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THE EFFECT OF AEROSOL OT ON THE ABSORPTION OF CARBON DIOXIDE
BY WATER IN A WETTED WALL COLUMN

A THESIS

Presented to
the Faculty of the Graduate Division
Georgia Institute of Technology

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Master of Science in Chemical Engineering

By
Lawrence James Engel
June 1954
THE EFFECT OF AEROSOL OT ON THE ABSORPTION OF CARBON DIOXIDE
BY WATER IN A WETTED WALL COLUMN

Approved:

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FOREWORD

The author wishes to express his sincere thanks to Dr. William M. Newton for his guidance and encouragement in the prosecution of this work and to Dr. R. F. Sessions who was consulted frequently during the course of the investigation. He also wishes to gratefully acknowledge the assistance of Mr. T. S. Yu with whom he worked in conjunction with the experimental phases of this investigation.
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THE EFFECT OF AEROSOL OT ON THE ABSORPTION OF CARBON DIOXIDE
BY WATER IN A WETTED WALL COLUMN

I. INTRODUCTION—LITERATURE SURVEY

While gas absorption has been practiced in one form or another since the earliest days of chemistry, there still remains much to be learned about the theory. Today gas absorption is one of the basic industrial separation processes and finds extensive use in the manufacture of inorganic and organic chemicals and in petroleum refining.

Although gas absorption has been the subject of extensive investigations by many workers over the past half century, and the literature on this subject is voluminous, very little attention has been paid to the effect of the surface tension of the liquid phase on the rate of inter-phase mass transfer in packed and in wetted wall columns.

The purpose of this investigation was to study the effect of surface tension and the concentration of an added surface active agent upon the absorption rate of carbon dioxide from the various air and carbon dioxide mixtures passed through a wetted wall column.

The investigation was confined to one surface active agent, AEROSOL OT, which is dioctyl sodium sulfo succinate manufactured by the American Cyanamid Company.

A. Surface Films

Since there are many postulates as to the nature of the mechanism through which surface active agents influence absorption phenomena, it
seems in order at this point to present briefly the basic theories of 
surface films in order to develop some definite ideas for use in the 
course of the evaluation of the experimental data obtained in this in-
vestigation.

The basic relation used to determine the concentration of surface 
active agent in the liquid surface was the adsorption equation first de-

derived by J. W. Gibbs (1). This equation is $\Gamma = -(c/RT)(\partial \sigma / \partial c)$,

where $\Gamma$ is the excess of the surface active agent in the surface of the 

solution expressed in moles per square centimeter of surface area. $c$ is 
the concentration of the surface active agent in the bulk of the solution 
in moles of the agent per mole of the solution. $T$ is the temperature 
in degrees Kelvin. $\sigma$ is the surface tension of the solution in dynes 
per centimeter. $R$ is the gas constant in the appropriate units.

The assumptions used by Gibbs in the derivation of the adsorption 
equation limits its application to an isothermal, isobaric system in a 
state of static equilibrium. A further limitation is the postulation of 
a plane surface of negligible thickness, generally referred to as the 
Gibbs surface or film. The final condition is that of a dilute solution 
where the concentration of the solute is proportional to the mole frac-
tion of the solute in the solution or the assumption of unit fugacity and 
activity.

Langmuir (2) from his study of the films of insoluble substances 
upon water concluded that the film was but one molecule thick and that 
the molecules were definitely oriented. He suggested that in such cases 
for both soluable and insoluable substances and for pure liquids the 
Gibbs film may be regarded as but one molecule thick and consists of
pure solute molecules which lower the surface tension of the solution.

Lord Rayleigh (3) from his studies on a surface film of oleic acid spread upon water suggested that the film consisted of a single layer of molecules which could be regarded as floating objects.

DeVanx (4) and Labrouste (5) carried out similar experiments and postulated that the surface was only one molecule thick.

