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CONTACT ANGLE RELATIONSHIPS OF MODIFIED SOLID-LIQUID INTERFACES

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PREFACE

Cavitation of the liquid is one of the limiting factors involved in the transfer of acoustic energy from its source in the solid vibrator to the liquid medium. The role of air (or gaseous) nuclei in the creation of cavitation spots at or near the solid surfaces has been demonstrated to be an important one(48,49). The presence of an air bubble on the surface of an oscillating ADP crystal working into castor oil is certain to initiate a cavitation vortex at the spot at low energy levels. ~~The~~ control of the presence or absence of such ~~gaseous~~ nuclei should have a bearing on the ultimate transfer of ~~the~~ acoustic energy into the a ~~terminal~~ liquid medium, e. g. from a rubber (solid) window into sea water (liquid) where the surface condition of the rubber determines its wettability by sea water.

This report is concerned with a study of ~~the~~ conditions that promote adsorption of reagents on solid surfaces for the purpose of rendering such surfaces attractive or unattractive to air bubbles. The study is closely related to the behavior of surface active reagents used in flotation techniques. The reagents that promote attraction and adsorption of air bubbles are termed collectors, those that suppress the adsorption of air bubbles are termed depressants.

Captive bubble angle technique was used for the measurement of the effect of the surface active reagents. Improvements were made on the existing design of such apparatus(49). The solid-liquid system used was galena and distilled water. The surface active reagents were ethyl and amyl xanthates as collectors, and sodium sulphide as depressant. These components are frequently met in practical flotation work where a considerable practical background of data and technique is available, and the value of contact angle data by the captive bubble method in predicting the practical behavior of conditioned solid surfaces exposed to frothy water can be estimated.

ABSTRACT

A comprehensive study of equilibria was carried out for the systems:

(a) Potassium ethyl xanthate - galena.

(b) Potassium amyl xanthate - galena.

(c) Potassium ethyl xanthate - potassium amyl xanthate - galena.

(d) Potassium amyl xanthate - sodium sulfide - galena.

The procedure which was followed in the study of potassium ethyl xanthate-galena equilibria has been outlined previously by Wadsworth, Conrady and Cook(38). Contact angle-collector concentration curves, for concentrations of collector less than 50 mg per liter, were obtained for pH values of 5.50, 6.45, 7.35, 8.20, 9.40, 10.00, and 10.50. From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH were constructed. Assuming a single site adsorption of ethyl xanthic acid on galena, and also a linear relationship between contact angle and surface coverage the following equation was obtained:

$$HX = \frac{K^{-1}}{a} \frac{1}{(60-\phi)} - K^{-1}$$

in which, K is the equilibrium constant for the adsorption, ϕ is the contact angle, HX is the concentration of ethyl xanthic acid and a is a constant. A plot of HX vs $\frac{1}{(60-\phi)}$ was made using average values of HX which had been taken from a contact angle - log HX plot. 1/K, taken from the intercept of the HX - vs - $1/(60-\phi)$ plot was equal to 3.0×10^{-9}, giving a value of $K = 3.3 \times 10^{8}$. The slope was 2.33×10^{-7}, giving a value of $a = 0.013$. Substituting this value of a into the equation, $b = 1 - 60a$ gives $b = 0.22$

which is the fraction of the surface covered at zero contact angle. These values of a and b gave $\theta = .013\,\phi + .22$ which checks the relationship of Cook, Conrady, and Wadsworth and demonstrates that their relationship is applicable to systems with collector concentrations less than 50 mg. per liter. Using a dissociation constant of $Ka = 8.7 \times 10^{-7}$ obtained from studies of competitive adsorption of ethyl and amyl xanthates on galena, together with the constants evaluated above, calculated collector concentration - pH curves were constructed for comparison with experimental curves.

An identical procedure was followed to show that a linear relationship between contact angle and surface coverage exists in the case of amyl xanthate on galena. Contact angle-collector concentration curves were obtained for pH values of 5.50, 6.45, 7.35, 8.20, 9.40 and 10.00. From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH were constructed and compared with calculated curves. The calculated curves were obtained by using the following equation:

$$HX = \frac{K^{-1}}{a}\,\frac{1}{80-\phi} - K^{-1}$$

in which K^{-1} and a were evaluated by making a plot of HX vs $1/(80-\phi)$. 9.2×10^{-7} was used for the dissociation constant of amyl xanthic acid. 1/K, taken from the intercept was equal to 1.12×10^{-9}, giving a value of $K = 8.9 \times 10^{8}$. The value of $a = .009$ was obtained from the slope. Substituting $a = .009$ into the equation, $b = 1 - 80a$, gives $b = 0.27$, which resulted in the following relationship between contact angle and surface coverage for amyl xanthate on galena:

$$\theta = .009\,\phi + 0.27$$

Competitive adsorption data of amyl xanthate and ethyl xanthate on galena were used to evaluate the dissociation constants for amyl xanthic acid and ethyl xanthic acid. The characteristic contact angle for a monolayer of ethyl xanthic acid on galena is sixty degrees. The contact angle for galena covered with a monolayer of amyl xanthic acid is eighty degrees. The contact angle on galena coated with ethyl xanthic acid increased from sixty degrees to eighty degrees, when the specimen was placed in a sufficiently concentrated amyl xanthic acid solution. By adjusting the concentration of amyl xanthic acid intermediate values of contact angle between sixty and eighty degrees were obtained. Contact angle-collector concentration curves were determined at pH values of 3.80, 5.25, 5.70, and 8.10. By interpreting the data in terms of free acid adsorption, the following equation was developed to represent competitive adsorption of the two collectors:

$$\frac{HX_1}{HX_2} = \frac{m_1}{m_2} \frac{(Ka_2 + H^+)}{(Ka_1 + H^+)}$$

HX_1 and HX_2 are free acid concentrations obtained by the addition of amounts of collector m_1 and m_2. Ka_2 and Ka_1 are dissociation constants. Assuming that, for a constant value of contact angle HX_1/HX_2 is constant, the values of Ka_1 and Ka_2 were determined by adjusting these values to superimpose all experimental data on a contact angle - vs - HX_2/HX_1 curve. This method gave a value of $Ka_1 = 8.6 \times 10^{-7}$ and a value of $Ka_2 = 9.3 \times 10^{-7}$. While this study did not give precisely the absolute values of the equilibrium constants, it can be concluded that the dissociation constants for the two acids are of the same order of magnitude probably around 1×10^{-6}.

The data were inadequate to rule out the possibility of a linear relationship between contact angle and surface coverage for the two collector system.

A contact angle study of the $Na_2S.9H_2O$ - potassium amyl-xanthate-galena system was made using experimental procedure similar to that which was used in the study of single collectors. Contact angle measurements were made for various concentrations of collector and depressant at pH values of 5.50, 6.05, 7.45, 7.90, and 8.60. The concentrations of collector and depressant which were required to maintain a given angle were converted to free acid concentrations. By plotting the data, in terms of free acid, curves for different pH values were superimposed. Using contact angle - surface coverage relationships for amyl xanthate, which had been obtained earlier in this work in the constants in the following equation of Last and Cook representing collector-depressant equilibria were evaluated:

$$K_1 \, HX = K' + K'K_2 \, HD$$

Evaluating all of the contact angle data according to the above interpretation gave a constant value of $K_2 = 5.7 \times 10^8$ and a value of $K_1 = 1.35 \times 10^9$. $K' = \theta_{HX}/1 - \theta_{HX}$ was evaluated from the previously determined contact angle-surface coverage relationship for amyl xanthate, $\theta = .009 \phi + 0.27$. These constants were used to calculate a contact angle versus ratio of depressant to collector (ϕ vs HD/HX) curve which superimposed the experimental curve.

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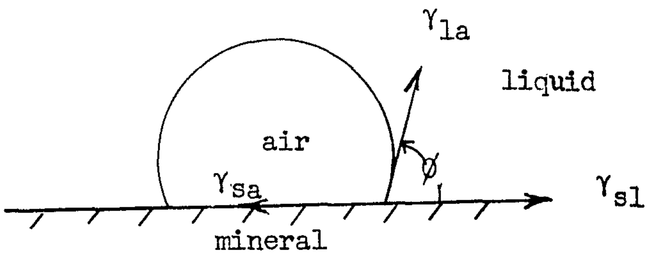
INTRODUCTION

The flotation process has made possible the beneficiation of tremendous tonnages of low grade ores which could not be otherwise utilized. This process concentrates low grade ores and, also, when properly controlled, permits the selective separation of different constituents of complex ores, which contain more than one valuable mineral.

Bulk flotation, in which the valuable minerals are separated as a single product from the waste material, depends upon inducing preferential adsorption of a "collector" upon surfaces of the valuable minerals. The collector is usually a soluble organic heteropolar compound. Selective flotation is accomplished by the addition of a "depressant," which is a compound added to prevent flotation of an otherwise amenable mineral.

Collectors increase the avidity of the mineral surface for air. Conversely, depressants increase the avidity of the mineral surface for water. If an air bubble is placed on the surface of a mineral which has been previously treated with a collector, the bubble will adhere to the surface. When the mineral has not been treated with a collector, the bubble will not adhere to the surface. The former condition is frequently termed "contact," whereas, the latter is termed "no contact" or "zero contact." Varying the amount of the collector on the mineral changes the attraction between the bubble and the surface, i.e., "changes the contact angle."

Sketch 1 is a schematic representation of a bubble in contact with a mineral surface. Since this investigation is not a study of the theory of contact angles, but merely utilizes contact angles in studying adsorption of collectors and depressants, this oversimplified model will be retained.



Bubble on Mineral
Surface

Sketch No. 1

γ_{sa}, γ_{la}, and γ_{sl}, represent the interfacial energies (numerically equivalent to the surface energies) of the solid-air, liquid-air, and solid-liquid interfaces respectively. γ_{la} is drawn tangent to the liquid-air interface, at the intersection of the three interfaces. The angle ϕ, between γ_{la} and γ_{sl}, measured across the liquid phase, is the contact angle.

γ_{la}, the surface tension of the liquid, may be determined experimentally. γ_{sa} and γ_{sl} are not measured ordinarily, however, the difference in interfacial tensions, $(\gamma_{sa} - \gamma_{sl})$, may be related to the work of adhesion of the solid to the liquid. $(\gamma_{sa} - \gamma_{sl})$ is a measure of the wettability of the surface; indirectly, it also may be considered a measure of the attraction of the air and the collector coating on the surface. The work of adhesion between the solid and the liquid is given by Dupre's equation,(2)

$$W_{sl} = \gamma_{sa} + \gamma_{la} - \gamma_{ls} \tag{1}$$

W_{sl} is the work of adhesion of the solid to the liquid. γ_{sa} is the interfacial tension between the solid and air, γ_{la} is the interfacial tension between the liquid and air, and γ_{ls} is the interfacial tension between the liquid and the solid. At equilibrium, the sum of the forces in the horizontal plane must equal zero, therefore, for a finite contact angle ϕ

$$\gamma_{sa} = \gamma_{ls} + \gamma_{la} \cos \phi \qquad (2)$$

Substituting $\gamma_{la} \cos \phi$ for $(\gamma_{sa} - \gamma_{sl})$ of equation 1, gives

$$W_{sl} = \gamma_{la} (1 + \cos \phi) \qquad (3)$$

After measuring the contact angle and the surface tension of the liquid, the work of adhesion may be determined by using equation 3. It should be noted that equation (3) breaks down for zero contact angles, i. e., W_{sl} is not necessarily 2 γ_{la} when $\phi = 0$.

Soon after the introduction of the first captive bubble apparatus, contact angle measurements were recognized as being a convenient experimental method for study of surface phenomena involved in flotation. Investigators used the simple interpretation which has been outlined in the preceding paragraph and proceeded to construct apparatus for measuring the angles.

The first apparatus(36) for measuring contact angles was simply constructed. Basically, most of the later equipment was similar to the original apparatus, however, some innovations were made to increase operating convenience. Early investigators soon realized that the experimental results were dependent upon laboratory techniques; and that a knowledge of the care with which experimental work was performed was vital for the evaluation of results.

Most of the early work was concerned with the development of experimental procedure. Results were reported in terms of "no-contact" or "contact" depending upon whether "zero contact," or a finite contact angle was obtained. Workers then became interested in studying contact angles at low collector concentration, to determine the threshold value required for "contact" to be established. They soon noted that a certain concentration of a given collector must be added to conditioning solutions before any "contact" was obtained. Further investigation showed that the change was not abrupt but was gradual. Also, a definite amount of collector was required for the attainment of a full angle. Radioactive tracer studies have reemphasized the importance of these studies at low collector concentrations. This type of study has also resulted quite naturally from considerations of the transition from regions of "no contact" to regions of "contact."

After the experimental procedure had become more or less standardized investigators used contact angle data as a basis for postulating a mechanism for the adsorption of collectors and depressants on mineral surfaces.

Studies of the transition zone have recently stressed the need for a knowledge of contact angle-surface coverage relationships. Investigators have used their proposed collector-depressant-mechanism for obtaining quantitative surface coverage - contact angle relationships.

This investigation is a continuation of the work of Wadsworth, Conrady, and Cook(38) in which quantitative surface coverage-contact angle relationships were obtained. The experimental procedures and interpretation are those which have been proposed by the above investigators.

Contact angle-surface coverage relationships were obtained for potassium ethyl xanthate, and for potassium amyl xanthate, on galena. In studying the potassium ethyl xanthate-galena system, emphasis was placed on contact angle readings taken at low collector concentrations.

Dissociation constants for amyl xanthic acid and ethyl xanthic acid were then determined. This resulted from a contact angle study of the competitive adsorption of ethyl xanthate and amyl xanthate on galena.

A contact angle study of the $Na_2S.9H_2O$ - potassium amyl xanthate-galena system was also made. The concentrations of collector and depressant which were required to maintain a given angle were converted to free acid concentrations. By plotting the data, in terms of free acid, curves for different pH values have been superimposed. Using contact angle-surface coverage relationships for amyl xanthate, which had been obtained earlier in this work, the constants of Last and Cook(22) which are involved in collector-depressant equilibria,were evaluated. These constants were then used to calculate a contact angle versus ratio of depressant to collector (ϕ - vs HD/HX) curve, which could be superimposed upon the experimental curve.

LITERATURE SURVEY

The literature survey has been divided into six sections. These categories seem to be representative of the trends which were followed in the development of contact angle measurements. Only the general scope of the work and the conclusions which are of current interest are given in each section. Much of the early work which could be included in the section on the "Construction of Apparatus and Development of Experimental Techniques" contains repetitions and has been omitted.

The section on "Collector-Depressant Studies" has also been shortened to avoid repetition. For example, several investigators have studied the depressant effects of sodium cyanide on galena. Since most of the work is not directly applicable to this investigation the references are not emphasized.

Reviews of the theories of flotation, despite their importance in interpreting the experimental data of this investigation, have been thoroughly given in other papers(20, 21, 23, 24, 37) and are not included in this survey.

Construction of Apparatus and Development of Experimental Techniques

Taggart, Taylor, and Ince(36) constructed the first contact angle apparatus. With the exception of minor modifications, this type of apparatus is still being used. Their results were reported in terms of "collecting index." This term was introduced to account for original contamination of the surface, and also served as a correction for bubble distortion. "Collecting index" has no theoretical or practical importance. The cell stage of the Taggart apparatus was modified by del Giudice(6), who also outlined a more elaborate method of cleaning the surfaces.

Wark(39) was instrumental in developing a standardized procedure for the preparation of the mineral surfaces, and listed main sources of contamination. These sources were briefly classified as follows: (a) polishing material and lap; (b) grease from fingers; (c) water, and (d) airborne contamination. Wark's recommendation of cleaning abrasives by ignition is still being followed. He also recommended that fine alumina be used for the final polishing of minerals prior to conditioning them with chemical reagents, and suggested that zero contact angle may be used as a criterion for a clean mineral surface.

Wark(41) also presented a detailed discussion of experimental techniques. This article is recommended for workers who are unfamiliar with the experimental procedure which is ordinarily followed in this type of investigation. Experimental data for several collector systems, as well as collector-depressant systems, are included in this article.

Some Early Results

Wark and Wark(46) presented experimental results showing that the contact angle is dependent only upon the non-polar group of the collector, is independent of the nature of the solid, and is independent of the polar or anchoring group. The following types of collectors were included in their investigation: xanthate, mercaptans, dithiocarbonates, dithiophosphates, trithiocarbonates, and monothiocarbonates. Fleming(10) recently made a study of the effects of alkalinity in flotation. In this work, the experimental procedure of Wark was applied to a study of cerussite. Sutherland(32) also used contact angle measurements to evaluate flotation reagents. In addition, he has noted temperature effects in the study of the adsorption of dithiophosphates on sulfide minerals. Cox, Wark and Wark,(5) discovered that only a trace of potassium ethyl xanthate in water leads to a contact angle, which is independent of the nature of the mineral. Also, it was noted that sodium diethyl dithiophosphate gave the same characteristic angle as did the ethyl xanthate. This fact resulted in the conclusion that the mineral was covered by a unimolecular film. It was also concluded that the alkyl group must be oriented outward from the mineral surface, and that the alkyl groups were packed as closely as their size would permit. Contact angle measurements were used extensively for testing previously untried organic compounds as collectors. Several different types of compounds were independently studied, all of which were of known structure. For example, Wark and Sutherland(44) have conducted single tests to evaluate mercapto benzthiazole as a flotation agent.

Studies of individual reagents were followed by studies outlined to show the effects of addition agents upon adsorption of collectors on minerals. The extensive commercial application of flotation to mineral beneficiation soon prompted this type of investigation. Wark and Sutherland(45) made an investigation of the influence of carbonate, chloride, nitrate, formate, acetate, propionate, and phosphate ions on the flotation of minerals by xanthates. They also investigated effects resulting from the addition of certain cations which are invariably present in flotation circuits.

Studies of Transition Region Between Contact and No Contact

Most of the work involved in early investigations was entirely qualitative. Investigators were interested only in determining whether a reagent produced "contact" or whether it had no effect at all, resulting in "no contact." Certain investigators soon noticed, however, that there was a gradual transition between "contact" and "no contact."

Plante(26) in studying the flotation of oxidized and unoxidized sulphide minerals, emphasized the fact that there is a marked transition zone between "no contact" and "contact." Gaudin and Vincent(15) also noted that there is a gradual transition between full appearance of a finite contact angle and "no contact." These investigators made a study of heptylic acid on siderite. They observed that not less than seven-fold change in heptylic acid is required to change the contact angle from 20° to 60°, within the pH range of 5-10.

Studies with Low Collector Concentrations

The studies of the transition range between "no contact" and "contact" emphasized the need for an investigation of the systems with low collector concentrations.

Edwards and Ewers(8) working with cassiterite and sodium cetyl sulphate, noted that only a very small portion of the mineral needed to be covered by collector in order to make flotation of the mineral possible. The contact angle tests of Taggart and Hassialis(35) indicated that the minimum concentration for establishing a coating of ethyl xanthate on galena is .0007 mg. per liter. They further stressed the importance of low concentration studies, by noting the effects of variations in induction times and total elapsed times upon the measured contact angles.

Recently, radioactive studies stressed the importance of studies at low collector concentrations. Judson, et al.,(18) used radioactive tracer techniques to study the distribution of dithiophosphates during the selective flotation of galena and sphalerite from quartz.

Studies of Contact Angle-Surface Coverage Relationships

Refined experimental techniques, with and without the aid of radioactive tracers led to the study of contact angle-surface coverage relationships. Postulated relationships may only be found in the more recent flotation literature.

Radioactive barium and lauric acid which had been labeled with radioactive carbon, were used by Gaudin and Chang(13) to study adsorption at equilibrium on ground quartz. They gave the surface coverage required for flotation of the quartz.

As is true with contact angle measurements, radioactive tracer techniques must be well developed in order to obtain precise experimental results. Consequently, well established techniques involved in contact angle measurements are still being adhered to by many investigators. Recent contact angle investigations have given results which are as reliable as radio tracer techniques.

Philippoff, Cooke, and Cadwell(25) correlated results which were obtained independently by contact angle measurements with results using radioactive techniques. They studied the adsorption of dodecylamine on a composite surface of glass and lucite. These results were used to formulate a relationship between surface coverage and contact angle. Comparison of their data with that obtained by a radioactive study of the adsorption of dodecylamine on quartz was used to substantiate their proposed contact angle-surface coverage relationship.

