponin best results were obtained in condensing the films by allowing them to continue through a small tube down near the lower end of a large separatory funnel. In this manner the films were broken by the pressure exerted by the incoming bubbles. At the end of a run the funnel was well stoppered and allowed to stand in a frigidaire for several hours. This proved to be the most satisfactory method as it allowed no loss by evaporation.

About 30 cubic centimeters of the solution from the end of the adsorption tube were collected and saved for analysis, and the remainder of the solution in the tubes was drained out and well mixed and a sample reserved for analysis. This made a total of five solutions that were reserved for analysis: the original solution, the condensed film solution, the trap solution, the solution last in contact with the bubbles, and the solution remaining in the tubes after adsorption had taken place.

After each run the whole apparatus was well cleaned and rinsed with conductivity water and at no time was it allowed to become completely dry. Before each run the apparatus was rinsed with the solution in use and if operations were not started immediately, it was well stoppered to prevent evaporation.

The solutions were made by dissolving a weighed amount of saponin in freshly boiled conductivity water of high purity and with a surface tension of 72.8 dynes. These solutions were freshly prepared before each run to prevent the action of molds which began to take place within three or four days.

The values of the surface tension of the saponin solutions were found by the use of the du Noüy tensiometer which has been proved to be the most accurate and consistent method for this substance. The drop weight and capillary height methods were useless due to the gel like surfaces that formed on the solution in a very short time. The readings on the tensiometer were taken in a short length of time under conditions comparable to those under which the bubbles were passed through the solutions. Throughout the surface tension measurements the solutions were kept well stirred as the surface tension changes with a change in time. Twelve to fifteen and sometimes more values were obtained for each concentration,and these agreed very closely with the mean value.

The solutions used in this experiment were very dilute consisting of concentrations of .00001, .00005,.0001, and .0005. According to Merck's Index the molecular weight of saponin is 726.5, but Donnan and Barker found it to be 1260 in dilute solutions. In this work 1260 is used as the molecular weight. In the case of the interferometer, precautions were taken to keep the temperature as near constant as possible, but with the temperature undergoing many changes in the course of analysis it was very difficult to work under ideal conditions. However, in most cases the change in temperature would not cause more than one degree deviation,and this would not give an appreciable increase in

Table II

Surface Tension of Solutions of Saponin

Du Noüy Method

Concentration	Dial Reading	Surface Tension
.00001	99.5	70.75
.00005	93.0	65.90
.00010	88.3	62.90
.00025	85.0	60.45
.00050	83.0	59.00
.00100	81.5	57.70
.00250	79.4	56.20
.00500	78.3	55.50

Table III

Calibration of Interferometer

Concentration	Drum Reading
.00001	-23
.00010	-13
.00025	02
.00050	29
.00075	55
.00100	82