Rideal (6) states that in mixtures of substances of markedly different surface tensions it has been found that over a considerable range of concentration the Gibbs film appears to behave as if it were unimolecular in character, but for strong solutions of these substances as well as for mixtures of liquids of similar surface activities the evidence is by no means conclusive. He states further that it must be assumed that in these cases the application of the principle of minimum surface energy to mixtures somewhat similar in internal pressures leads to the formation of a diffuse layer in which the concentration varies possibly in an exponential manner with the depth, the top layer alone may be said to be formed by the operation of chemical forces. Thus, he postulates, in the case of concentrated solutions of ethyl alcohol in water, that the subsequent decrease in the value of the excess surface concentration with the increase of the concentration of the alcohol in the liquid bulk might, on the assumption of an oriented layer of alcohol molecules in the Gibbs film, be accounted for by the decrease in the orientation of the surface molecules when the more polar water molecules in the bulk phase are displaced or replaced by the alcohol molecules. Rideal further says that although most mass interphase transfers take place at great speed as in the vaporization and condensation of water at the normal boiling point,
the life of a molecule on the surface is probably long enough to permit such adjustment as orientation requires.

There is no generally accepted work in the field of surface chemistry and physics which shows that an additional layer or layers of surface molecules in the surface constitute a stable and reproducible system. The works of McBain, Harkins, and Adam in the recent years indicate that the surface film is of one molecule thickness and consists of oriented or partially oriented molecules.

This brief presentation of the basic ideas accepted in the field of surface phenomena should be sufficient to establish the background for this investigation. Reference will be made to these points when the evaluation of the results of the investigation is presented.

B. Surface Tension in Gas Absorption

Consideration of the investigations reported in the literature on this topic does not reveal any agreement as to the effect of the surface tension of the liquid phase on the rate of interphase mass transfer.

Riou (7) noted that the rate of absorption of carbon dioxide by a water solution of sodium carbonate changes considerably upon the addition of different surface active agents. These changes were in both directions, that is in some an increase in the absorption rate was noted while in others a decrease was found. Riou explained this with the observation that the effect on the rate of absorption was due to the catalytic action of the surface active agents added.

Killefer (8) reinvestigated the work of Riou and decided that the change in the absorption rates was due to the lowering of the surface
tension of the solutions and was not related in any manner to a catalytic action of the added surface active agents.

Smith and Quinn (9) performed a similar investigation with the systems utilized by Riou and Killefer and decided that the answer to the effect observed on the absorption rate must be attributed to the change in the surface tension of the solution.

Rennolds (10) showed that the rate of desorption of carbon dioxide from water in the presence of any one of a series of surface active agents was lowered as compared to the desorption rate obtained with the use of pure water without any added surface active agents.

Sherwood (11) (12) (13) performed similar experiments to those of Rennolds and states that the addition of surface active agents affects the absorption rate when the liquid layer or film is the controlling factor and that the added agents have no effect upon the absorption rate when the gas film is the principle resistance to diffusion. Sherwood postulates that the decrease in the rate of absorption is due to the presence of the large molecules of the surface active agents upon the liquid surface which impede the movement of the diffusing molecules in the film, thus increasing the resistance of the liquid film to diffusion.

Pozin (14) investigated the absorption of ammonia by solutions of acetic, succinic, nitric, and hydrochloric acids. He stated that the rate of absorption is in no way related to the surface tension of the absorbing solution.

Trenovskaya and Belopolakii (15) have presented the most recent work on this topic. Their work was based on the absorption of sulfur dioxide by water solutions with various added surface active agents.
They found that the addition of soluble surface active agents as merzolyat, sulfonal, and nekale decreased the rate of absorption of the sulfur dioxide by the water considerably. They have further shown that as the concentration of the added agents is increased the absorption rate continues to decrease to a maximum lowering of the rate of absorption in the range of 25 to 35 percent less than the absorption rate obtained by the use of pure water. Their investigation disclosed that the change in the absorption rate ceased at very low concentrations of the surface active agents long before the inactive portion of the surface tension versus concentration isotherm was obtained, that is, that portion of the surface tension curve where a further increase in the concentration of the surface active agent will not alter the value of the surface tension of the solution.

They concluded that the change in the absorption rate could not be attributed to the change in the surface tension of the solution and that the answer must lie in the formation on the surface of the liquid layer consisting of molecules of the surface active agent.

Trenovoskaya and Belopolakii (16) in a further paper on this topic utilized the Gibbs adsorption equation in their analysis of the absorption phenomena. They stated that the limiting or minimum value for the absorption is found at the concentration corresponding to the formation of a saturated monolayer of the surface active agent molecules on the surface of the liquid. One of the surface active agents did not follow the theory presented and for this agent a change in the structure of the surface film through the reorientation of the surface action agent molecules was postulated.
C. Purpose of the Investigation

The purpose of the investigation was to study the effect of surface tension and the concentration of an added surface active agent, Aersol OT, upon the rate of absorption of carbon dioxide from various carbon dioxide and air mixtures passed through a two inch inside diameter wetted wall column at one atmosphere pressure and room temperature.