Wadsworth, Conrady and Cook(38) demonstrated that by proper interpretation of experimental data, the relationship between contact angle and surface coverage can be determined entirely from contact angle work. Their work includes consideration of ionic strength. Ionic strength has recently been emphasized in other types of adsorption(4).

Although not directly connected with the contact angle-surface coverage relationsip, Hagihara(16) by making an electron diffraction study of xanthate films on galena, verified that collector adsorption may be considered a single site free acid process.

Collector-Depressant Studies

As far as the general nature of the work is concerned, the studies on collector-depressant systems are quite similar to the work on single collector systems. The experimental techniques, number of investigations, types of collectors, and number of minerals studies, are essentially the same as have been considered in the single collector systems.

Again, the course of investigations has been influenced by the results which had been obtained in actual flotation circuits. Gaudin(12) noted that amyl xanthate is far superior to ethyl xanthate for collector-depressant studies. Plante(26) used captive bubble tests to show temperature effects on the depression of certain sulphide minerals by cyanide. Wark Cox(43) showed that, in the absence of copper sulphate, a change in temperature from 10°C to 35°C merely alters slightly the amounts of depressants necessary to prevent contact. The effects of addition of various cations on depressant action were studied by Sutherland(33). He has noted irregularties in the concentration of depressant-pH curves, when certain cations were present. Both amyl xanthate and ethyl xanthate were tested. The minerals included in this investigation were pyrite, chalcopyrite, sphalerite, and galena.

Using radioactive tracer techniques, Simard, Burke, and Salley(30) studied the interaction of dithiophosphate with galena. They concluded that the adsorption of dithiophosphate on galena is effected by the presence of phosphates. Gaudin and Charles(14) made a study of depressant effects of calcium and sodium on pyrite. Fleming(10) studied the effects of alkalinity on the flotation of lead minerals. He used potassium hydroxide for pH control, and worked entirely with oxidized lead minerals. The results were interpreted in terms of a three-stage reaction for depression of minerals. Wark and Cox(42) used captive bubble tests to study the $Na_2S.9H_2O$-galena-xanthate systems and noted that the concentration of Na_2S required for depression is a function of the pH of the system. They found that liberation of H_2S during the ordinary experimental procedure was sufficient to materially effect their results. When glass conditioning cells were covered with ground glass plates, the losses of H_2S as determined by chemical analysis, were negligible.

CONTACT ANGLE APPARATUS

Generally speaking, devices for making captive bubble tests must make provision for placing a bubble on the mineral surface, and must also provide a convenient means of measuring or recording the angle of contact. The prototype was constructed by Taggart, Taylor, and Ince(36) and practically all subsequent workers have used modifications of their apparatus.

Illustration 1 shows the contact angle apparatus used in this investigation. It is mounted on a reinforced angle iron base which is bolted directly to the table top. A mineral is placed in the glass absorption cell, positioned directly under the vertical capillary tube. The capillary tube, 3 mm. diameter, is mounted in the body tube of a microscope, which is bolted on a reinforced backing plate above the glass absorption cell. This arrangement provides a means of bringing the bubble into contact with a mineral surface. The bubble is either photographed, or its image is projected upon a screen. Using a protractor, one can measure the contact angle directly from the projected image. Photographs have the advantage that negatives may be kept for a permanent record.

The glass absorption cells were purchased from Schaar and Co., Chicago, Ill. They have diameters matched to within 0.002 inch, and their surfaces are formed to mirror smoothness. High quality cells are necessary to minimize dispersion and deflection of the light. Measurements of low angles are inherently difficult to make with precision, consequently, a sharp focus is particularly desirable.

Light is furnished by a 200-watt spherical lamp, equipped with a diaphragm which may be adjusted to give a nearly horizontal beam. When

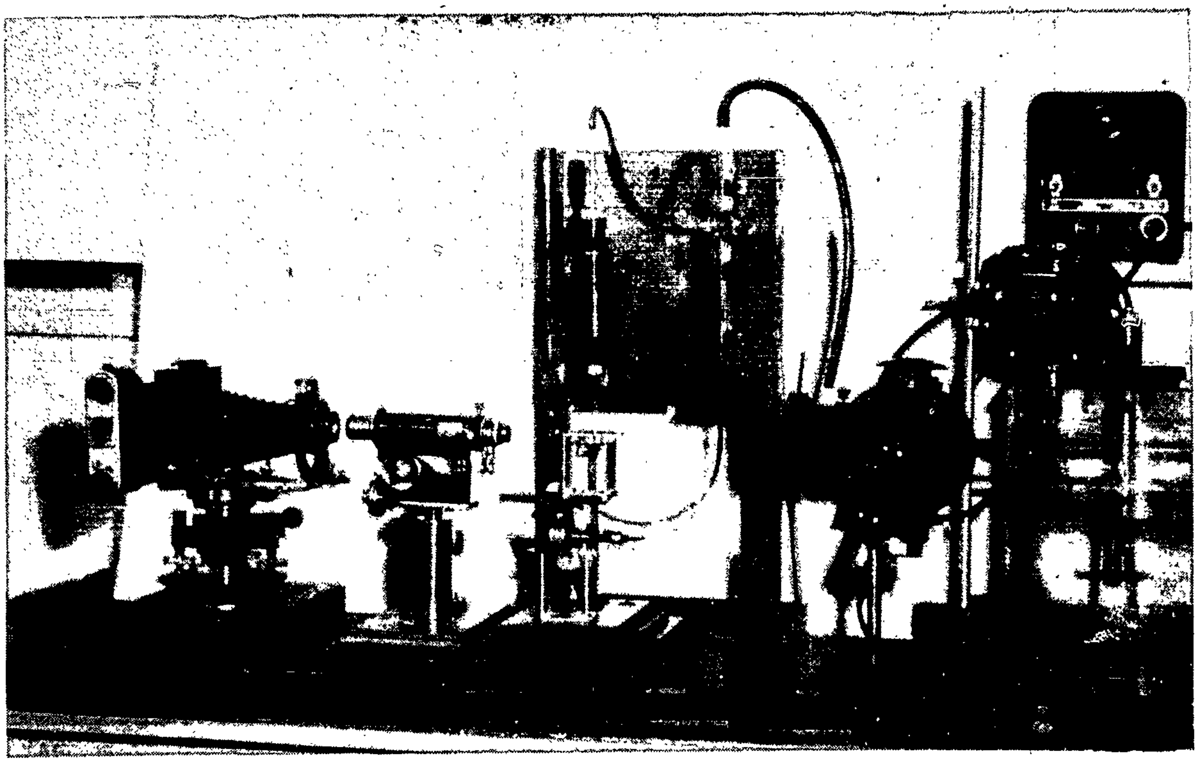


Illustration Number 1, Contact Angle Apparatus measurements which require extended periods of time are made, a water-filled cell is placed between the lamp and the absorption cell containing the mineral. This intermediate cell prevents appreciable increases in the temperature of the solutions in the test cell.

Magnification of the bubble image is produced by a Bausch and Lomb microscope, which is equipped with a 48 mm. objective and a 5X eyepiece. In order to allow focusing, both camera and microscope are mounted on steel rails. The camera is an Eastman Recomar No. 18 camera equipped with a 35 mm. film adapter.

The internal pressure of the captive bubble is controlled by a mercury-filled glass U-tube, having a micrometer adjustment on one side and a three-way stopcock on the other. This device is mounted on a reinforced backing plate above the bench and is connected to the capillary tube by thick-wall rubber tubing. The rubber tubing and all of the connections are coated with glyptal to make the system air tight.

The micrometer adjustment was constructed from a precision outside micrometer. A cylinder, having an inside diameter equal to the diameter of the spindle was mounted on the micrometer frame in such a manner that the spindle would act as a piston. The outside of the lower end of the cylinder was tapered to fit a ground glass joint on the U-tube. The micrometer adjustment provides positive displacement of mercury, which, in turn, displaces air and forms a bubble on the end of the capillary tube.

The three-way stopcock may be opened to the atmosphere, or may connect the U-tube with the capillary tube. This provides a means of cleaning and removing solution from the bottom of the capillary tube.

REAGENTS AND PREPARATION OF MATERIALS

The possibility of contamination is always a vital factor in this type of investigation. Impurities may be introduced inadvertently either by indiscriminate choice of chemicals or by inadequate preparation of materials prior to actual experimentation. For this reason, a complete description of the chemicals and a discussion of the preparation of the materials, despite the simplicity, is given in this section.

Galena

The galena was purchased from Ward's Natural Science Establishment, Rochester, New York, and was of the highest purity which could be obtained. The specimens, approximately one-inch cubes, were all single crystals. Microscopic and microchemical etch tests failed to show traces of impurities.

Considerable care was taken during the grinding process. It was found that this procedure saved time because samples did not require nearly as much polishing. Wark and Cox(41) investigated different methods of grinding galena, and concluded that, provided the galena surface is freshly prepared and is free of slimes, the actual method of preparation is immaterial. This factor is shown by the diversity of the following methods, all of which gave satisfactory results. The following methods of preparing the sample are included in their work: (a) grinding on a glass plate under distilled water, (b) grinding on a glass plate under running water, (c) grinding on a glass plate, followed by wiping the mineral surface with either linen or filter paper, (d) scraping the surface with a steel blade after the mineral has been ground level, (e) forming a new surface by cleaving the mineral under water, and, finally (f) first, polishing and then wiping the mineral surface with linen. All of these methods were tested, but were not used because the specimens required extra polishing in order to give acceptable surface.

For this work, the galena cubes were cut into halves, and the newly formed surfaces were polished with metallographic paper. The metallographic paper was pasted on a variable-speed, vertical disk sander equipped with a micrometer feed, in which the crystal could be rigidly supported. This sander produced a uniform surface on the mineral and, when rotated at low speeds, did not gouge out small particles from the surface of the galena. After successively grinding from 2/0 paper down through 00 paper, the specimens were mounted in lucite. A Buehler Mounting Press was used to mount the specimens. The final grinding was then done on a horizontal lap covered with broadcloth, using 600-mesh carborundum as an abrasive.

Following this final grinding there were two stages of polishing. All of the polishing was done on a Fisher Scientific Co., variable-speed metallographic polisher. After polishing the samples were stored in distilled water until needed. The water was changed daily in order to minimize contamination.

No attempt was made to obtain a particular orientation of the mineral surface. Wark and Cox(41) have considered surface orientation, and have shown experimentally that, as far as contact angle is concerned, orientation is unimportant. These workers made contact angle measurements on several different crystals of known orientation, some of which were parallel to the cleavage plane others on octahedral planes. No appreciable change in contact with variation in the orientation was noted.

Abrasives

The abrasives were of commercial quality and, with the exception of the minus-one-mesh alumina, were used as received without further purification or special treatment.

Coarse material scratched the mineral surface considerably and thereby necessitated considerable extra polishing whenever used. Since the finely divided alumina tends to agglomerate when traces of organic matter are present, the alumina was heated to 1600°F. After firing, the material was dispersed in distilled water, and the fine fraction was removed by elutriation. After allowing sufficient time for most of this fine material to settle, the excess water was decanted off. Use of flocculation reagents was avoided, because of the possibility that they might contaminate the galena surfaces during the polishing process. Until ready for use, the alumina was stored in glass containers. Polishing solutions were made up by merely diluting this stock solution. The solutions were made up daily, with small quantities of stock solution and high dilution being used in each batch. 600-mesh carborundum, a product of the Carborundum Company, was used for the final grinding. For the initial polish, 900-mesh alumina was used; for final polishing, and also for cleaning the galena between successive tests, minus-one-micron alumina was used.

Polishing Cloth

A high quality broadcloth, which had been boiled alternately in a sodium carbonate (analytical grade) solution, and then in a weak hydrochloric acid solution, was used for a polishing cloth. After boiling, the cloth was rinsed several times in distilled water and then stored under water in a covered glass container.

Preliminary tests showed that the cloth must be free of flaws in the weave and breaks in the thread, since it was noted that these were sufficient to cause considerable scratching of the mineral surface.

The same type of material as was used in polishing the galena, was used to wipe off the specimens prior to actually taking the contact angle readings.

Xanthates

Potassium ethyl xanthate and potassium amyl xanthate were the two collectors used in this investigation. The potassium ethyl xanthate was of special high purity, and was obtained from the American Cyanamid Company. The potassium amyl xanthate was synthesized in this laboratory by using analytical grade reagents.

The xanthates were purified periodically according to the method described by Foster(11), i. e., recrystallizing from mixtures of acetone and ether. Purification was done about once every four weeks, or more often, if deemed necessary. The reagents were stored in tightly stoppered bottles which were placed in a dessicator.

Cleaning Solution

Chromic acid cleaning solution was used throughout for cleaning glassware. The solution was made up daily, using technical grade potassium dichromate and concentrated sulphuric acid.

Distilled Water

Distilled water was made in the laboratory, using a Precision Instrument Co., block tin still, the runoff of which was adjusted so that only sufficient distillate for one day's consumption was produced. No further treatment was given the water prior to its use in the experiment. Distilled water was used for all of the polishing and the cleaning.

Buffers

All chemicals used in preparing buffer solutions were of analytical grade. Potassium dihydrogen phosphate-disodium acid phosphate buffers were used at pH values up to 8.50; and sodium carbonate-sodium bicarbonate buffers were used above a pH of 8.50. A Beckman pH meter was used for measurements for values up to pH of 8.50. Calculated values were used above pH of 8.50. Potassium chloride was used to adjust solutions to 0.1 ionic strength.

Depressant Solutions

Analytical grade $Na_2S.9H_2O$ was used in making up the depressant solutions. Since sodium sulfide loses its water of crystallization above

$50^{\circ}C^{(9)}$ the reagent was kept in a refrigerator until ready for use.

EXPERIMENTAL PROCEDURE

In the preliminary work of this investigation, it was noted that one must adhere strictly to a well defined experimental procedure, if consistent results were to be obtained. This was especially true, when working with low collector concentrations. Later, it was realized that, as an aid in the interpretation and evaluation of the experimental results, the actual techniques must also be well defined. This section contains a detailed description of the experimental procedure.

For all of the experimentation in this investigation the procedure was essentially the same. A slight modification was used in the collector-depressant equilibria studies. In this phase of the work, the low, wide form Kimble weighing bottles, equipped with Standard Taper interchangeable glass stoppers fitted on the outside of the bottles, were used as conditioning cells. This was done to prevent liberation of hydrogen sulphide. Otherwise, the technique was the same as that which was followed while working with the single and two-collector systems.

Cleaning Glassware

Before each run, all glassware was cleaned by washing with chromic acid cleaning solution. Since dichromate is a depressant for galena, the glassware was then rinsed several times with distilled water. The capillary tube was cleaned with cleaning solution prior to testing the mineral surface for cleanliness (see "Testing for Cleanliness"), and again before taking a series of readings. After cleaning with chromic acid, the end of the capillary tube was kept under distilled water to prevent contamination. The tube was rinsed thoroughly with distilled water between individual readings in the series.

Preparation of Solutions

The collector and depressant solutions were prepared daily. Siedler(29) has shown that there is no appreciable decomposition of the xanthate in thirty-six hours, however, in this investigation, it seemed important to minimize the time which the solutions were made up before the mineral was polished. This procedure allows less chance for contamination, and also cuts down on the possibility of decomposition when working with solutions of low pH.

The required amount of reagent was weighed on an analytical balance, and placed in a one-liter flask. Sufficient buffer was taken from a stock solution and added to the collector solution such that, when diluted to one liter with distilled water, the ionic strength of the resulting solution was 0.1. The collector solutions were kept in the stoppered flasks until just prior to polishing the minerals, at which time the collector solutions were pipetted into conditioning cells. The collector concentrations in the cells were then adjusted by the further addition of solution containing only the buffer.

Twenty-five milligrams of xanthate was the least amount weighed on the balance. This procedure was followed in order to eliminate errors which are inherent in weighing smaller quantities.

Polishing

Hassialis and Myers(17) have adequately demonstrated that, by using proper polishing technique, an adsorbed xanthate film can be removed from the surface of galena. The same specimens, twenty in number, were repeatly used throughout this investigation. Each sample was polished and checked for a zero angle, before being conditioned in the collector solution. Approximately ten samples were polished on a lap before changing the polishing cloth.

It was found that best polishing results were obtained when the lap was covered with two thickness of broadcloth. Until the new cloth had been properly conditioned with abrasive it frequently failed to clean the sample sufficiently. Conditioning the lap was accomplished by thoroughly moistening the new cloth, adding excessive amounts of abrasive, and then polishing a mineral specimen for only a short time. This procedure allowed the abrasive to work into the cloth and subsequently resulted in greater polishing action than would otherwise have been possible. Care was taken not to apply too much pressure to the mineral during this process because the excessive amounts of abrasive caused unnecessary scratching of the specimen.

After preparing the new cloth, the minerals were polished for testing. The lap was thoroughly rinsed off after each mineral had been polished. After rinsing, a small amount of abrasive was put on the lap. The mineral was held lightly against the lap for a short time before additional water was used. Best results were obtained by starting with a moist lap, adding a small amount of abrasive, and polishing for a short time with no additional water; water was then poured on the lap, slowly at first, and gradually increasing in amount, until a large excess was being used at the end of the polishing period. This procedure was necessary to insure that all slimes and abrasive had been removed from the surface. When the polishing had been completed, the mineral was rapidly transferred to an absorption cell containing distilled water in which the mineral could be checked for cleanliness.

Testing for Cleanliness

When a bubble is held on a coated mineral surface there is very definite attraction of the air and the surface, the measure of which is indicated by the angle of contact. On the other hand, when a mineral has been thoroughly polished a bubble may be held on the surface indefinitely without any evidence of attraction between the air and the mineral surface. This latter case is termed "zero angle."

Early workers(7,19) have shown that sulfide minerals are wetted by water, however, there has been some question(27, 28) as to the validity of early conclusions. More recently, however(34, 40, 41, 47) investigators have assumed that zero contact angle is adequate criterion for a clean surface. Unfortunately, this does not mean that the surface is absolutely free of contamination, but can only be interpreted as meaning that the concentration of the contaminant, if present at all, is insufficient to affect the angle of contact.

After testing and having been found clean, the mineral was transferred to cells containing the collector, or collector-depressant solution. Transferring the mineral from one container to another, and from the lap to the test cells was accomplished very rapidly in order to minimize chances of contamination. The specimens were handled only with tongs and were not touched with bare hands.

Conditioning the Minerals

The time which is allowed for the establishment of equilibrium on the collector film is important in contact angle studies. This is discussed by Taggart(34) and emphasized by Taggart and Hassialis(35).

Wark and Cox(41) have shown that equilibrium is established in ten to thirty minutes for most cases, however, periods up to two hours may occasionally be required. At least one and one-half hours was allowed for establishment of equilibrium in all of this work. After conditioning the minerals the contact angle readings were taken.

When polished surfaces are left in distilled water for several hours, they cannot be treated chemically so that they will become responsive to xanthate. For this reason, Wark and Cox(41) have recommended wiping the surface with either filter paper or cloth before taking the contact angle readings. In this investigation, the surfaces were wiped prior to taking the readings, using the same type broadcloth as was used for polishing the minerals.

Induction Time

The induction time, defined as the time during which the bubble is actually in contact with the mineral, is important when working with low collector concentrations(35). Induction times varied from a minimum of ten minutes, for high collector concentrations, up to periods of 60 minutes, for low collector concentrations.

Wark and Cox(41) have shown that the readiness with which equilibrium is established is also a function of the smoothness of the surface. Since the same samples were used repeatedly in this work the resulting surfaces were highly polished, thus minimizing the required induction periods.

Measurement of Contact Angle

The bubble was pressed down on the mineral by means of the capillary tube. After contact had been established, the capillary tube was raised very slowly until the area of contact of the bubble on the mineral just began to diminish. Subsequent adjustment, when necessary, was made with the micrometer pressure control.

In the past, tapping of the cell has been recommended for initiating contact (1, 19). This method was sometimes resorted to when measuring contact angles in solutions of low collector concentration.

Advancing and receding angles may be quite different. Edser(7) using Sulman's experimental data, which admittedly was a result of questionable technique, shows hysteresis values of 28-38° in the case of galena. Ablett's work(1) has shown that the mean of the advancing and the receding angle is represented by the equilibrium angle.