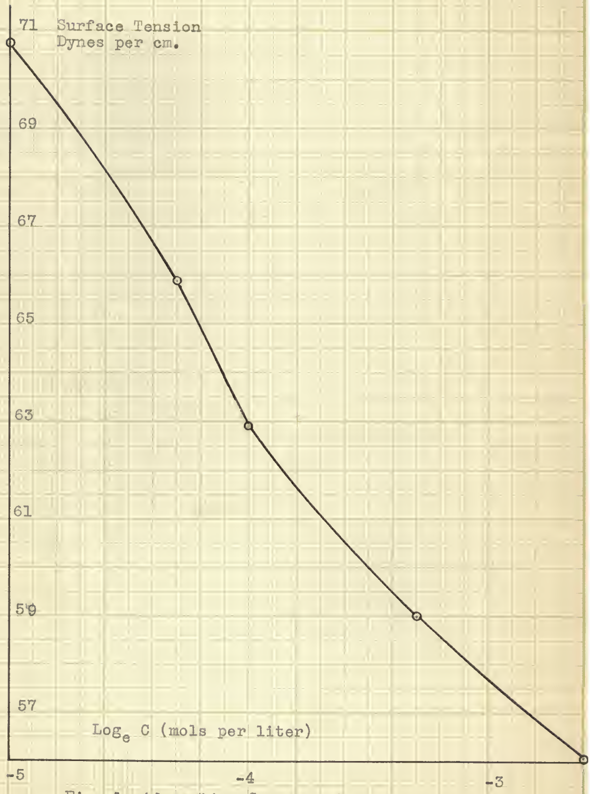

Fig. 1. Adsorption Curve of Saponin Solutions

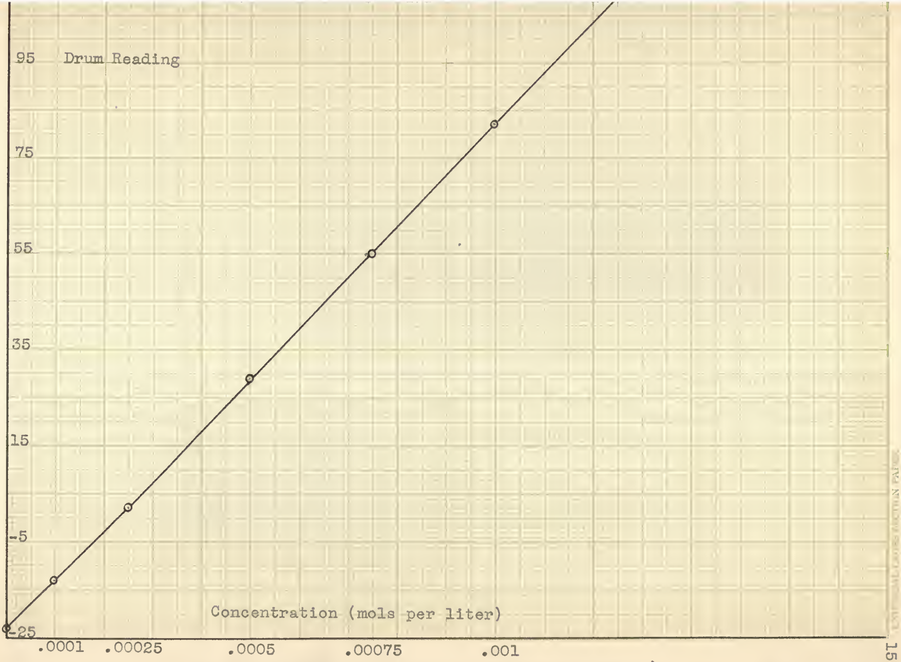

Fig. 2. Calibration Diagram for Interferometer

the experimental error. It was found in the standardization of the interferometer that one degree on the dial was equal to 10^{-8} mols per cubic centimeter.

DIMENSIONS OF THE ADSORPTION APPARATUS

Tube	Inside diameter	Length	Slope
Saturation	1.75 cm.	180 cm.	5 per cent
Adsorption	1.75 cm.	150 cm.	9 per cent
Vertical	0.87 cm.	15 cm.	Vertical

Volume of tubes - - - - - 800 cc.

CALCULATION OF RESULTS

The formula of McBain and DuBois was used in the calculation of the observed adsorption.

$$u = \frac{1^\circ \text{ x } r \text{ x } V_c \text{ x } S_c}{2V_g + 2\pi r^3 B}$$

1° is the mols per cc represented by one degree on the drum of the interferometer. r is the radius of the bubble when it is considered as a cylinder. In this case it is equal to the radius of the vertical tube. V_c is the volume on the collected film solution. S_c is the change in the interferometer reading in degrees. V_g is the volume of the air passed through the solution in the bubbles. B is the total number of bubbles passed through the solution. u is expressed in mols per square cm x 10^{-10}.

DISCUSSION OF RESULTS

The use of the very dilute solutions made it possible to get much more accurate results than with concentrated solutions. The changes in the concentration of the condensed film solution was very great compared to the concentration of the original solution, so this allowed the concentrations to be determined more accurately. When concentrated solutions are used a very slight change in the concentration relative to the original would cause a large shift in the reading of the interferometer. This would give more chances for a larger experimental error in the determination of the concentrations,as the interferometer is more accurate over a small range of concentration.

The analysis of the solutions collected in the trap at no time showed any marked increase or decrease in concentration as is shown in Table IV.

McBain and DuBois suggested that it was possible for the more loosely held molecules in the film to be pulled from the film due to the friction of the liquid and the glass. The results obtained in this experiment in the analyses of the trap solutions have shown that no changes in concentration have taken place, and this would indicate that the solute adsorbed in the film has been disturbed in no manner by its passage through the solution or the trap