Four fixed gas rates were chosen as 0.25, 0.50, 0.75, and $1.0 \times 10^{-3}$ pound moles of gas per minute at one atmosphere pressure and 80° F. Liquid rates were set as 0.6, 2.02, 3.03, and 5.1 pounds of water per minute at 80° F. The gas compositions of the inlet gas were fixed as 100, 80, 40, and 20 percent of carbon dioxide by volume. With these fixed flow rates and compositions the rate of absorption of the carbon dioxide from the air-carbon dioxide was determined using tap water.

Added amounts of the surface active agent were used to alter the surface tension of the tap water. The concentration of the surface active agent ranged from 0.0025 to 0.200 weight percent giving a corresponding range for the surface tension of the solution from 54 to 29 dynes per centimeter. The rate of absorption of the carbon dioxide was then determined for the systems with the added surface active agents using the same combinations of flow rates and gas compositions as those chosen previously for the tap water system.
II. EXPERIMENTAL EQUIPMENT AND MATERIALS

A. Equipment

The equipment consisted essentially of a liquid supply reservoir, a liquid pump, a carbon dioxide cylinder, an air compressor, and a glass column together with various devices for controlling and metering the gas and liquid phases.

The column was constructed of a two inch inside diameter laboratory glass cylinder, four feet high, mounted in a supporting structure as shown in Figures II through IV, inclusive. This investigation was confined to wetted wall operations and therefore no packing was placed in the column. A leveling device was included in the structure at the top and by adjustment of a bolt mechanism the column was aligned in a perpendicular position. The device for the control of the liquid overflow, consisting essentially of a circular weir, was attached to the glass cylinder by an eight inch steel flange with gaskets. The overflow weir was carefully machined to insure an even distribution of the liquid over the walls when the column was adjusted to the perpendicular position.

The bottom of the column was connected to a drain through a U type liquid trap. The water was pumped to the top of the column from a standard fifty gallon drum which served as a reservoir and was fitted with an outlet for draining. Power was supplied for the liquid by a 1/4 HP centrifugal pump. The water flowed from the reservoir to the pump by gravity and then through either of two rotameters, both of which
had been previously calibrated. The rotameter flow rates were from 0.2 to 1.0 pounds of water per minute at 80° F and 1.0 to 6.0 pounds of water per minute at 80° F. Thermometers were placed in the water lines entering and leaving the column.

A take off point was provided at the bottom of the column for the removal of a liquid sample. There was a connection at the bottom of the column for a line to a water manometer to record the pressure at that point.

The air was supplied by a laboratory compressor. The pressure was reduced and the air was filtered by passing it through glass wool to remove any particles in the stream. The air rate was measured by a standard orifice, 0.082 inches in diameter, placed in a one inch pipe. The pressure drop across the orifice was indicated by a water manometer and the upstream pressure was measured with a mercury manometer. The orifice was calibrated by the use of a wet test meter. The air flow in the system was controlled with two manually operated valves and a spring activated pressure regulator.

The carbon dioxide entered the system from a standard commercial cylinder. A machined connection was fitted to the gas cylinder outlet and a spring activated diaphragm pressure regulator was attached to the brass fitting. This system is shown in detail in Figure IV. The cylinder pressure was thereby reduced to the operating pressure desired. The carbon dioxide was passed into a surge tank and then through the upstream pressure control valve to a standard sharp edged orifice. The pipe diameter was one inch and the orifice was 0.082 inches in diameter. This orifice was also calibrated using standard procedure. The pressure drop
through the orifice was measured with a water manometer and the upstream pressure was obtained by the use of a mercury manometer. The carbon dioxide then passed through the downstream control valve. The pressure reduction system shown with the carbon dioxide cylinder controlled the upstream pressure very well and was superior to all previous arrangements tried. Facilities were provided for the addition of heat to the brass fitting connected to the carbon dioxide cylinder to prevent the solidification of the carbon dioxide in the pressure reduction system.