Wark(41) has shown that small variations in the size of the bubble have little or no effect on the contact angle. In this work, the size of the bubble (5 mm. diam.) was maintained as near constant as was possible by using guide lines on the projection screen.

All of the contact angle measurements were made at room temperature.

POTASSIUM ETHYL XANTHATE ON GALENA

Experimental Procedure

The procedure for the study of the potassium ethyl xanthate-galena equilibria has been outlined previously by Wadsworth, Conrady, and Cook(38). These investigators used collector concentrations of fifty milligrams per liter or more. In the present investigation nearly all of the collector concentrations were less than fifty milligrams per liter.

Using the experimental techniques which have been outlined in the previous section, contact angle-collector concentration curves were obtained for pH values of 5.50, 6.45, 7.35, 8.20, 9.40, 10.00, and 10.50.

The preparation of the mineral surface seemed to be more critical than the actual measurement of the contact angle. Rather than recording two or three readings on the same sample, several different samples were prepared, and a single reading was recorded for each sample. Freshly prepared xanthate solutions were used for individual tests.

Special precautions were necessary when single readings were recorded on each sample. Minute flaws and scratches in the mineral surface distort the bubble sufficiently so that the true equilibrium angle may not be obtained. If there seemed any doubt as to the validity of a reading the sample was moved and a second reading was taken.

Experimental Results

Figure 1 is a composite of the averaged values taken from experimental readings as shown in Figure 2 through Figure 9, in which the data are indicated as experimental bands. All readings were included in these bands.

Figure 1

Contact Angle - Concentration Potassium Ethyl Xanthate

(Averaged Contact Angle Readings)

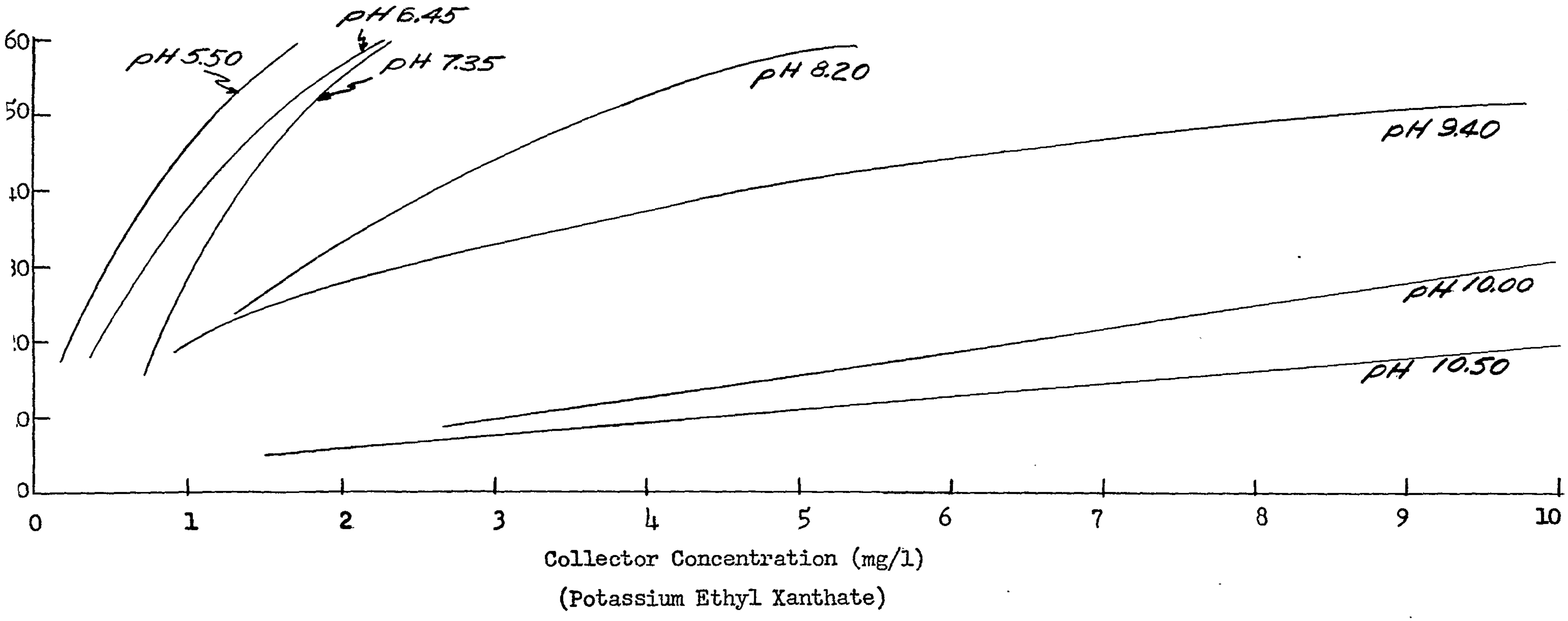


Figure 2

Contact Angle - Concentration Potassium Ethyl Xanthate

pH 5.50

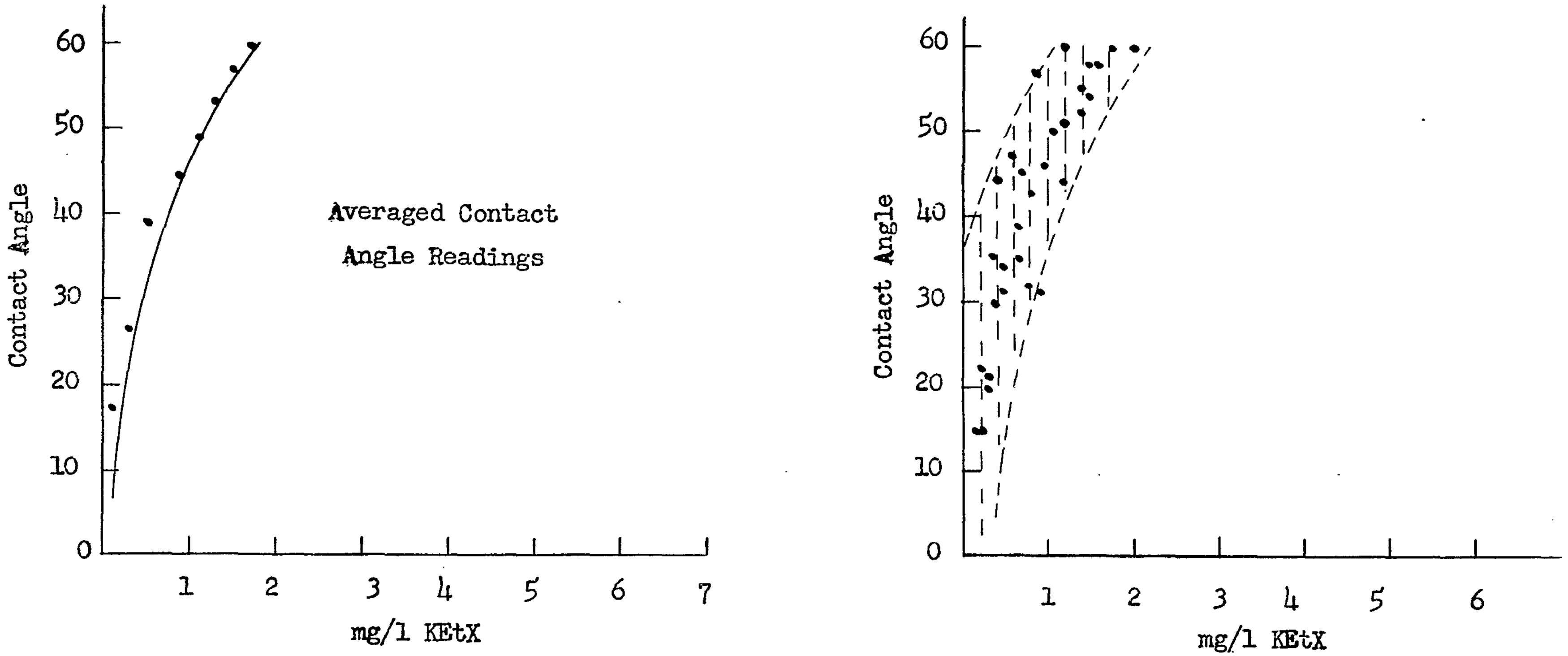
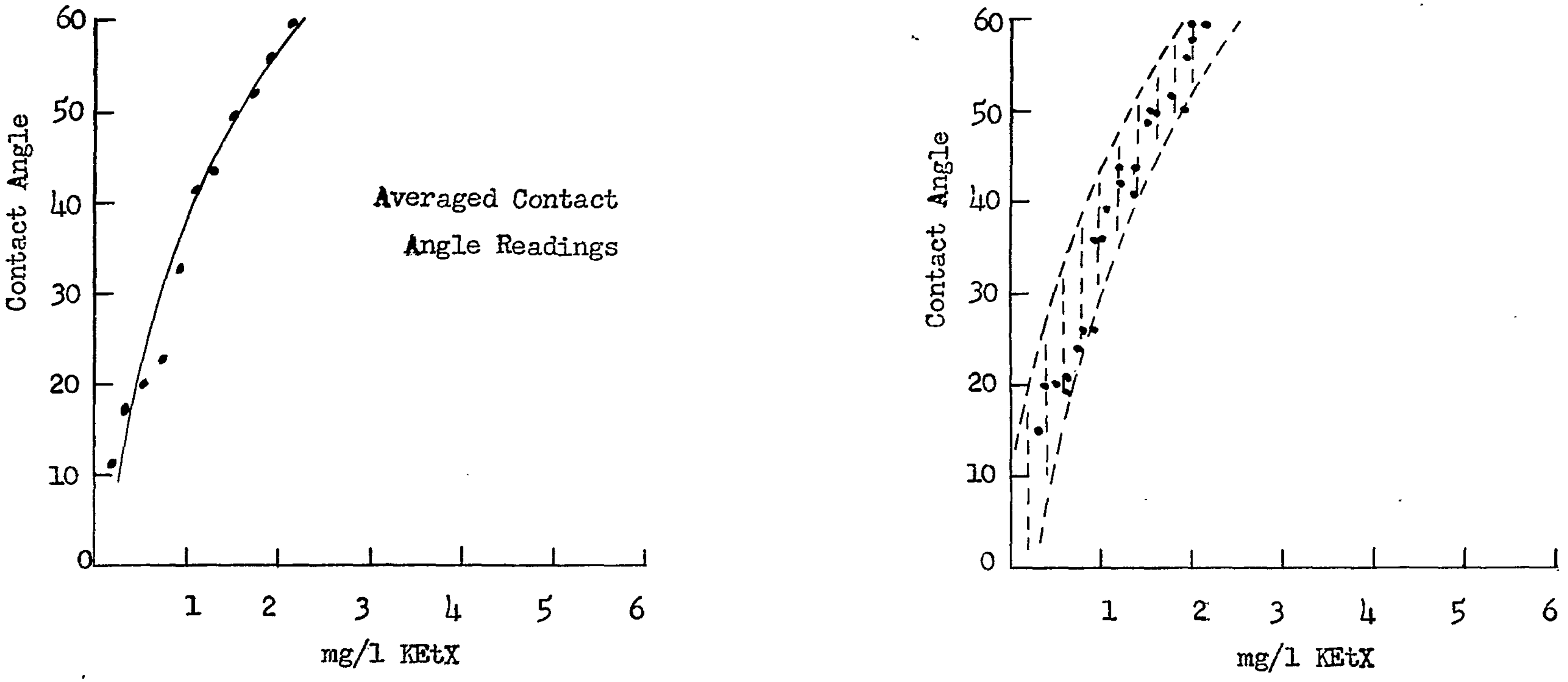


Figure 3
Contact Angle-Concentration Potassium Ethyl Xanthate
pH 6.45



Contact Angle - Concentration Potassium Ethyl Xanthate

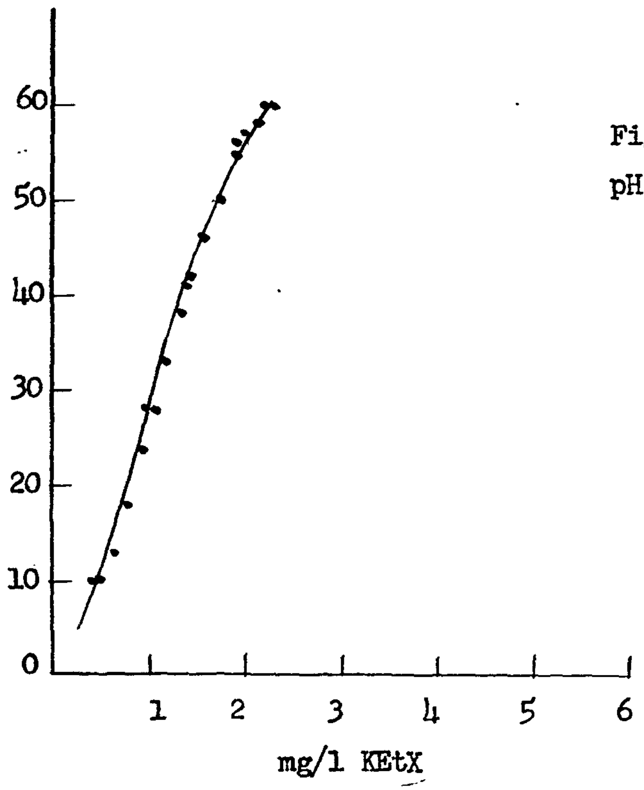


Figure 4
pH 7.35

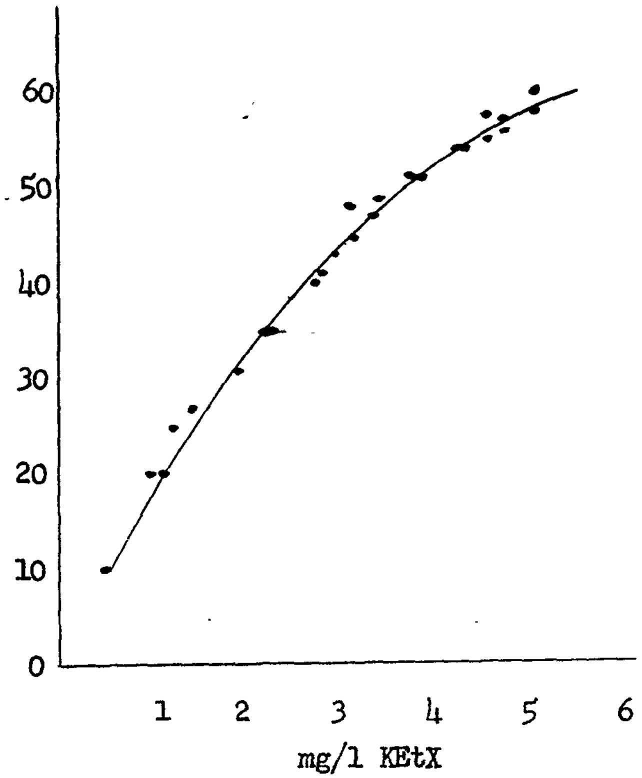


Figure 5
pH 8.20

Figure 6

Contact Angle - Concentration Potassium Ethyl Xanthate

pH 9.40

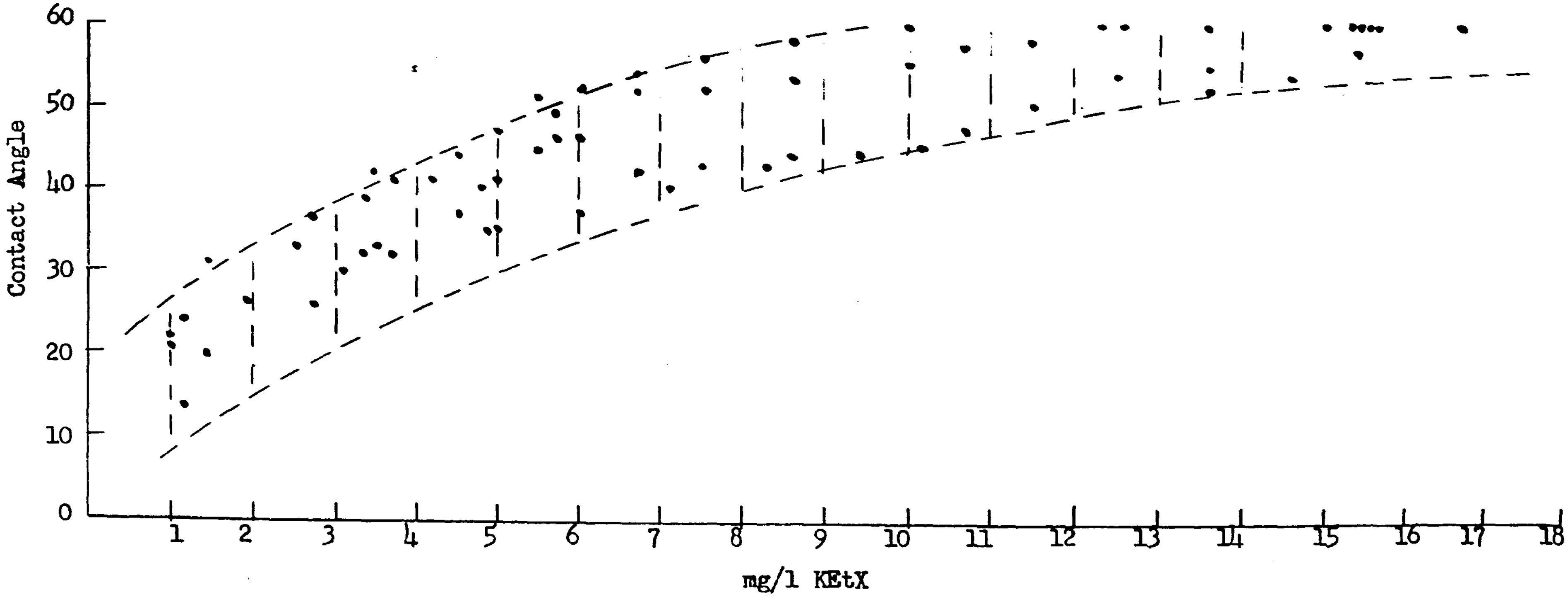


Figure 6a

Contact Angle - Concentration Potassium Ethyl Xanthate

(Averaged Contact Angle Readings)