Table IV

Conc. Original Solution Mol/liter	Surface Tension Dynes/cm^2	Temp.	Film Solution		Adsorption Mol/cm^2 x 10^{-10}		Trap Soln. Vol.	Change in Concentration Mol/cc x 10^{-8}		
			Vol.	Change in Conc. Mol/cc x 10^{-8}	Calc.	Observed		Trap Soln.	End Soln.	Final Soln.
.00001	70.75	23.0	14.28	21	1.799	2.748	7.83	0	0	0
.00001	70.75	25.0	09.83	24	1.787	2.161	20.79	0	0	0
.00001	70.75	26.5	19.93	12	1.779	2.184	4.44	0	0	0
.00001	70.75	25.5	08.43	24	1.784	1.989	15.22	0	0	0
.00005	65.90	26.5	16.77	17	2.806	2.591	8.09	1	0	0
.00005	65.90	25.0	20.27	16	2.819	2.966	3.59	0	0	0
.00005	65.90	26.0	16.80	22	2.811	3.354	8.22	-2	0	0
.00005	65.90	25.0	19.15	18	2.819	3.148	3.90	0	0	0
.00010	62.90	26.0	14.69	21.5	2.379	2.927	6.08	1	3	-1
.00010	62.90	23.0	12.37	25.5	2.404	2.852	14.63	0.5	1	-0.5
.00010	62.90	22.0	14.60	23	2.412	3.267	7.65	-1	1	-0.5
.00010	62.90	22.5	14.41	26.5	2.407	3.688	8.70	1	0.5	-1
.00050	59.00	27.0	14.22	24	1.774	3.420	11.86	0	-1	0
.00050	59.00	25.0	18.32	32	1.786	5.370	8.88	5	0	-1
.00050	59.00	28.0	20.43	24	1.767	4.400	5.22	0	-1	0
.00050	59.00	27.0	14.52	24	1.774	3.185	10.83	0	-2	-2
.00050	59.00	29.0	12.97	27	1.762	3.189	8.27	8	0	0

and vertical glass tube.

If there were negative adsorption at the liquid-glass interface,the molecules of the solute would be forced into the film, and the liquid that drained from the film into the trap would be deficient in the amount of solute present, but evidently there is neither negativenor positive adsorption on glass for the results show no change in concentration that could be expected if adsorption took place. It is possible that adsorption could have taken place on the glass with the adsorbed layer being so stable that the passage of the films would not appreciably affect this layer. This slight amount adsorbed would not affect the concentration of the trap solution. When the height of the liquid in the adsorbing tube was raised considerable more solution was collected, but this did not affect the concentration of the trap solution. At the beginning of the experiment a few of the solutions showed an increase in the concentration. This was due to the difficulty in getting the proper drainage started in the trap. Instead of entering the vertizal tube the films came through the trap and caused the increase in concentration. In calculating the observed adsorption allowance was made for the increase shown in these solutions. From the great number of runs in which the trap solution showed no gain it can be readily seen that the higher concentration in the few cases was due to the films that came through the trap. This defect was noticed early in the experiment and was remedied to prevent its recurrence.

The samples of the final solution were analyzed but they showed very little decrease in concentration due to the very large volume and to the small amount of solute removed by the bubbles. The interferometer was sensitive to 10^{-8} moles/cc and in most cases the change was too small to show with the interferometer. It would have been possible to read the concentration more accurately if an 80 mm cell could have been used instead of the 20 mm in the interferometer.

In the analyses of the solutions obtained from the upper end of the adsorption tube there was no decided increase or decrease in the concentration at any time. This would indicate that very few, if any, molecules of the solute had been pulled from the films by the liquid in the tube. All these facts indicate that the excess concentration of the solute in the films would give very near the true adsorption. The solution at the highest concentration showed some deviation from the expected, but the total change was within the range of experimental error.

In every case the analysis of the collapsed film solution showed a remarkable increase in concentration, sometimes as great as 20 times that of the original solution. This indicates a decided tendency on the part of the solute to become more concentrated in the surface of the moving films. This agrees with the conclusions of McBain and DuBois. However, in the calculation of the observed values of the adsorption it was found that these values for the .00001 and .00005 solutions showed a very close agreement with the values obtained from Gibbs' equation.

It is true that complete adsorption may not have taken place but in this experiment the bubbles were in contact with the solution longer than in the experiments of McBain and DuBois, so there is every reason to assume that the observed values are very near the true adsorption in these dilute solutions. These results indicate that in very dilute solutions the molecules of the solute are oriented in a monomolecular layer in the air-liquid interface of the adsorbing solution. From the experimental results obtained for the adsorption in the .0001 and .0005 molal solutions it was found that the actual adsorption was two times that calculated from the Gibbs equation.

These results offer further evidence in the support of the theory of McBain and Davies on the structure of the surfaces at liquid-air interfaces. In order to have an adsorption greater than that calculated from Gibbs' equation for a monomolecular layer, the surface must consist of a completed monomolecular layer that further acts as a support for the excess molecules of the solute. These could possibly be in long chains or oriented with respect to the molecules already in the surface. The action of the surface on exposure to air offers further evidence in the support of the doubling up theory. On exposure to air the bubble film seems to turn to a gel having very little water along with the solute. This also affected the drop weight method of measuring the surface tension. From all indications the molecules are so thickly packed in the surface that the film appears more like a solid than a liquid.