The air and carbon dioxide lines were joined and the resulting mixture was passed through a system of flow restrictions to obtain proper mixing of the gases. The mixture line was provided with a control valve to close off this portion of the system in the event of improper functioning of the column.

Thermometers located in the gas streams recorded the gas inlet and outlet temperatures. A take off point was provided in the gas mixture line to enable a gas sample to be taken for analysis. The top of the column was at atmospheric pressure.

A barometer was provided on the control panel for a convenient source of atmospheric pressure data.

B. Materials

The carbon dioxide was obtained from the Liquid Carbonic Corporation of Atlanta, Georgia and had the specifications of 99.7 plus percent carbon dioxide with approximately 0.3 percent nitrogen.

The water used was tap water as provided the municipal system by the City of Atlanta Water Works.
The surface active agent, Aerosol OT, was provided by the manufacturer, the American Cyanamid Company.
Figure II. View of Column
Figure IV. View of Pressure Reduction System
III. EXPERIMENTAL PROCEDURE

A. General

Since in the course of the investigation the same type of experimental data for all the systems was to be collected, a general procedure common to all of the runs was established.

The gas rate, gas composition, and liquid rate to be investigated were chosen and the control equipment was adjusted until the column was operating in a steady state under the arbitrarily chosen conditions. The column was allowed to run for about fifteen minutes after constant flow rates were attained to establish operation at equilibrium. During this interval gas and liquid samples were analyzed and a material balance was made to insure that the column was functioning properly and that there were no leaks in the system. Then consecutive liquid samples were taken for analysis over a period of about ten minutes and if the results were in agreement, the values were recorded. During this period all the thermometers and the manometers giving the pressure drops through the orifice meters were read and recorded. The pressure at the bottom of the column was recorded along with the barometric pressure and room temperature which completed this particular run.

Another run followed immediately with the same gas rate and gas composition, but with a different liquid rate using the same general procedure as outlined above. This procedure was repeated until the data for four liquid rates all with the same gas rate were obtained. Then the next gas rate desired was chosen with the fixed gas composition and
four liquid rates were again run off as before. This procedure was fol-
lowed until the experimental data was obtained for all the gas and liquid
rates and the gas compositions within the range of the investigation.

If the experimental run involved water with the surface tension
lowered, the surface active agent (Aerosol OT) was first added to the
supply reservoir and the water system thoroughly agitated by recycling
from the drum through the pump and back into the drum for several hours
to insure a homogenous liquid phase with a constant surface tension.
The same procedure as for the case of tap water was followed to obtain
the necessary experimental data for the arbitrarily chosen flow rates
and gas compositions.

B. Comments on the General Procedure

Further discussion is in order on some details of the operation
not taken up in the general coverage of the experimental procedure.

The brass fitting connecting the carbon dioxide cylinder to the
pressure reduction system was heated when relatively large flow rates
of carbon dioxide were used in the system. This was to prevent the
solidification of the carbon dioxide in this portion of the system as
the gas cooled upon expansion to the lower operating pressure.

The upstream pressure in both the air and the carbon dioxide lines
was maintained at a constant value during all of the experimental work.
Variation of the flow was obtained by control valves on the downstream
side of the orifices. This was required since the orifice meters were
calibrated for the same upstream pressure, ten pounds per square inch,
gauge, and any deviation from this setting would alter the flow rate of
the gases entering the system. Due to the relatively small flow rates used in the investigation a minor variation of the upstream pressure would produce a noticeable effect upon the absorption rate of the carbon dioxide.

The liquid sample was removed from the bottom of the column by the use of a calibrated pipette. This was to reduce the possibility that some of the carbon dioxide in the sample solution would be liberated as the liquid was passed from the pressure in the bottom of the column to atmospheric pressure. The pressure in the bottom of the column was less than one inch of water so this effect would be small in any case.

The liquid sample was added to the barium hydroxide solution immediately keeping the mouth of the pipette below the surface of the barium hydroxide solution to provide good initial contact for the chemical reaction between the solutions. The sample was then analyzed as quickly as possible to minimize the amount of carbon dioxide escaping from the solution to the air to which the solution was exposed in the stoppered flasks.

The surface tension of the solutions to which the surface active agent had been added was checked during the mixing period to see if the desired surface tension value had been obtained. The surface tension of the solution was also tested during the experimental runs to insure that the value remained constant.