pH 9.40

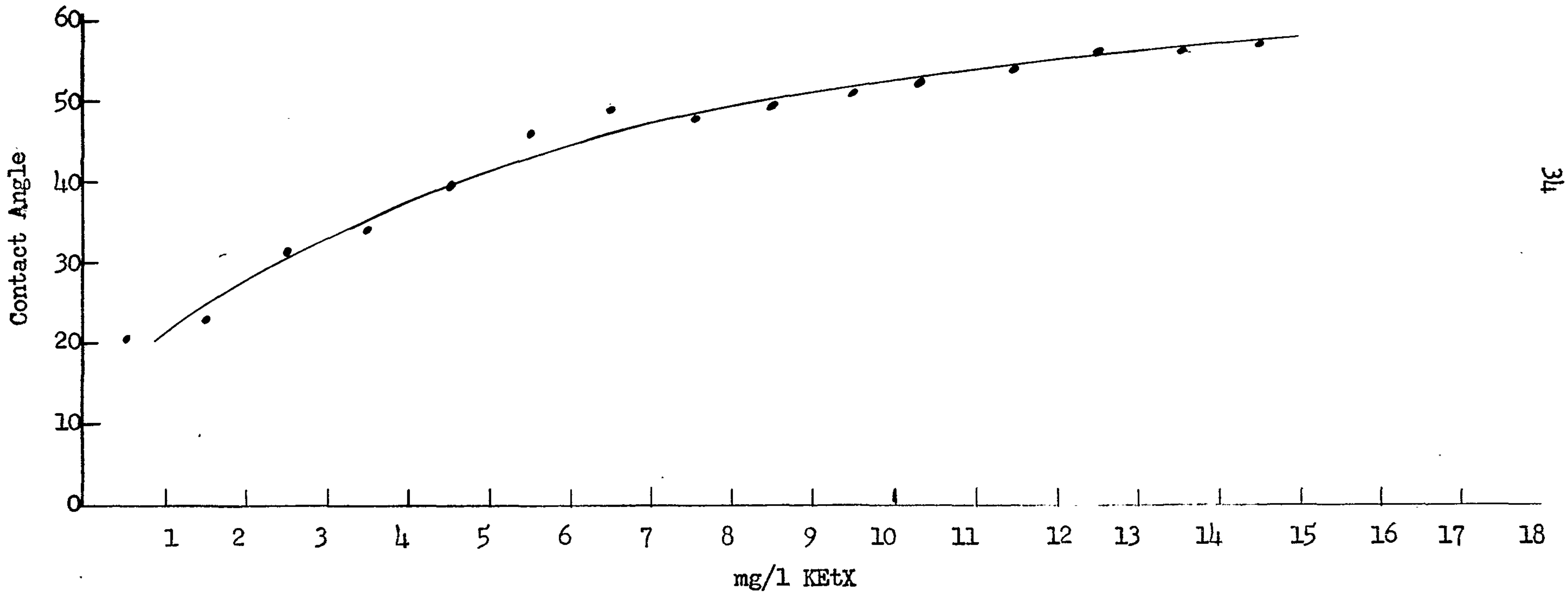


Figure 7

Contact Angle - Concentration Potassium Ethyl Xanthate

pH 10.00

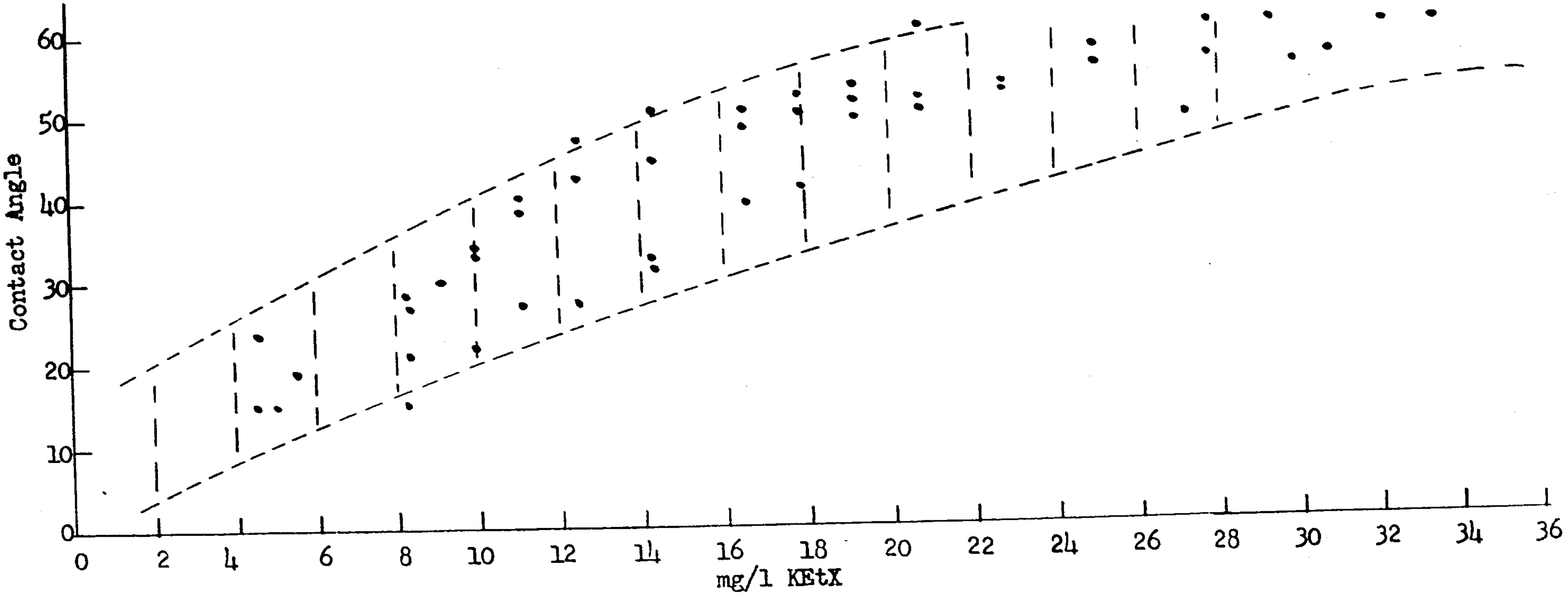


Figure 8
Contact Angle - Concentration Potassium Ethyl Xanthate
pH 10.00

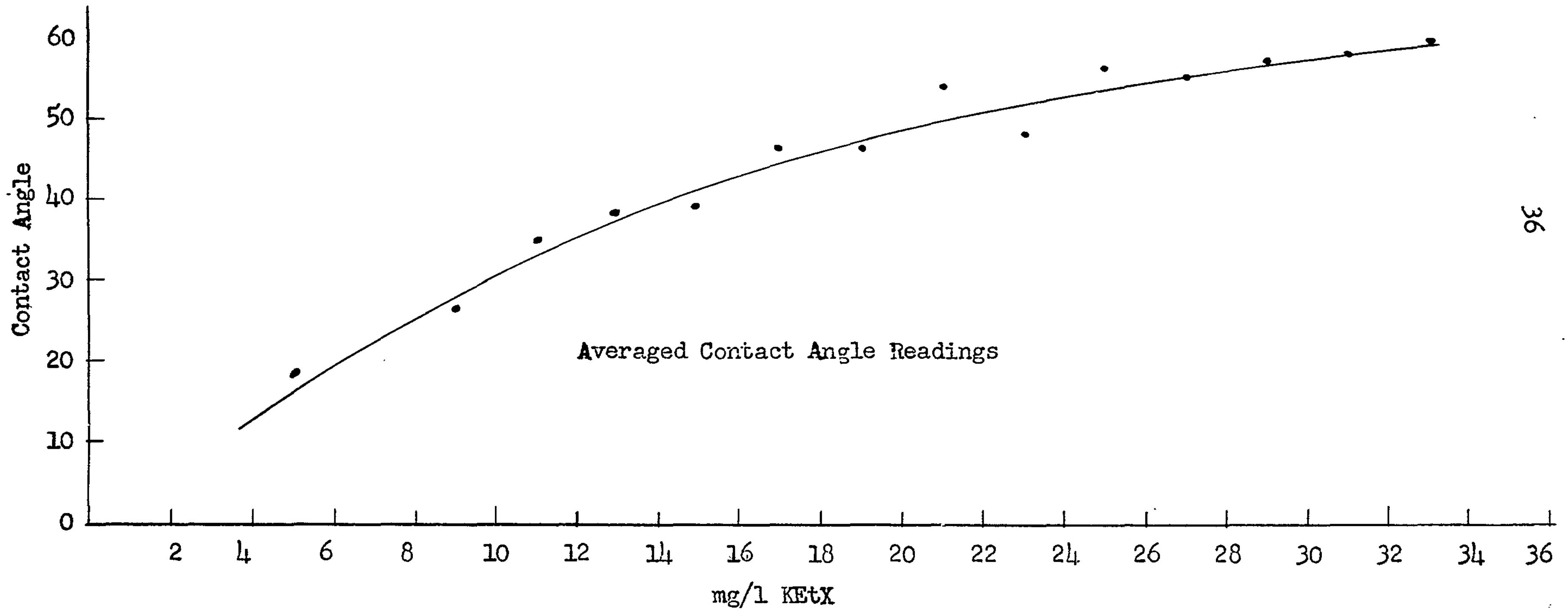
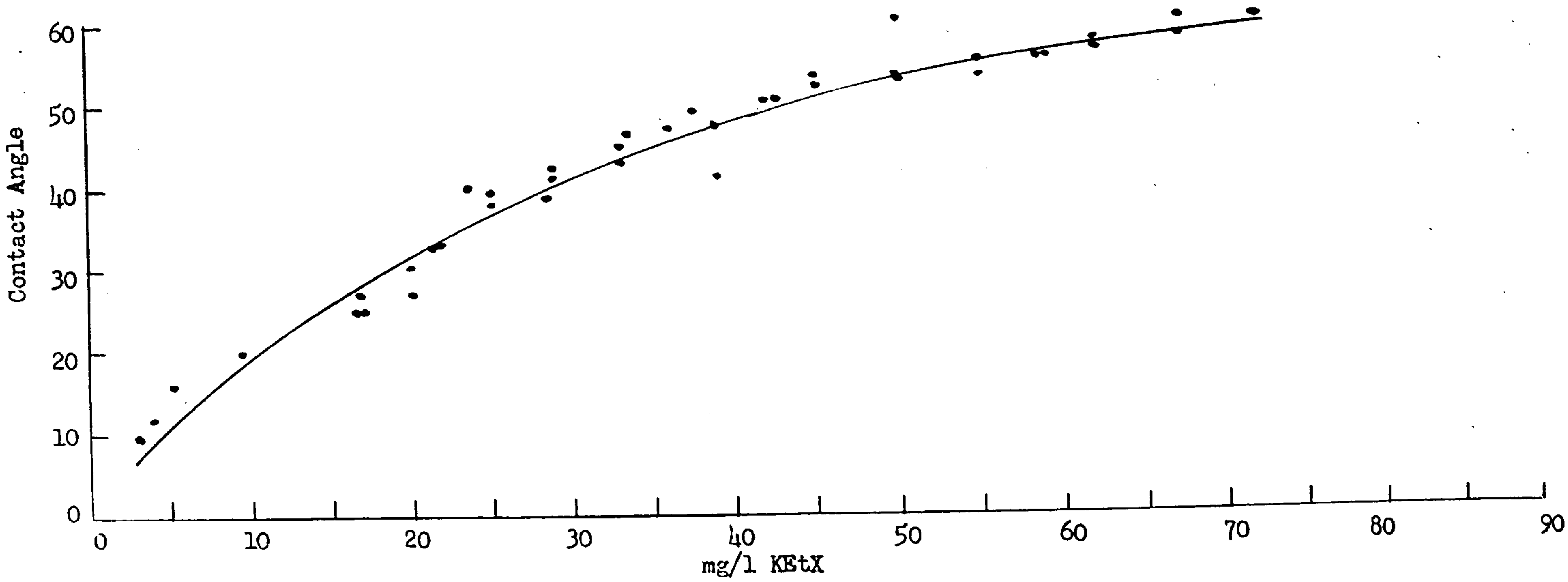


Figure 9

Contact Angle - Concentration Potassium Ethyl Xanthate

pH 10.50



Each point is an average of two readings, one reading having been taken on each side of the bubble.

The dotted lines outlining the bands are, therefore, an indication of the limits of experimental error. Limits of experimental error attributed to the actual measurement of the angle, i.e., disregarding the differences due to preparation of the mineral surface, are plus or minus 2 degrees. The chainomatic analytical balance allows the collector to be weighed to 1/10 milligram, consequently, the concentration measurements are much more accurate than are the contact angle readings.

Figures 2, 3, 6 and 7, representing readings taken at pH values of 5.50, 6.45, 9.40, and 10.00, show that there is a considerable spread in the actual readings. From the bands, it may be noted that, for a given collector concentration, the readings of contact angle are spread over as much as twenty degrees; conversely, for a given contact angle, the spread in concentrations is as much as 10 mg/liter, in the case of pH of 10.00.

Since the limits of experimental error encountered in weighing the collector are much less than limits encountered in measurement of the contact angle, the abscissa was divided into equal regions for averaging. For different pH values the divisions were of different magnitude, as is indicated by vertical lines drawn through the bands (Figures 2, 3, 6, and 7). Readings which fell on division lines were averaged with points representing lower collector concentrations.

The readings taken at a pH of 5.50 were also averaged by taking the root mean squares, but comparison with the results obtained by the method of averaging outlined above showed little difference in the final results.

When necessary, this method of approximating averages has been used throughout this work for interpreting the experimental data. In Figures 4, 5, 8, and 9 the experimental results were not averaged.

Values used for calculations in theoretically interpreting these data were taken from the curves of Figure 1.

Interpretation of Results

The experimental data were interpreted by assuming that the effective collector is xanthic acid, and also that a single site mechanism applies(23, 37, 38). The theoretical interpretation has been given by Wadsworth, Conrady, and Cook(38) and is included in this paper to provide a basis for comparison of the experimental results.

The following equation represents the dissociation of the xanthic acid:

$$HX \rightleftharpoons H^{+} + X^{-} \qquad (1)$$

from which the dissociation constant may be written,

$$K_a = \frac{[H^{+}][X^{-}]}{[HX]} \qquad (2)$$

Using a dissociation constant of 8.6×10^{-7}, which was evaluated as described elsewhere in this paper, the concentrations of added collector were converted to free acid concentrations. If it is assumed that the following material balance applies:

$$m = HX + X^{-} \qquad (3)$$

(where m is the concentration of collector added, X^{-} is the concentration of the xanthate ion, and HX is the concentration of free acid collector, all in equivalent units), the relationship between added collector and the free acid concentration was obtained by substituting equation 3 into equation 2, and then solving equation 2 for HX:

$$HX = \frac{[m][H^+]}{[K_2 + H^+]} \qquad (4)$$

For convenience, these data are plotted as contact angle versus log HX in Figure 11. The values are also included in the tables at the end of this section, page 49.

From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH, for constant values of contact angle were constructed. This plot is shown in Figure 10. The concentration of free acid is constant for a given contact angle. After evaluating equilibrium constants and those constants involved in assuming a linear relationship between contact angle and surface coverage, these experimental concentration-pH curves may be compared with the calculated curves.

The equilibrium constant and the contact angle-surface coverage relationship were determined by the method described in the following paragraphs.

An equilibrium equation for the adsorption of the collector on the surface may be written in the following manner:

$$S + HX \rightleftharpoons SHX \qquad (5)$$

or, writing the equilibrium constant,

$$K = \frac{[SHX]}{[S]\,[HX]} \qquad (6)$$

S is the concentration of unoccupied surface sites. If θ is the fraction of the surface covered by the collector, $\theta = SHX$, and $S = 1 - \theta$. Substituting these values into equation 6 gives

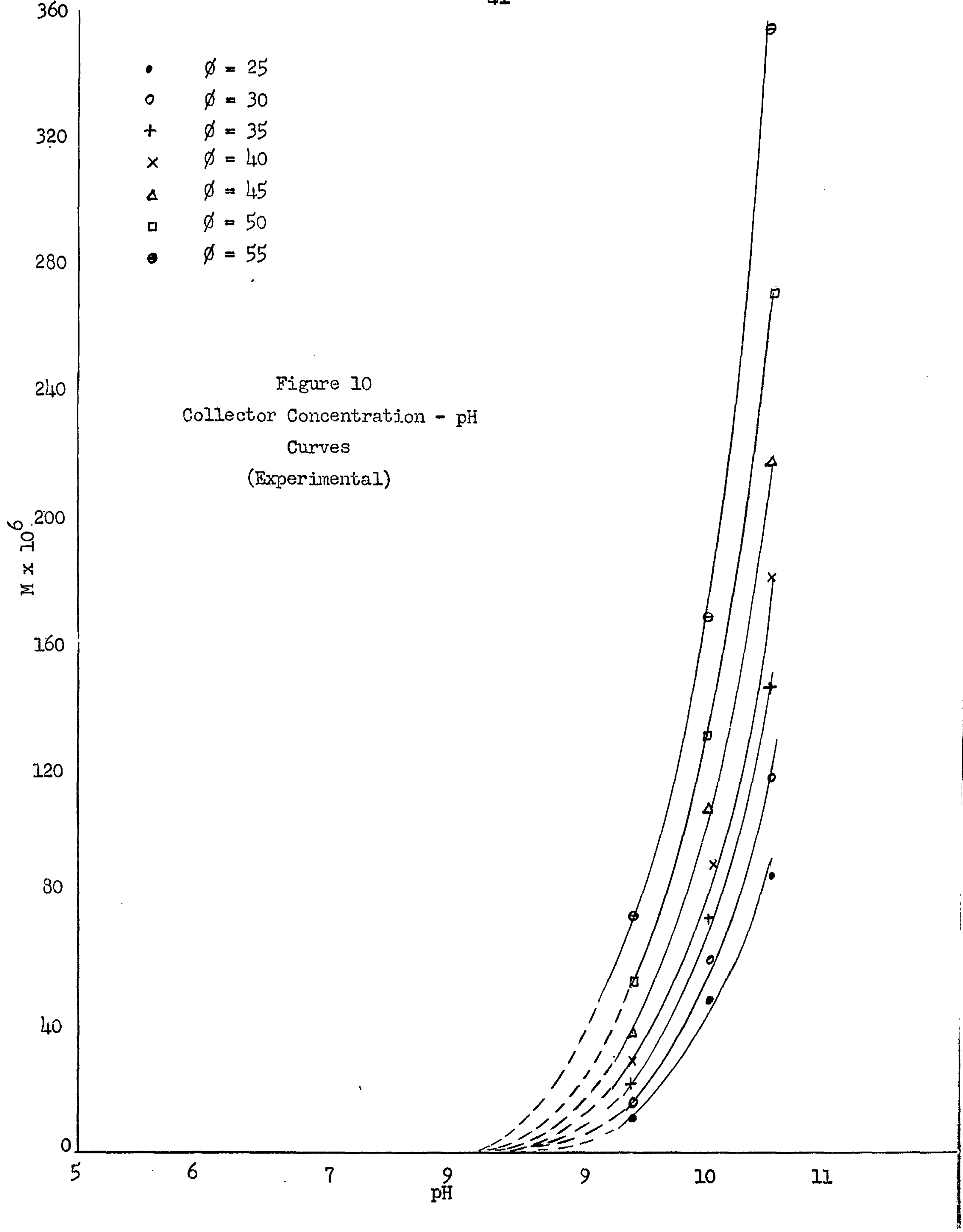
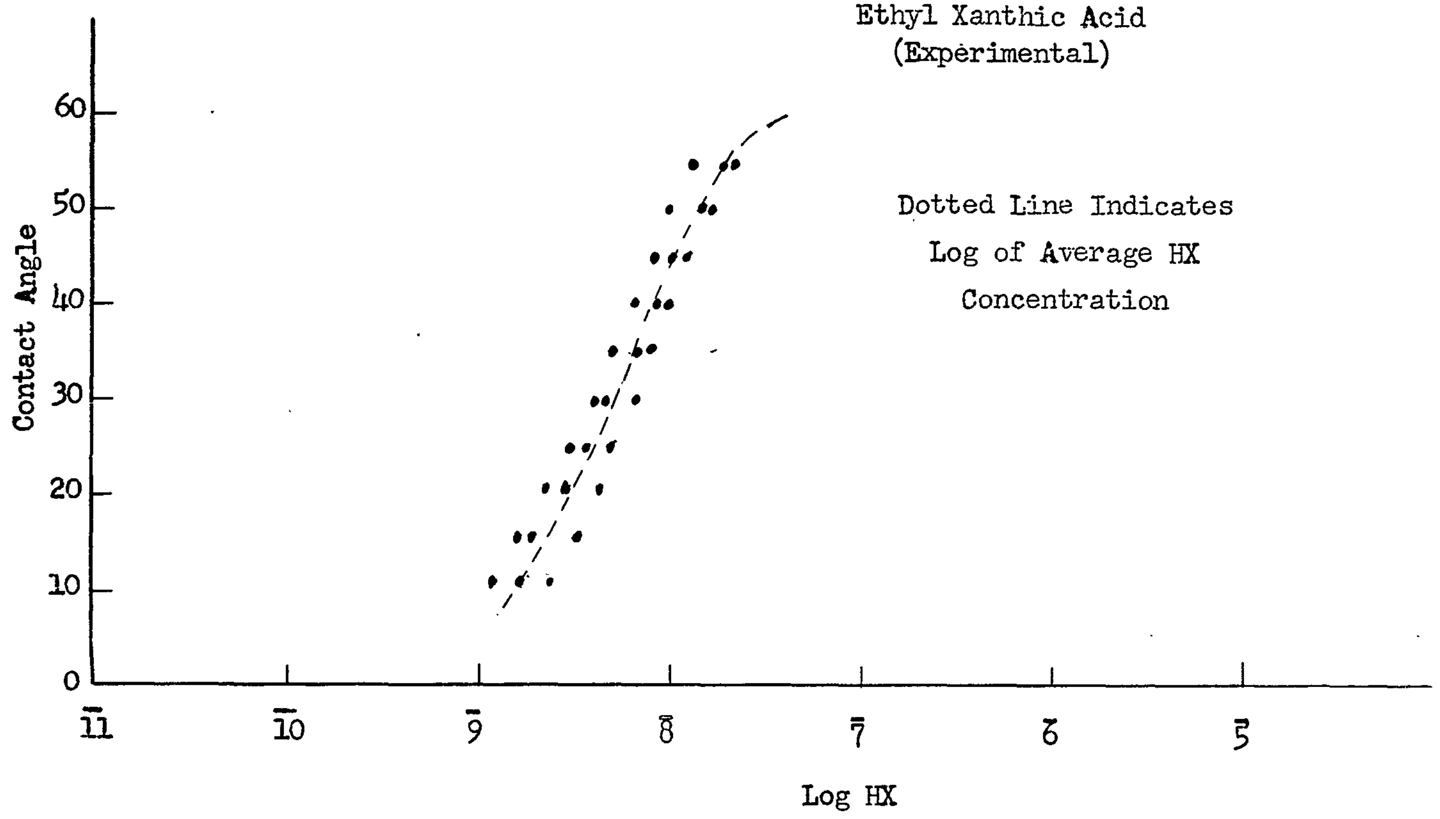


Figure 10
Collector Concentration - pH
Curves
(Experimental)

Figure 11

Contact Angle - Log Concentration of
Ethyl Xanthic Acid
(Experimental)



Dotted Line Indicates
Log of Average HX
Concentration

$$K = \frac{\theta}{1 - \theta} \frac{1}{[HX]} \qquad (7)$$

In order to obtain a relationship between free acid concentration and contact angle, the following assumption is made:

$$\theta = a\phi + b \qquad (8)$$

where θ = surface coverage, ϕ = contact, and a and b are constants. b is the fraction of the surface covered when the contact angle is zero. When $\phi = 60^\circ$, $\theta = 1$, therefore equation 8 may be written:

$$b = 1 - 60a$$

which when substituted back into equation 8 gives:

$$\theta = 1 + a\ (\phi - 60) \qquad (9a)$$

therefore,

$$\frac{\theta}{1 - \theta} = \frac{1}{a(60 - \phi)} - 1 \qquad (10)$$

Equation 10, substituted into equation 7, gave HX in terms of contact angle, and two constants, both of which were evaluated.

$$HX = \frac{K^{-1}}{a} \frac{1}{(60 - \phi)} - K^{-1} \qquad (11)$$

If a plot of HX versus $1/(60-\phi)$ is made, the slope should be equal to 1/aK and the intercept should be equal to 1/K. This plot is shown in Figure 12.