In the experiment on phenol extraordinary results were obtained. A solution of phenol approximately one-half molar was used, and as this solution does not form stable films the method of McBain and DuBois was used in obtaining a liquid to use in the calculation of the adsorption. This lets the bubbles pass through the adsorption tubes and forces a little of the solution over into the trap where it can be collected. In the bubbling process it was noticed that there were two phases instead of one in the solution that was collected in the trap. The concentration increase in the films had been so great that the phenol was thrown out of solution. This liquid could not be used in the interferometer on account of the excess phenol. While this method is not accurate for the determination of the actual adsorption in phenol it shows that the adsorption is very much more than would be expected from the Gibbs' equation.

The same method was used in an attempt to find the adsorption in a 2 molar sodium chloride solution. The solution collected was analyzed in the interferometer, but it appeared that the solute was positively adsorbed on the glass of the cell,and this would not permit an accurate determination of the concentration. A solution of one hundreth molar concentration was used and on analysis of the collected solution an increase was shown indicating positive adsorption. However, this increase was very small compared to the original concentration,and the total change was not out of the range of the expected experimental error. No definite conclusions could be made on the adsorption in sodium chloride solutions on account of the inability to obtain consistent results. If stable films could be formed, the adsorption could be accurately determined. The method of allowing the films to force over the liquid is not to be recommended for accuracy in determining the adsorption.

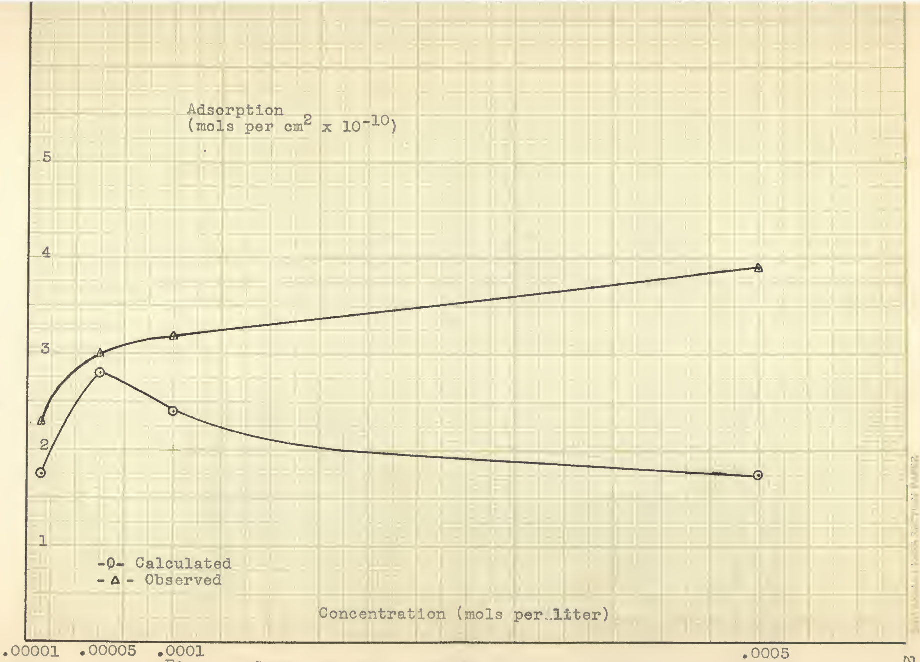

Fig. 3. Change of Adsorption with Change of Concentration.

CONCLUSIONS

1. In solutions approaching infinite dilution the experimental values of the adsorption agree very closely with the values calculated from the Gibbs adsorption equation.

2. In the more concentrated solutions the surfaces consist of more than one layer of molecules.

3. There is little, if any, adsorption at a liquid-glass interface in a saponin solution.

4. The results found in this experiment show no agreement with those of Donnan and Barker.

5. The ring method is the most consistent in the determination of the surface tensions of saponin solutions.

6. The value of the observed adsorption for phenol is very high.

7. This bubbling method is not recommended for solutions that do not form stable films.

LITERATURE CITED

James W. McBain and Robert DuBois 1929 — Further Experimental Tests of the Gibbs Adsorption Theorem. The Structure of the Surfaces of Ordinary Solutions. J. Am. Chem. Soc. 51: 3534

James W. McBain and George P. Davies 1927 — An Experimental Test of the Gibbs Adsorption Theorem. A Study of the Structure of the Surfaces of Ordinary Solutions. J. Am. Chem. Soc. 49: 2230

F. G. Donnan and J. T. Barker 1911 — An Experimental Investigation of Gibbs Thermodynamical Theory of Interfacial Concentration in the Case of an Air-water Interface. Proc. Roy. Soc. 85 A: 557

Leason H. Adams 1915 — The Use of the Interferometer for the Analysis of Solutions. J. Am. Chem. Soc. 37: 1181.