The reservoir was drained frequently to remove rust and other particles from the liquid system. After the experimental runs on a specific concentration of the added surface active agent were completed, the whole system was flushed thoroughly to remove all traces of the added agent.
IV. METHODS OF ANALYSIS

Three types of analysis were made during the course of the experimental runs.

The gas composition was determined through the use of standard Orsat equipment. The gas analysis was used in the initial testing of the apparatus and in the determination of the overall material balance for the system. After the orifices were calibrated the Orsat equipment was available for occasional material balance checks on the operation of the column and the connected apparatus.

The liquid samples were analyzed by the following procedure. A standard solution of barium hydroxide with a known concentration, in the range of 0.05 Normal, was prepared. A definite amount of the barium hydroxide was placed in a clean stoppered flask. A definite amount of liquid was removed from the bottom of the column through the liquid take off line with a calibrated pipette. When this sample was added to the barium hydroxide solution a white precipitate of barium carbonate was formed. The resulting mixture was titrated with a standardized solution of dilute hydrochloric acid, in this case in the range of 0.025 Normal, to determine the excess of barium hydroxide present. A test blank was run on a sample of the liquid from the reservoir to determine what correction must be made for the amount of hydrochloric acid used in the titration of the liquid solution removed from the bottom of the column. The flasks were thoroughly washed with water and hydrochloric acid to remove the traces of the solutions and the precipitate. The flasks were dried in a
moisture oven and stoppered for further use. This procedure was used to eliminate any errors in the chemical analysis of the liquid samples due to absorbed carbon dioxide. The indicator used in the titrations was phenolphthalein.

The barium hydroxide standard solution was checked against a standard solution of hydrochloric acid before, during, and after the lengthy experimental runs to insure that the normality of the solution remained unchanged. The solution container was equipped with calcium chloride and ascrite adsorption tubes for the removal of water vapor and carbon dioxide from the air entering as the solution was displaced which would alter the normality of the solution. The burette for the barium hydroxide was also equipped with similar adsorption tubes.

The surface tension of the liquid was determined through the use of a DuNouy Tensionometer. This apparatus was calibrated with distilled water and with weights of known mass. The calibration of the Tensionometer was rechecked before each set of experimental determinations of the surface tension of the solution.
V. CALCULATION AND EVALUATION OF DATA ON SURFACE AREA

In most research investigations some basis must be advanced for the evaluation of the experimental data.

The basic relation used in this investigation for the determination of surface concentration of the surface active agent was the Gibbs adsorption equation. The limitations of the Gibbs equation have already been pointed out and for this reason the equation was taken only as an indication of the concentrations of the surface active agent where the surface concentrations of the surface agent were of interest with respect to their effect of the absorption rate of carbon dioxide.

The experimental runs were made at conditions of constant temperature and pressure, satisfying the first condition imposed by Gibbs in the derivation. Streamline flow down the sides of the column gave the condition of a smooth liquid surface being presented to the gas phase and it was postulated that this gave a condition of dynamic equilibrium similar to the condition of static equilibrium imposed as a limitation of the Gibbs equation.

The condition of a dilute solution was satisfied since the concentration of the surface active agent was very small. It was assumed that the solutions were ideal in as much as the concentration of the solute was very small so that unit activity and fugacity could be postulated.

From the surface tension-concentration data for Aersol OT the value for the excess surface concentration of the surface active agent on the liquid surface was calculated by the use of the Gibbs adsorption
equation, utilizing the surface tension vs concentration curve for Aersol OT, Figure V, Appendix, for the evaluation of the function \( \frac{\partial \gamma}{\partial c} \).

If the total concentration of the Aersol OT on the liquid surface is examined, it is seen that the contribution of the Aersol OT molecules in the bulk of the solution may be neglected in the concentration range of 0.00 to 0.099 weight percent. This may be shown by calculating the contribution of the bulk molecules to the total surface coverage at the highest concentration in this range, 0.099 weight percent. This concentration would give \( 9.9 \times 10^{-4} \) grams of Aersol OT per cc of solution. If equal distribution of the molecules in the solution is postulated and if the grams of solute per cc of solution is divided by the density of the Aersol OT, the volume fraction of the Aersol OT in the solution or the fraction of any plane surface that is covered by the Aersol OT molecules is obtained. For the 0.099 weight percent concentration only five hundredths of one percent of the surface would be covered by the contribution of the bulk solution molecules. The percent of the surface covered by the excess concentration of the Aersol OT on the liquid surface, reference to Figure VI, Appendix, is seen to be 17.5 percent at this point. As the concentration of the Aersol OT in the solution is decreased, the contribution of the molecules of the Aersol OT in the bulk becomes smaller and approaches zero as a limit. For this reason the total concentration of the Aersol OT molecules on the surface of the solution in the concentration range 0.00 to 0.099 weight percent was taken as the excess surface concentration of the Aersol OT molecules as calculated from the Gibbs adsorption equation, i.e., the contribution of the bulk molecules in this concentration zone was neglected. This produces no appreciable error in
the resulting conclusions.