In constructing Fig. 12, the average values of HX were used. These values had been taken from the contact angle-log HX plot, Figure 11. Figure 11, being a log plot, together with the fact that the function $1/60 - \phi$ changes rapidly with ϕ values approaching 60°, makes Figure 12 a very sensitive plot. HX concentrations which were obtained by using the extreme values of log HX for a given contact angle are represented by the dotted line in Figure 12.

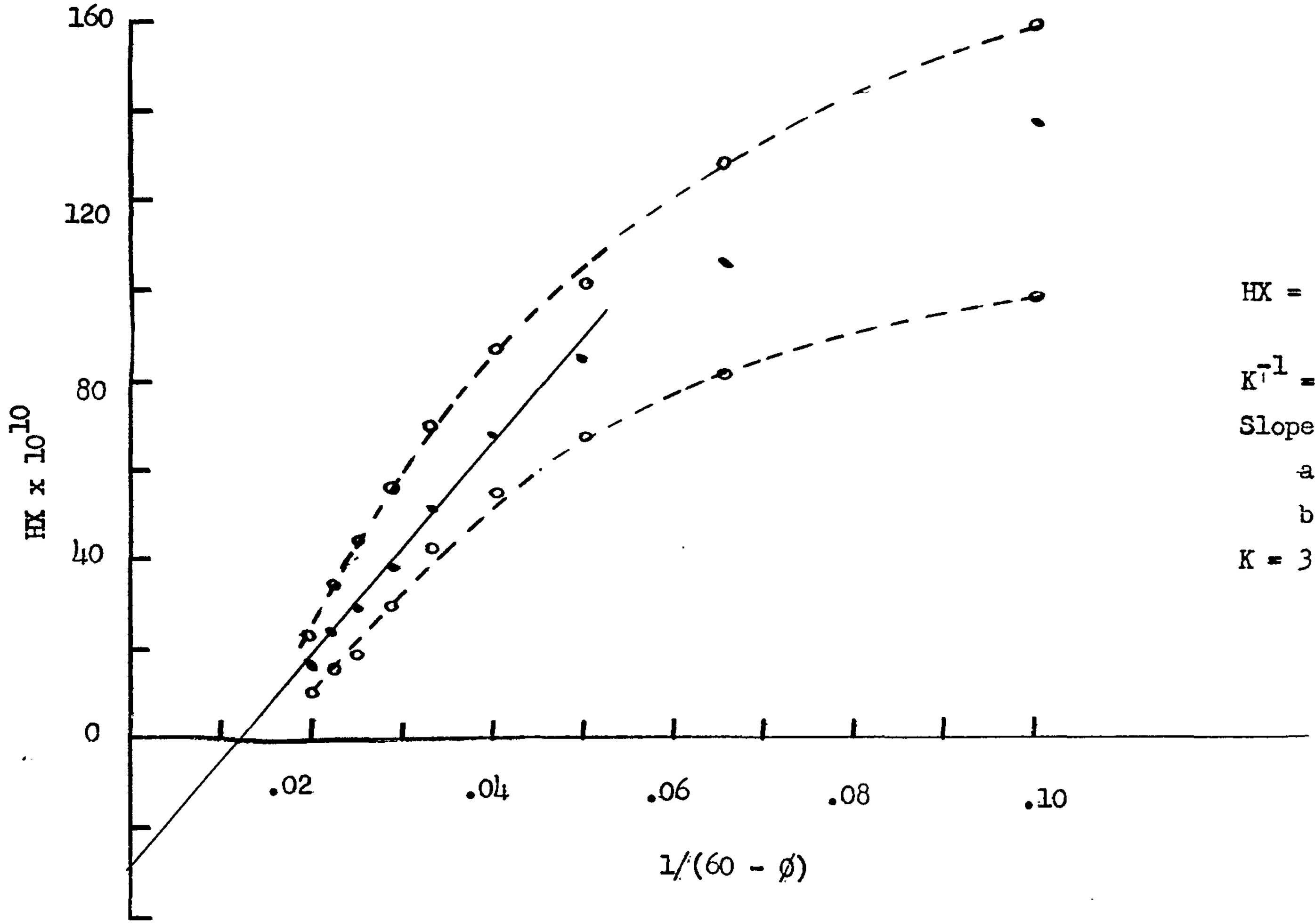


Figure 12
Plot of Equation:

$$HX = \frac{K^{-1}}{a} \frac{1}{(60-\emptyset)} - K^{-1}$$

$K^{-1} = 3.0 \times 10^{-9}$

Slope = 2.33×10^{-7}

a = .013

b = .22

$K = 3.3 \times 10^{8}$

1/K, taken from the intercept of Figure 12, was equal to 3.0×10^{-9}, giving a value of $K = 3.3 \times 10^{8}$. The slope was 2.33×10^{-7}, giving a value of $a = .013$. Substituting this value of (a) into equation 8 gives $b = .22$, which is the fraction of the surface covered by the collector at "bubble pickup."

Substituting these values of a, b, and K into equation 11 gives the following equation relating free acid concentration to contact angle:

$$HX = \frac{2.3 \times 10^{-7}}{(60-\phi)} - 3.0 \times 10^{-9} \qquad (12)$$

By substituting equation 4 into equation 11, the relationship between m and pH, at constant contact angle, may be obtained: (See Table II).

$$\frac{H^{+}}{8.6 \times 10^{-7} + H} = \frac{1}{m} \; \frac{2.3 \times 10^{-7}}{(60-\phi)} - 3.0 \times 10^{-9} \qquad (13)$$

By equation 13, m-pH curves may be calculated and compared with the experimental curves of Figure 10.

The results of these calculations are shown in Table I. Figure 13 is a comparison of the calculated and experimental values.

Discussion

Some of the experimental data have been omitted in evaluating the equilibrium constants, and in obtaining the contact angle-surface coverage relationships. These readings have been intentionally disregarded because of the possibility that phosphates could be acting as a depressant. The concentrations involved at the lower pH readings are so small that even the slightest depressant action of the buffer could very easily give misleading results.

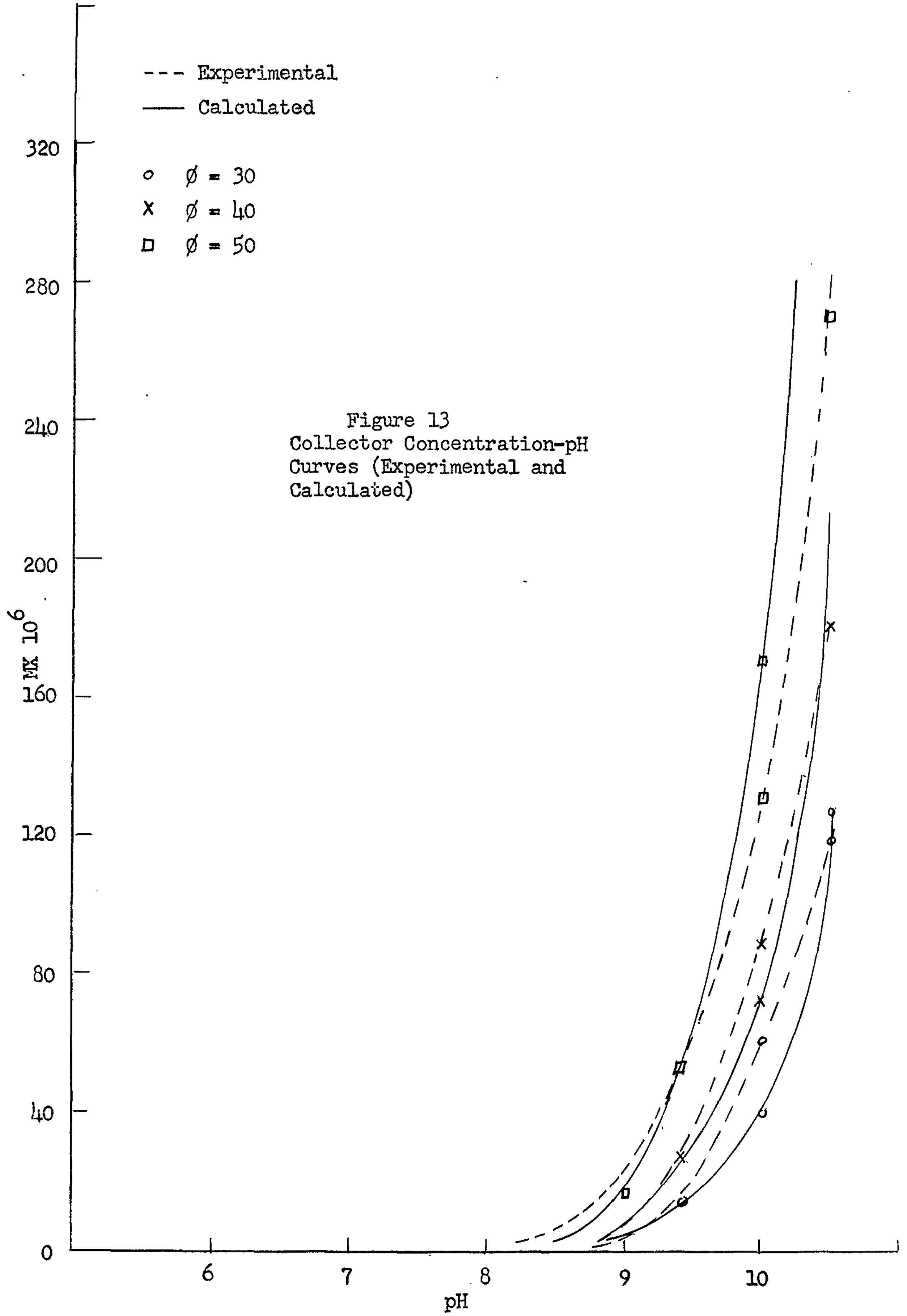


Figure 13
Collector Concentration-pH Curves (Experimental and Calculated)

Other investigators have studied the adsorption of carbonates and phosphates on galena. Most of the evidence indicates that carbonates are not adsorbed, however, there is the possibility that the phosphates are adsorbed.

Ravitz(27) has concluded that sodium phosphate has no effect on cleaned galena when there are no oxidation products present on the mineral surface with which the phosphates could react. This would seem to indicate that there was a possibility that the surface had not been properly cleaned prior to testing, and does not entirely discount the fact that phosphates could be adsorbed on cleaned galena.

Simard, Burke, and Salley(30) have used radioactive tracer techniques to study the effects of various concentrations of carbonates and phosphates upon the adsorption of dithiophosphates on galena. Their work indicates conclusively that the phosphates are adsorbed sufficiently to effect the adsorption of the dithiophosphate. Also, their work indicated little or no carbonate was adsorbed with dithiophosphates. In the latter tests, their solutions were buffered at a pH of 7.8, with 20×10^{-8} moles per cubic centimeter of sodium carbonate.

Simard, Chupak, and Salley(31) have made tracer measurements with radiocarbonate. Their results indicated that little or no carbonate ion could be removed by galena in the presence of dithiophosphate, although in the absence of dithiophosphate some carbonate abstraction was possible.

In view of the foregoing evidence the possibility that phosphates are adsorbed must be considered, and consequently, the experimental data, which was obtained using phosphate buffers in this investigation has not been considered in evaluating the theoretical constants.

Wark(41) conditioned some galena samples in sodium carbonate solutions, and then transferred the samples to xanthate solutions. No decrease in the effectiveness of the xanthate was noted. In making studies of collector-depressant systems, Wark uses 150-250 mg/liter of sodium carbonate. Wark and Sutherland(45) made a study of the influence of certain anions on air-mineral contact. They have concluded that, in the absence of heavy salts, apart from pH value, sodium carbonate has no influence on contact.

Comparison of results of the final relationship between contact angle and surface coverage shows that the linear relationship proposed by Wadsworth, Conrady, and Cook is applicable to regions of low collector concentration.

Further verification of this interpretation is indicated by comparison between experimental and calculated curves of Figure 13.

Table 1

Conversion of Concentration of Added Collector
(mg/l) to Concentration of Ethyl Xanthic and (molar).

m_c (mg/l)	pH	$m \times 10^6$	mH^+	[HX]
$\phi = 10^\circ$				
3.0	10.0	18.7	1.9×10^{-15}	2.2×10^{-9}
4.25	10.5	26.5	8.4×10^{-16}	9.8×10^{-10}
$\phi = 15^\circ$				
4.5	10.0	28.1	2.8×10^{-15}	3.3×10^{-9}
7.0	10.5	43.7	1.4×10^{-15}	1.6×10^{-9}
$\phi = 20^\circ$				
1.0	9.6	6.2	1.56×10^{-15}	1.8×10^{-9}
6.25	10.0	38.9	3.9×10^{-15}	4.5×10^{-9}
10.0	10.5	62.4	2.0×10^{-15}	2.3×10^{-9}
$\phi = 25^\circ$				
.35	5.50	2.18	6.7×10^{-12}	
.55	6.45	3.43	12.2×10^{-13}	
.90	7.35	5.61	25.1×10^{-14}	
1.35	8.20	8.42	53.1×10^{-15}	
1.55	9.40	9.67	2.4×10^{-15}	2.8×10^{-9}
7.80	10.00	48.7	4.8×10^{-15}	5.6×10^{-9}
14.0	10.50	87.3	2.8×10^{-15}	3.2×10^{-9}
$\phi = 30^\circ$				
.45	5.50	2.81	8.9×10^{-12}	
.70	6.45	4.37	15.5×10^{-13}	
1.05	7.35	6.55	29.3×10^{-14}	
1.75	8.20	10.92	68.9×10^{-15}	
2.35	9.40	14.66	3.7×10^{-15}	4.3×10^{-9}
9.80	10.00	61.1	6.1×10^{-15}	7.1×10^{-9}
19.0	10.50	118.5	3.7×10^{-15}	4.4×10^{-9}
$\phi = 35^\circ$				
.60	5.50	3.74	11.8×10^{-12}	
.90	6.45	5.61	19.9×10^{-13}	
1.15	7.35	7.17	32.0×10^{-14}	
2.15	8.20	13.4	84.6×10^{-15}	
3.45	9.40	21.5	5.4×10^{-15}	6.3×10^{-9}
12.0	10.00	74.9	7.5×10^{-15}	8.7×10^{-9}
23.5	10.50	146.6	4.6×10^{-15}	5.4×10^{-9}

Table 1 (Continued)

m_c (mg/l)	pH	$m \times 10^6$	mH^+	$[HX]$
$\phi = 40^\circ$				
.75	5.50	4.68	14.8×10^{-12}	
1.10	6.45	6.86	24.4×10^{-13}	
1.35	7.35	8.42	37.6×10^{-14}	
2.60	8.20	16.2	102.2×10^{-15}	
4.50	9.40	28.1	7.1×10^{-15}	8.3×10^{-9}
14.4	10.0	89.8	8.9×10^{-15}	1.03×10^{-9}
29.0	10.5	180.9	5.7×10^{-15}	6.7×10^{-9}
$\phi = 45^\circ$				
.95	5.50	5.93	18.7×10^{-12}	
1.30	6.45	8.11	28.8×10^{-13}	
1.50	7.35	9.36	41.8×10^{-14}	
3.10	8.20	19.3	121.7×10^{-15}	
6.0	9.40	37.4	9.4×10^{-15}	1.0×10^{-8}
17.4	10.00	108.5	1.1×10^{-14}	1.3×10^{-8}
35.0	10.50	218.3	6.9×10^{-15}	8.0×10^{-9}
$\phi = 50^\circ$				
1.15	5.50	7.17	22.6×10^{-12}	
1.55	6.45	9.67	34.3×10^{-13}	
1.70	7.35	10.60	47.4×10^{-14}	
3.65	8.20	22.8	143.9×10^{-15}	
8.7	9.40	54.3	1.4×10^{-14}	1.6×10^{-8}
21.0	10.00	130.9	1.3×10^{-14}	1.5×10^{-8}
43.5	10.50	271.4	8.6×10^{-14}	10.0×10^{-9}
$\phi = 55^\circ$				
1.40	5.50	8.73	27.6×10^{-12}	
1.85	6.45	11.54	41.0×10^{-13}	
2.00	7.35	12.48	55.8×10^{-14}	
4.30	8.20	26.8	169.1×10^{-15}	
12.0	9.40	74.9	1.9×10^{-14}	1.3×10^{-8}
27.0	10.00	168.4	1.7×10^{-14}	1.95×10^{-8}
57.0	10.50	355.6	1.12×10^{-14}	1.3×10^{-8}

Table 2

Calculated values of ethyl xanthate concentration required to maintain a given contact angle.

$$\frac{H^+}{8.6 \times 10^{-7} + H^+} = \frac{1}{m}\left[\frac{2.3 \times 10^{-7}}{(60 - \phi)} - 3.0 \times 10^{-9}\right]$$

$\phi = 30^\circ$

pH	H^+	$H^+/(8.6 \times 10^{-7} + H^+)$	$m = \frac{4.7 \times 10^{-9}}{f(H^+)}$
6.0	10^{-6}	.54	8.8×10^{-9}
7.0	10^{-7}	.10	4.5×10^{-8}
8.0	10^{-8}	1.2×10^{-2}	4.1×10^{-7}
9.0	10^{-9}	1.2×10^{-3}	4.1×10^{-6}
10.0	10^{-10}	1.2×10^{-4}	4.1×10^{-5}
10.5	3.2×10^{-4}	3.7×10^{-5}	1.3×10^{-4}

$\phi = 40^\circ$

pH	H^+	$m = \frac{8.5 \times 10^{-9}}{f(H^+)}$
6.0	10^{-6}	1.6×10^{-8}
7.0	10^{-7}	8.2×10^{-8}
8.0	10^{-8}	7.4×10^{-7}
9.0	10^{-9}	7.3×10^{-6}
10.0	10^{-10}	7.3×10^{-5}
10.5	3.2×10^{-11}	2.3×10^{-4}

$\phi = 50$

pH	$m = \frac{20.0 \times 10^{-9}}{f(H^+)}$
6.0	3.7×10^{-8}
7.0	1.9×10^{-7}
8.0	1.7×10^{-6}
9.0	1.7×10^{-5}
10.0	1.7×10^{-4}
10.5	5.4×10^{-4}

POTASSIUM AMYL XANTHATE ON GALENA

Potassium amyl xanthate is more stable than postassium ethyl xanthate, consequently contact angle measurements involving systems containing amyl xanthate should give more precise experimental data. This fact has been shown by applying the method outlined in the last section to the potassium amyl xanthate-galena system.