The fraction of the surface covered with Aersol OT molecules was determined by using Sally's (17) value of 65 square Angstrom units for the surface area covered by one molecule of Aersol OT. The fraction of the surface covered was obtained by multiplying the value of the total surface concentration of the surface active agent in moles per centimeter square of surface area first by Avagadro's number to obtain the number of molecules present and then by the area of the Aersol OT molecule. Multiplication by 100 gives the percentage of the surface that is covered by the Aersol OT molecules. These calculations are expressed graphically in Figures VI and VII of the Appendix, in which the calculated surface coverage is plotted against the concentration of the Aersol OT in the solution.

Referring to Figure VI, Appendix, it is seen that the surface coverage afforded by the excess concentration of the Aersol OT molecules on the liquid surface becomes very small for the 0.100 and higher weight percent concentrations. Further enlargement of this concentration zone is shown in Figure VII in which the contribution of the bulk and of the surface excess concentrations to the total surface coverage is shown. In this region it is seen that the bulk concentration comprises approximately one sixth of the total surface coverage. At this point as will be discussed later, the Gibbs adsorption equation gives little insight as to the surface condition and since the calculated percent surface coverage is so small no attempt will be made to explain the effect upon the absorption rate observed in this region other than postulation that a complex surface has been formed.
The most plausible explanation of the effect on the absorption of the carbon dioxide by Aerosol OT seems to be that the relatively large molecules of the surface active agent concentrate on the surface layer and offer resistance to the diffusion of the carbon dioxide through the liquid film. Consequently, the experimental work was designed so as to throw as much light as possible on this phenomena.
VI. RESULTS AND DISCUSSION

The results of the experimental runs when put into graphical form were a series of absorption isotherms at 80°F and approximately 735 mm of mercury pressure for the carbon dioxide, air, water, and Aersol OT combinations in a two inch wetted wall column.

The absorption isotherms were determined for all combinations of the liquid rates of 0.6, 2.02, 3.03, and 5.10 pounds of water per minute at 80°F, gas rates of 0.25, 0.50, 0.75, and $1.0 \times 10^{-3}$ pound moles of gas per minute at 80°F, and gas compositions of 100, 80, 60, and 20 percent by volume of carbon dioxide, for each concentration of the added surface active agent, Aersol OT, from 0.00 to 0.20 weight percent Aersol OT. These isotherms are presented in the Appendix, Figures VIII to XII, inclusive, in which the absorption rate in pound moles of carbon dioxide absorbed per minute is plotted against the concentration of the Aersol OT in the solution at one constant gas rate and one constant liquid rate for the various gas compositions. The data used for these curves is presented in tabulated form in the Appendix, Tables I through V, inclusive.

The experimental data for the investigation exhibited very good agreement. From the plots of the experimental data for all of the various gas and liquid rates and gas compositions it was found that the decrease in the absorption rate was relatively constant for any one surface active agent concentration. This decrease in the absorption rate when expressed as a percentage of the rate for the tap water was approximately 72 percent at 0.02 weight percent Aersol OT concentration, 65 percent and the
minimum decrease at the 0.04 weight percent, and 75 percent for 0.10 weight percent concentration and higher.

Visual observation of the column during the experimental runs disclosed that the flow characteristics of the liquid phase flowing down the inside of the walls changed upon the addition of the surface active agent. When the tap water was used the usual pattern of concentric water rings down the column sides was noticed. Upon the addition of the surface active agent it was difficult to decide whether or not there was actually any liquid flow in the column whatsoever as the surface took on a glass like smoothness giving the appearance of a dry column.