Experimental Procedure and Results

The same experimental procedure and analysis of the data as was shown in the previous section has been applied to the potassium amyl xanthate-galena system. Contact angle curves for potassium amyl xanthate on galena at pH values of 5.50, 6.45, 7.35, 8.20, 9.40, and 10.0 were determined experimentally, see Figures 14-20. From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH for constant values of contact angle were constructed (Figure 23). These data were also plotted as contact angle versus log HX (Figure 21).

Discussion

Again, a linear relationship between contact angle and surface coverage has been assumed.

Assuming the single site mechanism,

$$S + HX \rightleftharpoons SHX \qquad (1)$$

the equilibrium constant may be written

$$K = \frac{SHX}{[S]\,[HX]} = \frac{\theta}{1-\theta}\,\frac{1}{HX} \qquad (2)$$

Figure 14

Contact Angle - Concentration

Potassium Amyl Xanthate

(Averaged Contact Angle Readings)

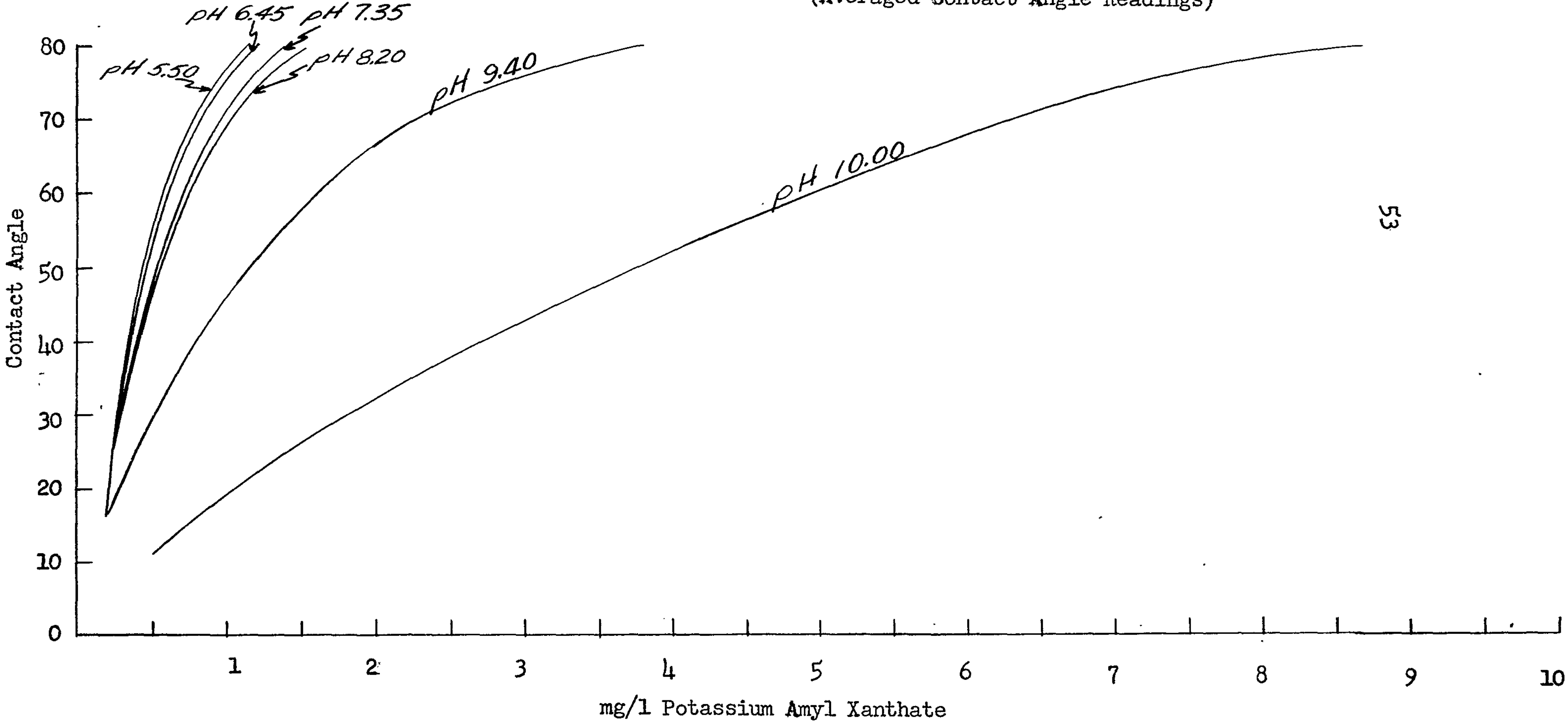


Figure 15
Contact Angle - Concentration Potassium
Amyl Xanthate
pH 5.50

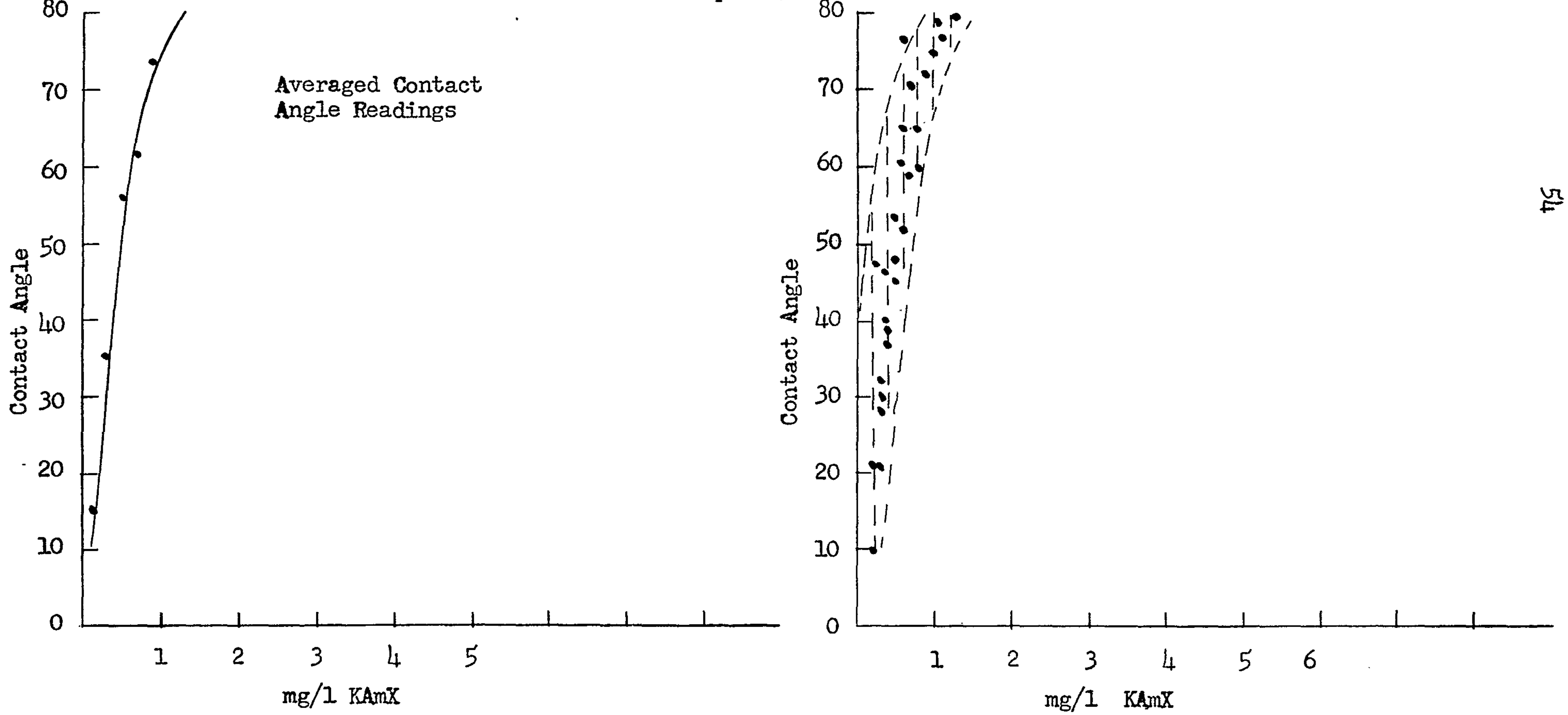


Figure 16
Contact Angle - Concentration Potassium Amyl Xanthate
pH 6.45

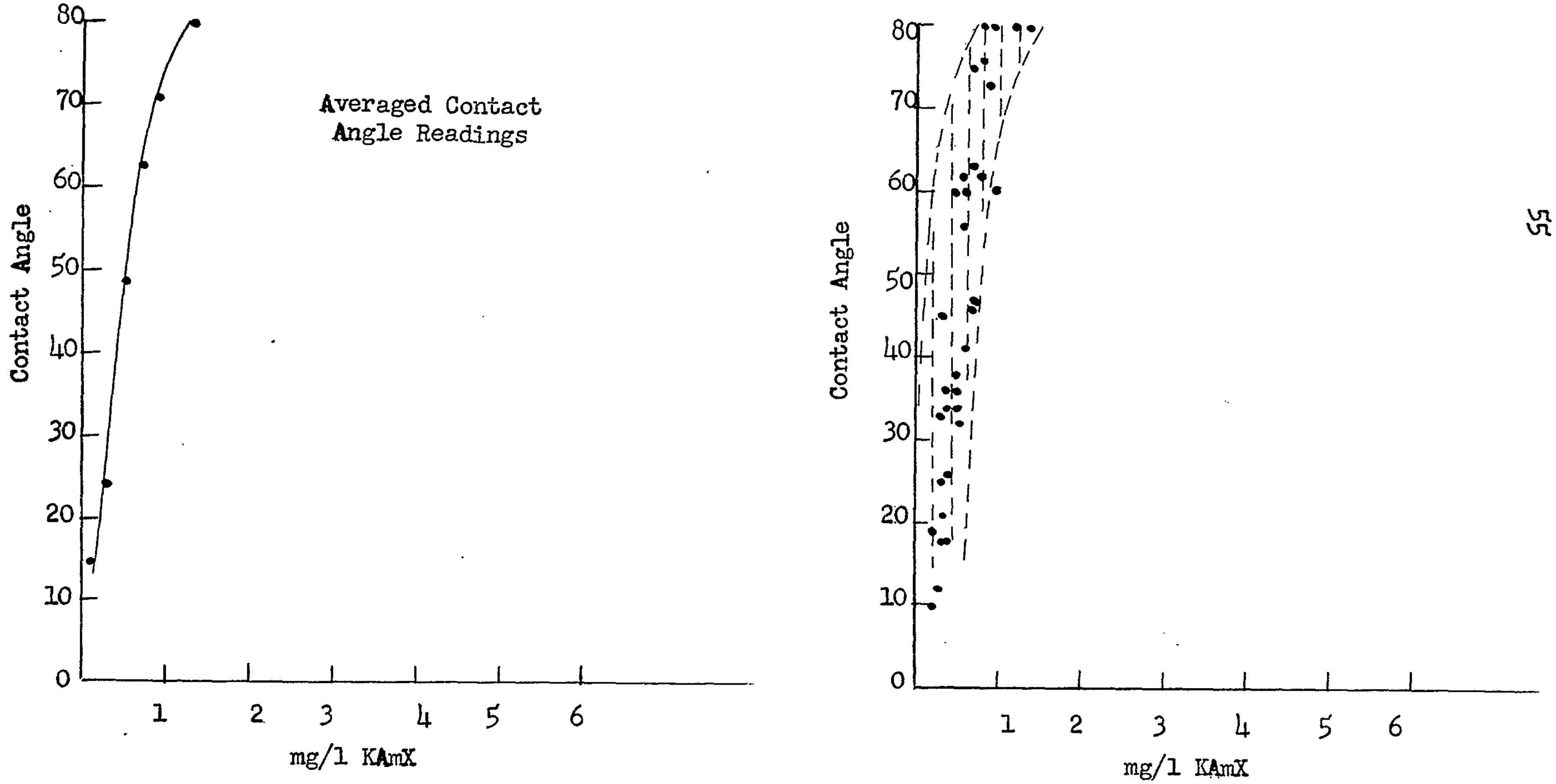


Figure 17
Contact Angle - Concentration Potassium Amyl Xanthate
pH 7.35

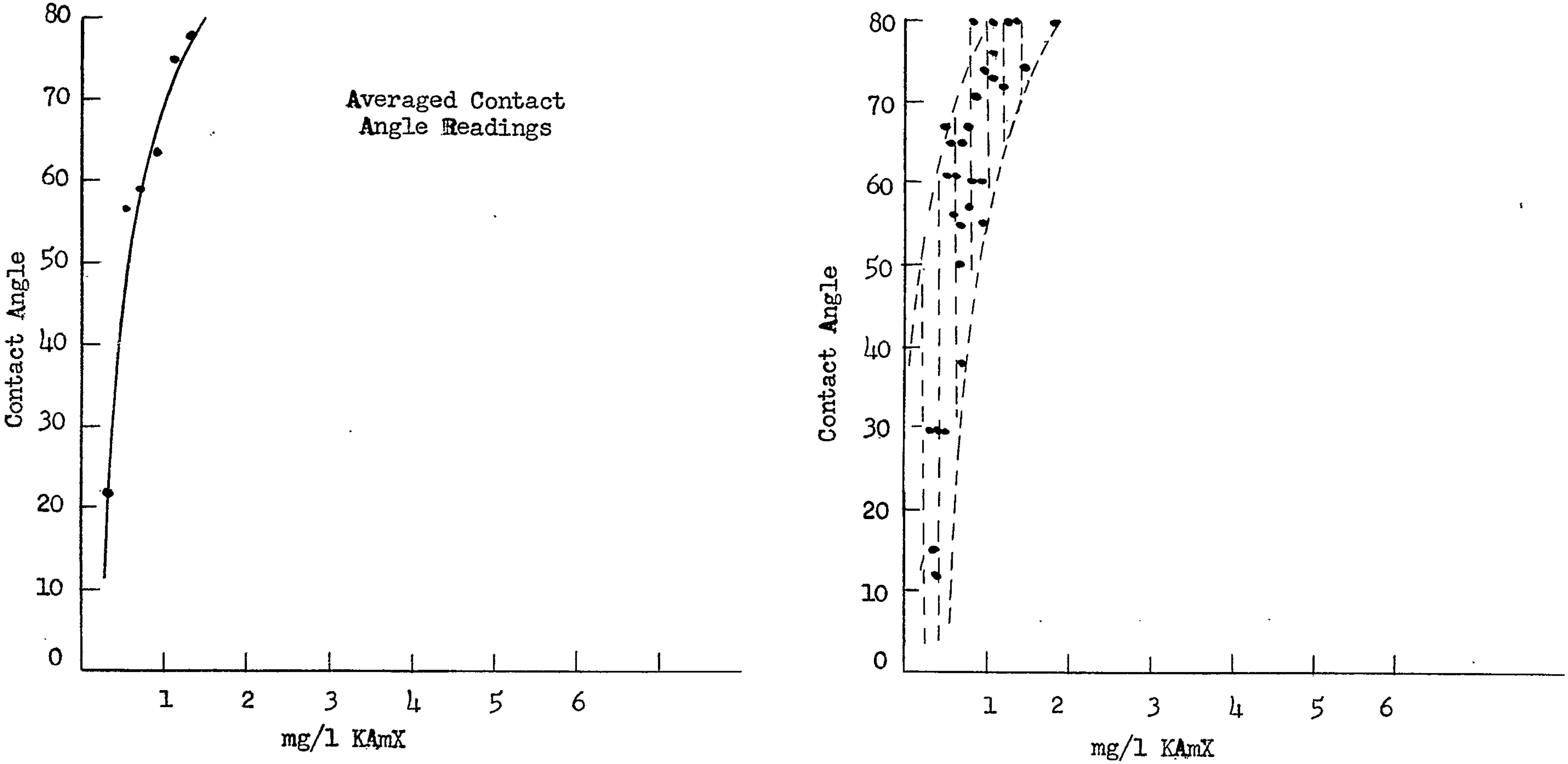


Figure 18

Contact Angle - Concentration Potassium Amyl Xanthate

pH 8.20

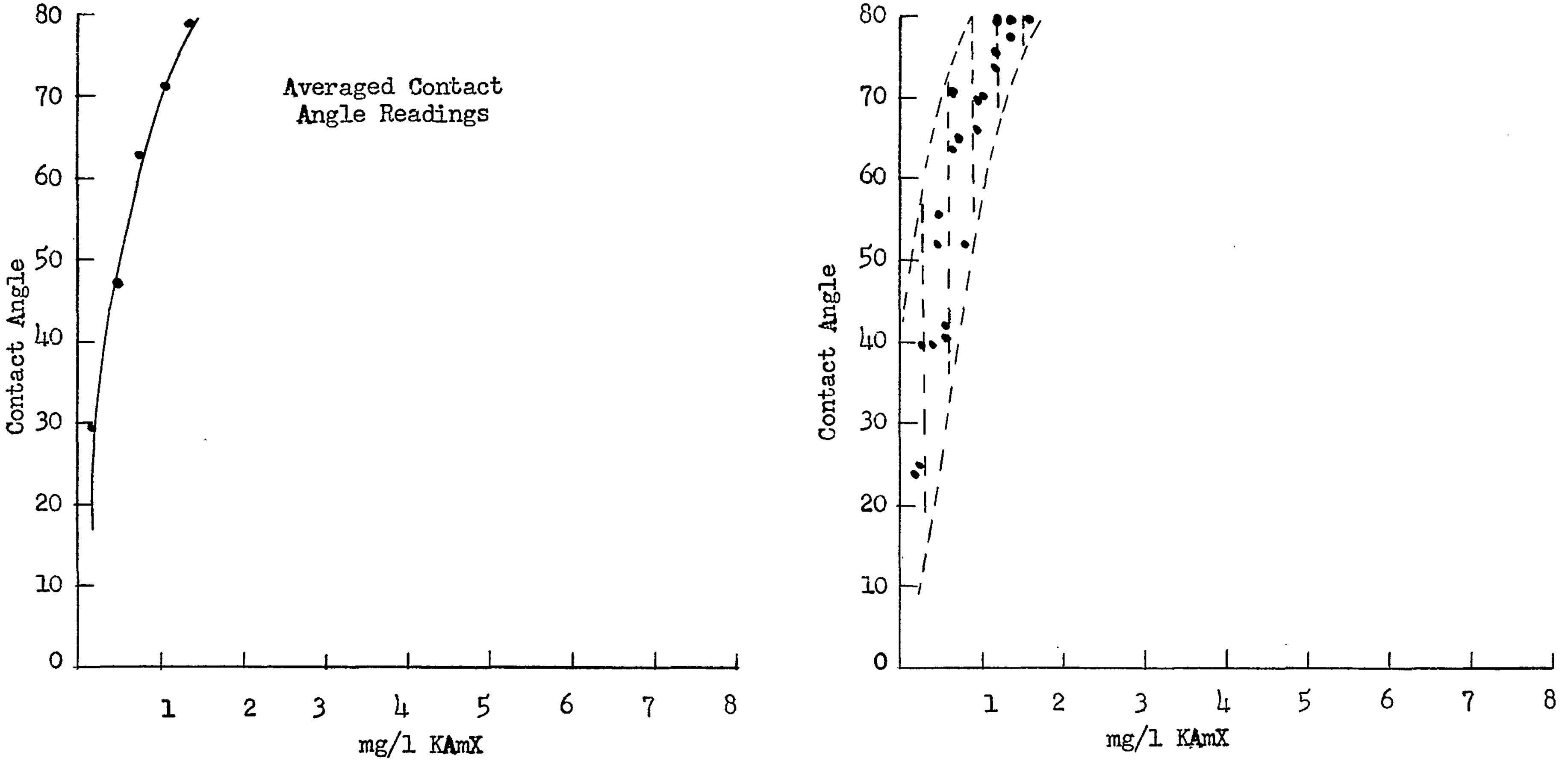


Figure 19

Contact Angle - Concentration Potassium Amyl Xanthate

pH 9.40

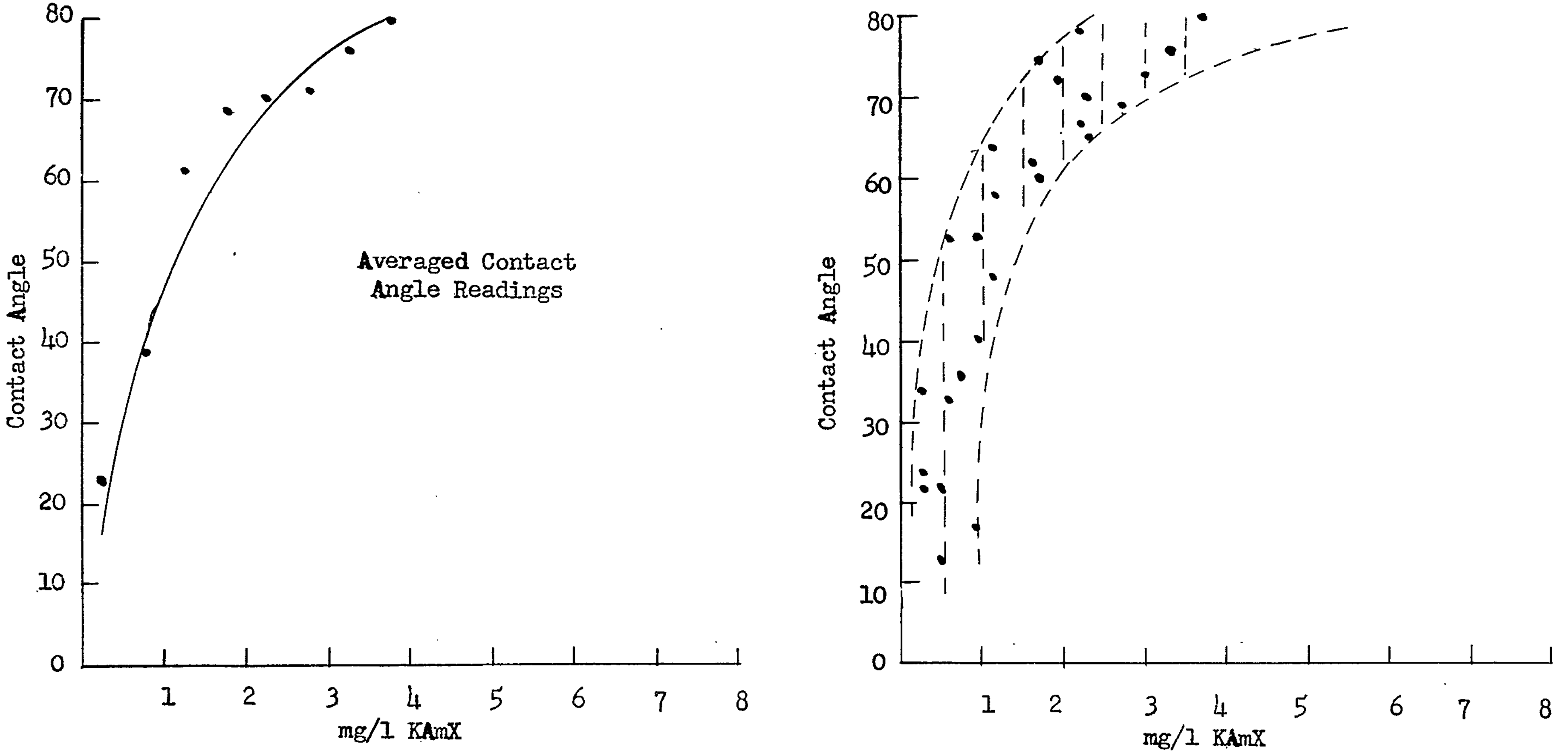
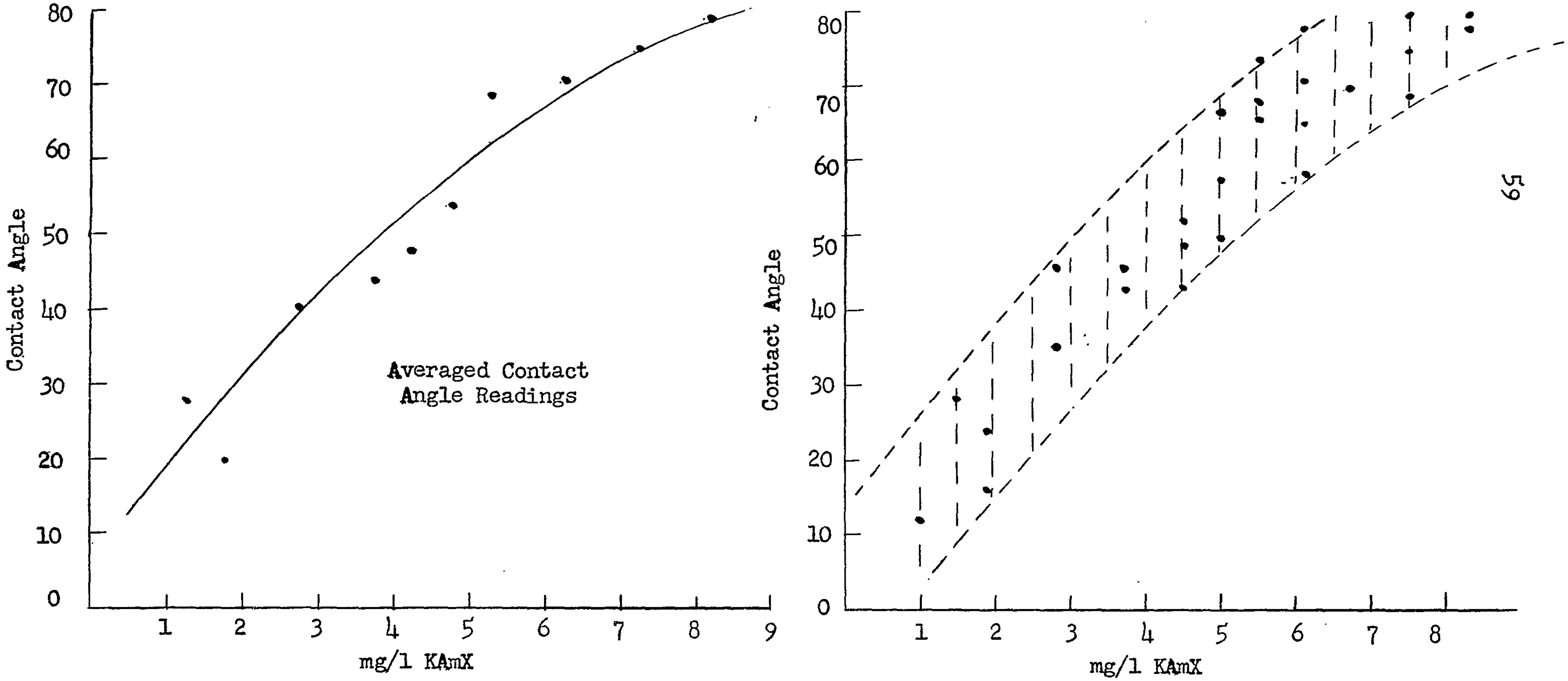


Figure 20

Contact Angle - Concentration Potassium Amyl Xanthate
pH 10.00



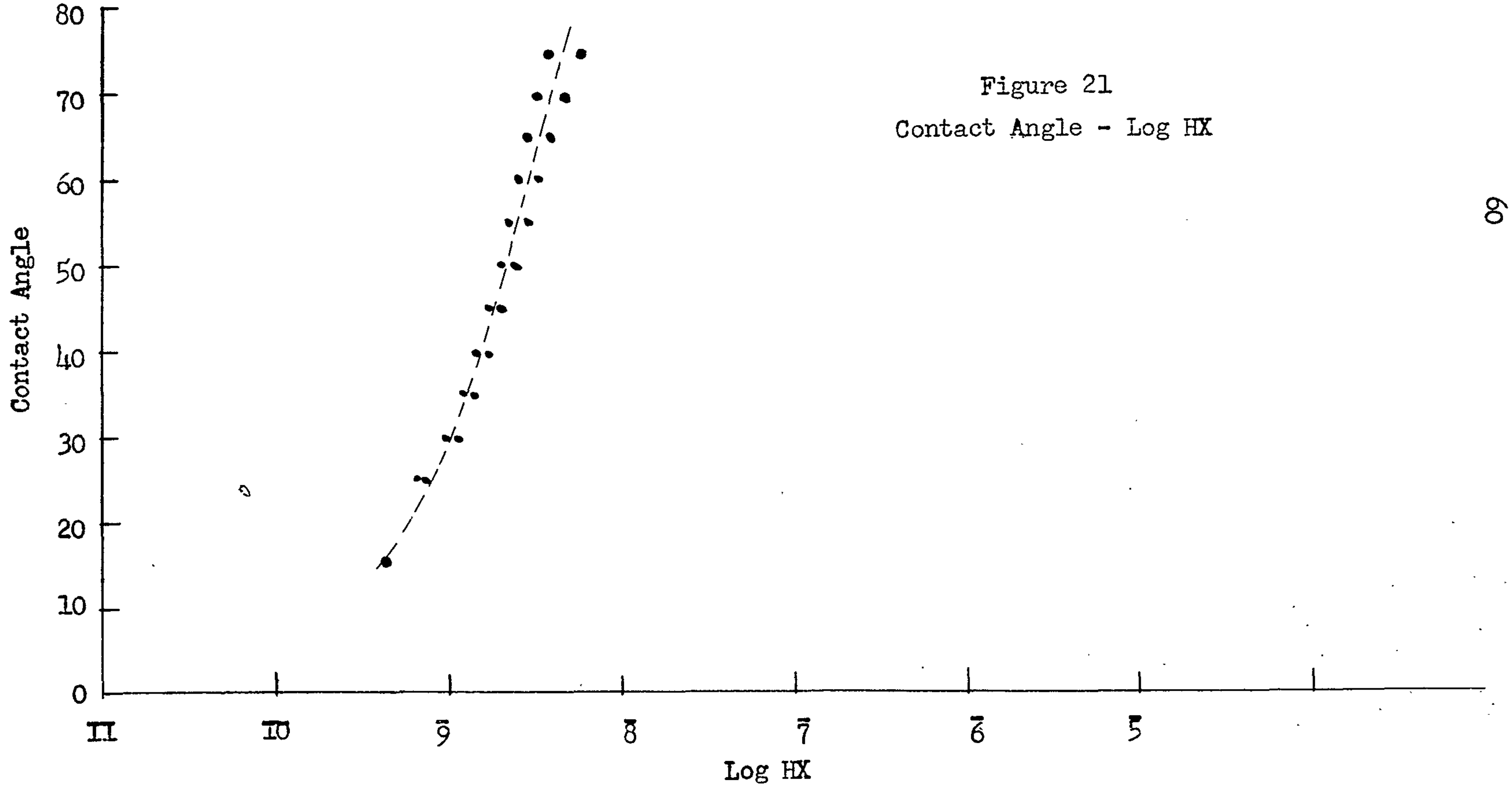


Figure 21

Contact Angle - Log HX

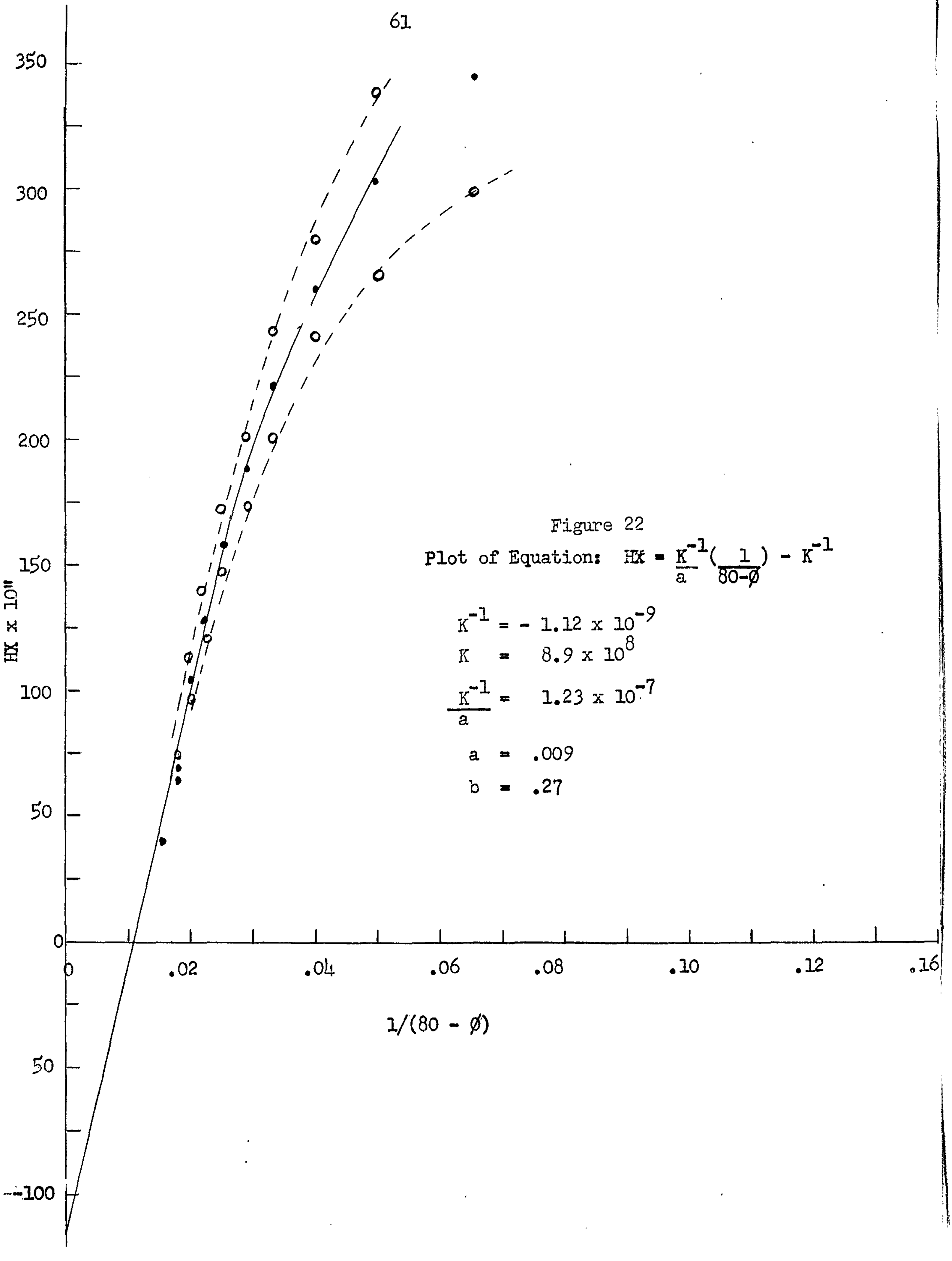


Figure 22

Plot of Equation: $HX = \frac{K^{-1}}{a}\left(\frac{1}{80-0}\right) - K^{-1}$

$K^{-1} = -1.12 \times 10^{-9}$

$K = 8.9 \times 10^{8}$

$\frac{K^{-1}}{a} = 1.23 \times 10^{-7}$

$a = .009$

$b = .27$

where θ = fraction of the surface covered by the collector, S = the concentration of unoccupied surface sites. Substituting the limits, $\theta = 1$ when $\phi = 80$, into the linear relationship,

$$\theta = a\phi + b \qquad (3)$$

gives

$$b = 1 - 80\ a \qquad (4a)$$

$$\text{or} \quad \theta = 1 + a(\phi - 80) \qquad (4b)$$

$$\text{and} \quad \frac{\theta}{1-\theta} = \frac{1}{a(80-\phi)} = 1 \qquad (4c)$$

Substituting this value of $\theta/1(1 - \theta)$ in equation 2 gives,

$$HX = \frac{K^{-1}}{a(80-\phi)} - K^{-1} \qquad (5)$$

A plot of HX versus $1/(80-\phi)$ is shown in Figure 22. 1/K, taken from the intercept is equal to 1.12×10^{-9}, giving a value of $K = 8.9 \times 10^{8}$. The slope is 1.23×10^{-7}, giving a value of $a = .009$. Substituting this value of a into equation 4b gives $b = 0.27$. Equation 5 may therefore be written

$$HX = \frac{1.24 \times 10^{-7}}{80-\phi} - 1.12 \times 10^{-9} \qquad (6)$$

Using equation 6 the relationship between collector concentration and pH, at contact angle, may be obtained.

$$\frac{H^{+}}{9.3 \times 10^{-7} + H^{+}} = \frac{1}{m} \left(\frac{1.24 \times 10^{-7}}{80-\phi} - 1.12 \times 10^{-9} \right) \qquad (7)$$

The value of $Ka = 9.3 \times 10^{-7}$ was determined by a study of a two collector system. (See Section on "Two Collector System"). Calculated concentration of collector versus pH curves are compared with experimentally determined curves in Figure 24. Calculated results have also been tabulated in Tables 3 and 4.

Comparison of these results with the results obtained with potassium ethyl xanthate on galena shows that the same relationships are valid.

The difference in surface coverage for amyl xanthate and for ethyl xanthate at the threshold of contact may be accounted for by considering the accuracy of the extrapolation in the HX - vs ($\frac{1}{60-\phi}$) and HX vs $\frac{1}{(80-\phi)}$ curves. For the HX vs $\frac{1}{80-\phi}$ curve, a change of ten units in the value of the intercept is sufficient to account for the total discrepancy in surface coverage values at zero contact angle.