In the analysis of the data a study was made to see if the surface tension of the solution was an influencing factor in the effect observed on the absorption rate of carbon dioxide or whether the major factor could be attributed to the presence of the molecules of the surface active agent in the surface layer of the liquid without regard to surface tension.

An examination of the surface tension vs concentration curve for Aersol OT, Figure V, Appendix, shows that in the range of 0.1 to 0.2 weight percent concentration there is relatively little change in the surface tension of the solution. This concentration range was investigated and the results are shown graphically in Figures VIII through XII, inclusive, where the absorption rate of carbon dioxide in pound moles absorbed per minute is plotted against the concentration of the Aersol OT in the solution. In this concentration zone there was found to be no appreciable change in the absorption rate. It would appear that the surface tension of the solution is a major factor in this concentration
region, since the surface tension also exhibits very little change.

In the lower concentrations of Aersol OT from zero to 0.04 weight percent, the absorption rate exhibits a constant decrease. Reference to the surface tension curve, Figure V, shows that the surface tension of the solution also decreases in this range, so that again there seems to be a relation between the surface tension of the solution and the absorption rate.

If the concentration region from 0.04 to 0.10 is examined, it is seen that the postulation that the surface tension of the solution is the major factor does not apply. In this concentration range the absorption rate shows an increase, but the surface tension of the solution continues to decrease.

Thus it may be concluded that although the surface tension of the solution appears to afford some correlation with the observed effect on the absorption rate, this correlation is not followed in the concentration range of 0.04 to 0.10 weight percent Aersol OT. It is obvious therefore that some other answer must be found for the observed absorption phenomena.

If reference is made to the calculated surface coverage by the molecules of the Aersol OT on the liquid surface, Figure VI, it is seen that there is an increase in this function in the range from 0.00 to 0.04 weight percent concentration Aersol OT. Figures VIII through XII show that the absorption rate for the carbon dioxide decreases in this region.

Examination of the concentrations of 0.10 weight percent and higher reveals that the absorption rate for the carbon dioxide exhibits no appre-
ciable change. The calculated surface coverage in this region is also noted to be relatively constant as shown in Figure VII. The surface coverage obtained by calculation using the Gibbs adsorption equation was a very small value leading to the belief that the absorption rate should be almost equal to that for the tap water system where the concentration of the Aersol OT was zero, while examination of the absorption curves, Figures VIII through XII, show no such trend. This leads to the postulation that for the concentration regions of 0.1 and higher weight percent a complex surface is formed and the Gibbs equation is no longer applicable.

It is postulated that the Gibbs adsorption equation is not applicable to the concentration range of 0.10 weight percent Aersol OT and higher. In this region the absorption rate is approximately 75 percent of the value obtained with the use of tap water with no added surface active agent. It is thought that a complex surface is formed and/or in conjunction with the disorientation of the Aersol OT molecules on the surface, subsequently giving an increase in the surface coverage due to the random distribution of the molecules on the surface and the spreading out of the two long chains associated with the Aersol OT molecule. In this case the calculated area covered would be lower than the actual surface coverage since the area of the molecule was assumed to be a constant value of 65 square Angstrom units.

Beyond the point of maximum surface coverage and maximum surface concentration at 0.04 weight percent Aersol OT, it is postulated that the formation of large attractive force within the bulk of the solution starts due to the larger amount of Aersol OT present in that phase and some of the Aersol OT molecules from the surface film are drawn into the
bulk of the liquid. This would agree with the results of the experiment as it would mean a decrease in the concentration of the molecules on the surface, a decrease in the calculated surface coverage, and a corresponding increase in the absorption rate, if the postulations presented are correct.

Reference to the surface coverage curve, Figure VI, reveals that at the point of maximum surface coverage, 0.04 weight percent, there are enough molecules to form a complex layer or surface since there is a 40 percent excess in the surface coverage. This is definitely not a true picture since the introduction one of the basic ideas expressed was that there is no generally accepted work in the field of surface chemistry today which postulates the formation of a stable surface composed of multilayers. A more logical explanation of this fact is that the Gibbs equation can be used as a guide only and does not apply exactly to this system. Another reason may be that the area of the Aersol OT molecule was taken as a constant and actually may be somewhat smaller value due to the close packing of the molecules on the liquid surface. Thus it is possible that the value used for the area of the Aersol OT molecule was too large, giving a larger value also for the surface coverage.

The change in the flow characteristics of the solution in the column upon the addition of the surface active agent gives an additional factor which was unaccounted for in this investigation. It is entirely possible that this charge in the liquid flow might have some influence upon the column operation and the absorption rate, which at present is not clear to the investigator.
VII. CONCLUSIONS

From the results of the investigation the following conclusions were drawn:

1. The rate of absorption of carbon dioxide was decreased upon the addition of Aersol OT in various concentrations to the water and this is in some way related to the presence of the Aersol OT molecules on the surface of the solution as predicted by the Gibbs equation. It is postulated that the observed absorption phenomena was due to the presence of the relatively large molecules of the surface active agent on the surface of the liquid phase restricting the diffusion of the carbon dioxide molecules through the liquid film.

2. The correlation of the data obtained indicates that the same percentage decrease of the absorption rate for carbon dioxide is obtained at any specific concentration of the Aersol OT for all combinations of the liquid and gas rates and gas compositions.

3. The surface tension of the water solution containing small concentrations of Aersol OT has no effect on the absorption rate of carbon dioxide.

4. The nature of the flow of the liquid phase down the inside of the column walls was changed from the normal concentric ring pattern to that of a glass like smooth surface.
VIII. RECOMMENDATIONS

It is recommended that further studies be made as to the effect of surface active agents upon absorption. It is further recommended that various types of surface active agents exhibiting different surface tension characteristics be employed to study the effect of an excess of concentration of a surface active agent on the surface of the liquid phase in an attempt to see if the theory advanced here applies in general to all surface active agents.

It is also recommended that various other gases be employed to study this effect where the liquid film is not controlling. When further studies are made it is urged that the theoretical surface excess concentration curve as predicted by the Gibbs adsorption equation be used.
IX. BIBLIOGRAPHY


X. APPENDIX
TABULATED DATA

Notes:

Liquid rates are expressed in pounds per minute at 80° F.
Gas rates are in pound moles per minute at 80° F.
Concentrations are in weight percent Aerosol OT.
Gas compositions are in volume percent carbon dioxide.
Carbon dioxide absorbed is in pound moles per minute at 80° F.
Temperature for all data is 80° F.
Pressure for all data is 735 mm of mercury.

Table 1. Liquid Rate 3.03: Gas Rate $1.0 \times 10^{-3}$

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### Table 2. Liquid Rate 3.03: Gas Rate $0.76 \times 10^{-3}$

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Table 5. Liquid Rate 2.02: Gas Rate $0.76 \times 10^{-3}$

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FIGURE V
SURFACE TENSION – CONCENTRATION CURVE
FOR AEROSOL OT
At 80° F
Surface Tension in dynes/cm vs Concentration of Aerosol OT in weight percent
FIGURE VI
CALCULATED THEORETICAL PERCENT SURFACE COVERAGE
At 80° F
FIGURE VII

Calculated Percent of Surface Covered

\[ \text{vs} \]

Concentration of Aersol OT

at

80 °F

Contribution of Excess Surface Concentration

Contribution of Bulk Concentration

Concentration of Aersol OT in Weight Percent
Figure VIII

Liquid Rate 3.03
Gas Rate 1.0 x 10^-3
Temperature 80°F

100% Carbon Dioxide

80% Carbon Dioxide

40% Carbon Dioxide

20% Carbon Dioxide

Concentration of Aerosol OT in Weight Percent

Pound Moles of Carbon Dioxide Absorbed per Minute x 10^5
FIGURE IX

Liquid Rate 3.03
Gas Rate $0.76 \times 10^{-3}$
Temperature 80°F

Concentration of Aerosol OT in Weight Percent

Pound Moles of Carbon Dioxide Absorbed per Minute $\times 10^5$

- 100% Carbon Dioxide
- 80% Carbon Dioxide
- 40% Carbon Dioxide
- 20% Carbon Dioxide
FIGURE X

Liquid Rate 3.03
Gas Rate 0.50 x 10^{-3}
Temperature 80 °F

100 % Carbon Dioxide

80 % Carbon Dioxide

40 % Carbon Dioxide

20 % Carbon Dioxide

Pound Moles of Carbon Dioxide Absorbed per Minute x 10^7

Concentration of Aersol OT in Weight Percent
FIGURE XI

Liquid Rate 3.03
Gas Rate 6.25 \times 10^{-3}
Temperature 80 °F