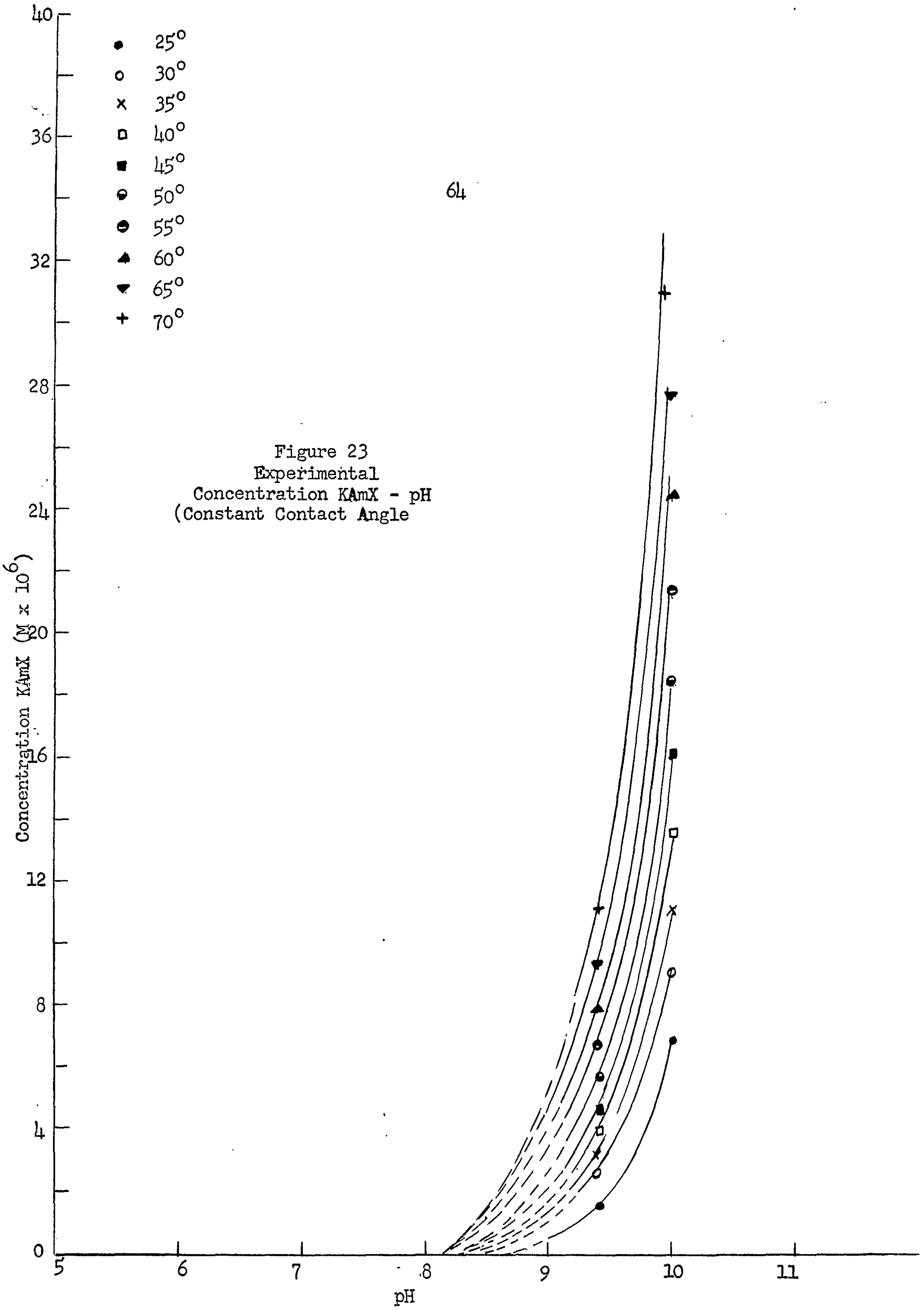


Figure 23
Experimental
Concentration KAmX - pH
(Constant Contact Angle

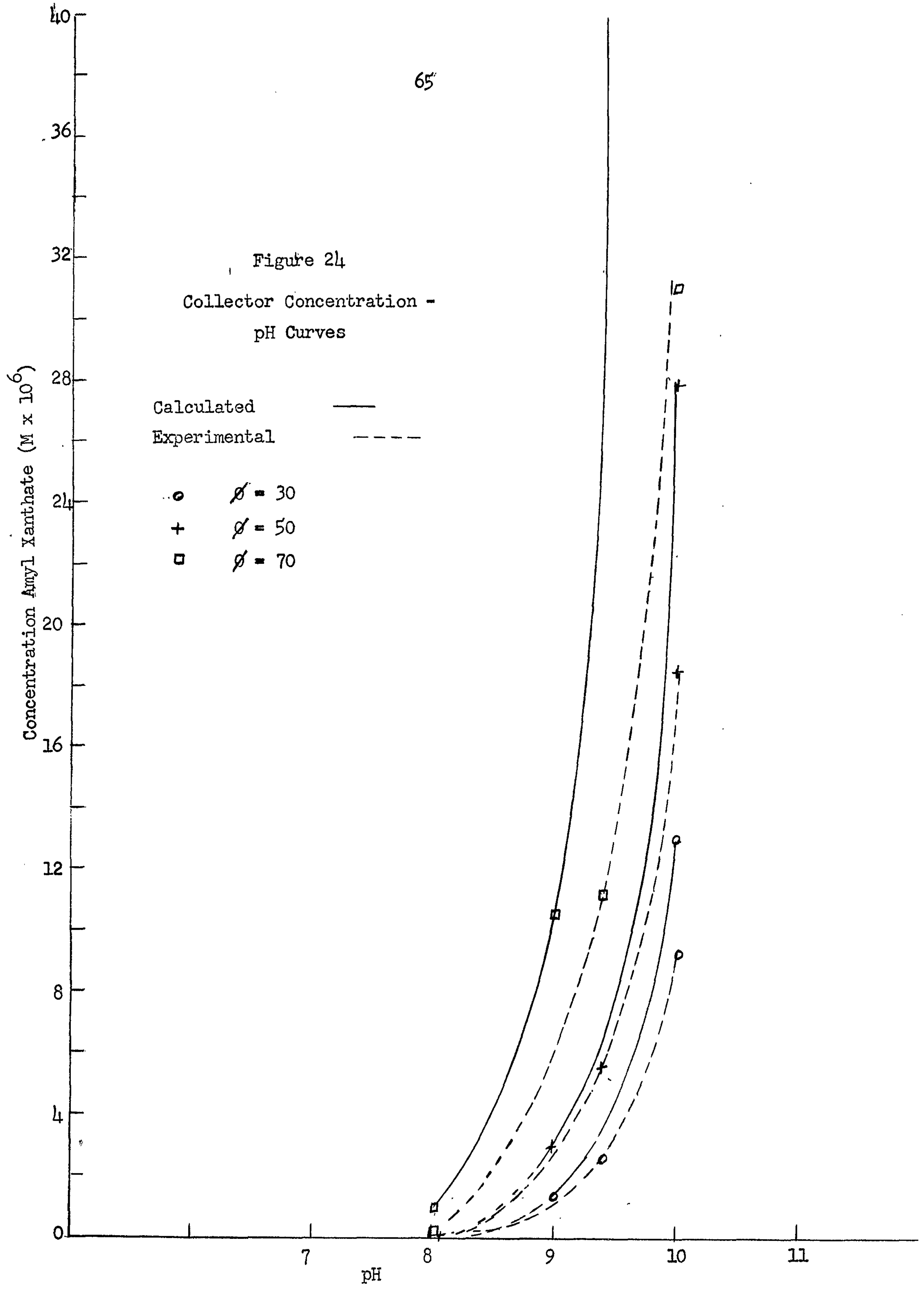


Figure 24

Collector Concentration - pH Curves

Table 3

Conversion of Concentration of Added Collector (mg/l) to Concentration of Amyl Xanthic Acid (molar)

m_c (mg/l)	pH	$m \times 10^6$	m_{H^+}	[HX]
$\phi = 25^\circ$				
.25	5.50	1.24	3.9×10^{-12}	
.25	6.45	1.24	4.4×10^{-13}	
.25	7.35	1.24	5.5×10^{-14}	
.25	8.20	1.24	7.8×10^{-15}	
.30	9.40	1.48	5.9×10^{-16}	6.4×10^{-10}
1.40	10.0	6.92	6.9×10^{-16}	7.5×10^{-10}
$\phi = 30^\circ$				
.27	5.50	1.33	4.2×10^{-12}	
.27	6.45	1.33	4.7×10^{-12}	
.27	7.35	1.33	5.9×10^{-14}	
.27	8.20	1.33	8.4×10^{-15}	
.53	9.40	2.62	1.1×10^{-15}	1.1×10^{-9}
1.83	10.00	9.04	9.0×10^{-16}	9.8×10^{-10}
$\phi = 35^\circ$				
.32	5.50	1.58	4.99×10^{-12}	
.32	6.45	1.58	5.61×10^{-13}	
.32	7.35	1.58	7.06×10^{-14}	
.32	8.20	1.58	9.97×10^{-15}	
.65	9.40	3.21	1.28×10^{-15}	1.4×10^{-9}
2.25	10.0	11.1	1.11×10^{-15}	1.2×10^{-9}
$\phi = 40^\circ$				
.35	5.50	1.73	5.47×10^{-12}	
.35	6.45	1.73	6.14×10^{-13}	
.40	7.35	1.98	8.85×10^{-14}	
.40	8.20	1.98	1.25×10^{-14}	
.80	9.40	3.95	1.58×10^{-15}	1.71×10^{-9}
2.75	10.0	13.6	1.36×10^{-15}	1.47×10^{-9}
$\phi\ 45^\circ$				
.40	5.50	1.98	6.26×10^{-12}	
.40	6.45	1.98	7.03×10^{-13}	
.45	7.35	2.22	9.92×10^{-14}	
.45	8.20	2.22	1.40×10^{-14}	
.95	9.40	4.69	1.87×10^{-15}	2.02×10^{-9}
3.25	10.0	16.1	1.61×10^{-15}	1.74×10^{-9}

Table 3 (Continued)

m_c (mg/l)	pH	$m \times 10^6$	m_{H^+}	[HX]
$\phi = 50^\circ$				
.45	5.50	2.22	7.01×10^{-12}	
.45	6.45	2.22	7.88×10^{-13}	
.50	7.35	2.47	1.10×10^{-13}	
.50	8.20	2.47	1.56×10^{-14}	
1.15	9.40	5.68	2.26×10^{-15}	2.4×10^{-9}
3.75	10.00	18.5	1.85×10^{-15}	2.0×10^{-9}
$\phi = 55^\circ$				
.53	5.50	2.62	8.28×10^{-12}	
.53	6.45	2.62	9.30×10^{-13}	
.60	7.35	2.96	1.32×10^{-13}	
.63	8.20	3.11	1.96×10^{-14}	
1.35	9.40	6.67	2.66×10^{-15}	2.9×10^{-9}
4.33	10.00	21.4	2.14×10^{-15}	2.3×10^{-9}
$\phi = 60^\circ$				
.59	5.50	2.92	9.23×10^{-12}	
.61	6.45	3.01	1.07×10^{-12}	
.70	7.35	3.46	1.55×10^{-13}	
.75	8.20	3.71	2.34×10^{-14}	
1.60	9.40	7.91	3.16×10^{-15}	3.4×10^{-9}
4.95	10.0	24.5	2.45×10^{-15}	2.7×10^{-9}
$\phi = 65^\circ$				
.67	5.50	3.31	1.05×10^{-11}	
.70	6.45	3.46	1.23×10^{-12}	
.82	7.35	4.05	1.81×10^{-13}	
.87	8.20	4.30	2.71×10^{-14}	
1.90	9.40	9.39	3.74×10^{-15}	3.9×10^{-9}
5.60	10.0	27.7	2.77×10^{-15}	3.0×10^{-9}
$\phi = 70^\circ$				
.80	5.50	3.95	1.25×10^{-11}	
.83	6.45	4.10	1.46×10^{-12}	
.97	7.35	4.79	2.14×10^{-13}	
1.05	8.20	5.19	3.27×10^{-14}	
2.25	9.40	11.1	4.42×10^{-15}	4.8×10^{-9}
6.30	10.0	31.1	3.11×10^{-15}	3.4×10^{-9}

Table 4

Calculated Values of Amyl Xanthate Concentration Required to Maintain a Given Contact Angle

$$\frac{H^+}{9.3\times10^{-7}+H^+} = \frac{1}{m}\left(\frac{1.24 \times 10^{-7}}{80 - \phi} - 1.12 \times 10^{-9}\right)$$

$\phi = 30$

pH	H^+	$H^+/(93 \times 10^{-7} + H^+)$	$m = 1.36 \times 10^{-9}/f(H^+)$
6.0	10^{-6}	.52	2.6×10^{-9}
7.0	10^{-7}	9.7×10^{-2}	1.4×10^{-8}
8.0	10^{-8}	1.06×10^{-2}	1.3×10^{-7}
9.0	10^{-9}	1.07×10^{-3}	1.3×10^{-6}
10.0	10^{-10}	1.07×10^{-4}	1.3×10^{-5}

$\phi = 50$

pH	$m = 3.01 \times 10^{-9}/f(H^+)$
6.0	5.8×10^{-9}
7.0	3.1×10^{-8}
8.0	2.8×10^{-7}
9.0	2.8×10^{-6}
10.0	2.8×10^{-5}

$\phi = 70$

pH	$m = 11.3 \times 10^{-9}/f(H^+)$
6.0	2.17×10^{-8}
7.0	1.16×10^{-7}
8.0	1.07×10^{-6}
9.0	1.06×10^{-5}
10.0	1.06×10^{-4}

COMPETITIVE ADSORPTION OF ETHYL AND AMYL XANTHATES ON GALENA

The first two sections of this paper have demonstrated the validity of interpretation of contact angle measurements in terms of free acid adsorption and single site mechanism. Using a similar experimental procedure, dissociation constants of amyl xanthic acid and of ethyl xanthic acid have been determined by studying the competitive adsorption of ethyl xanthate and amyl xanthate on galena.

The characteristic contact angle on a monolayer of ethyl xanthic acid on galena is sixty degrees. The contact angle for galena covered with a monolayer of amyl xanthic acid is eighty degrees. The contact angle on galena coated with ethyl xanthic acid increases from sixty degrees to eighty degrees when the specimen is placed in a sufficiently concentrated amyl xanthic acid solution. Also, the concentration of amyl xanthic acid may be adjusted so that intermediate angles are obtained.

Experimental Procedure

The cleaned mineral was first conditioned in ethyl xanthate, and then was placed in a solution which contained a mixture of potassium amyl xanthate and potassium ethyl xanthate. Ethyl xanthate concentrations were constant for solutions of various pH values. For pH 3.80, m_c = 45 mg/l.; pH 5.25, m_c = 60 mg/l.; pH 5.70, m_c = 60 mg/l, and pH 8.10, m_c = 75 mg/l. All ethyl xanthate values were above critical concentrations required for full values of contact angles.

Experimental Results

The results are shown in Figures 25-33 which are plots of contact angle versus mole percent amyl xanthate. Figures 27, 29, 31 and 33 show the actual experimental points, whereas, Figures 25, 26, 28, 30, and 32 show the aver-

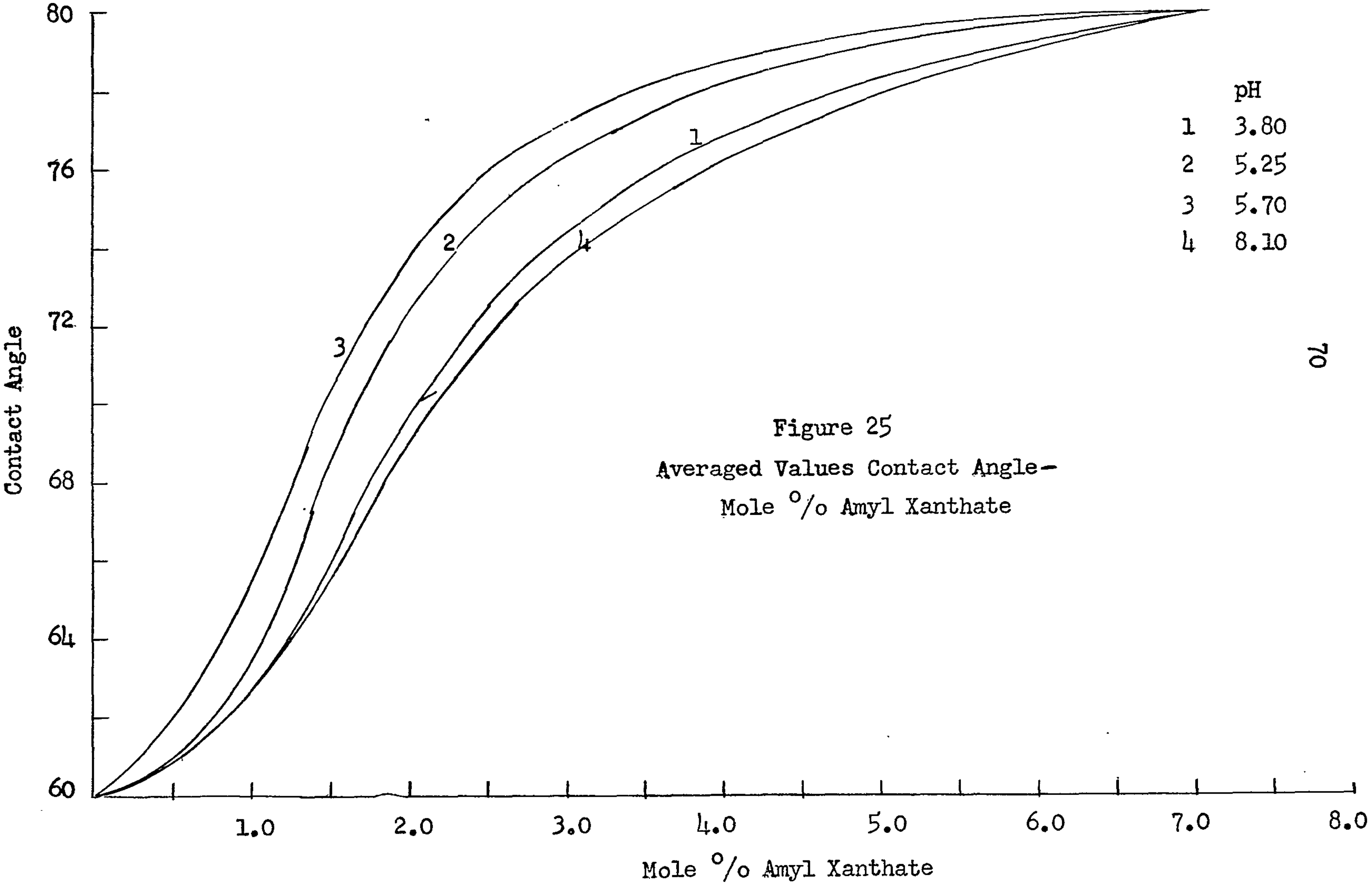


Figure 25
Averaged Values Contact Angle—
Mole °/o Amyl Xanthate

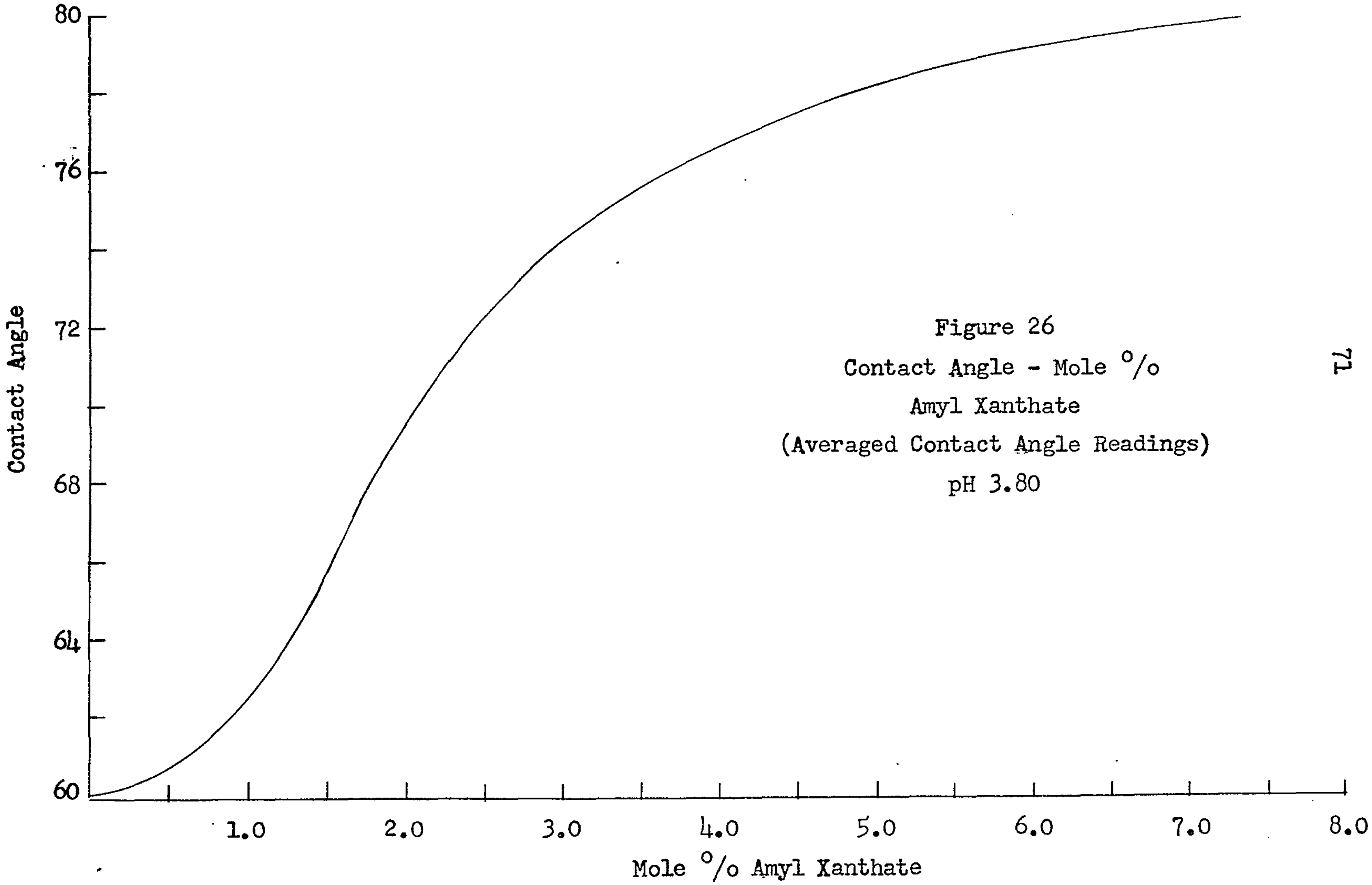


Figure 26
Contact Angle - Mole °/o
Amyl Xanthate
(Averaged Contact Angle Readings)
pH 3.80

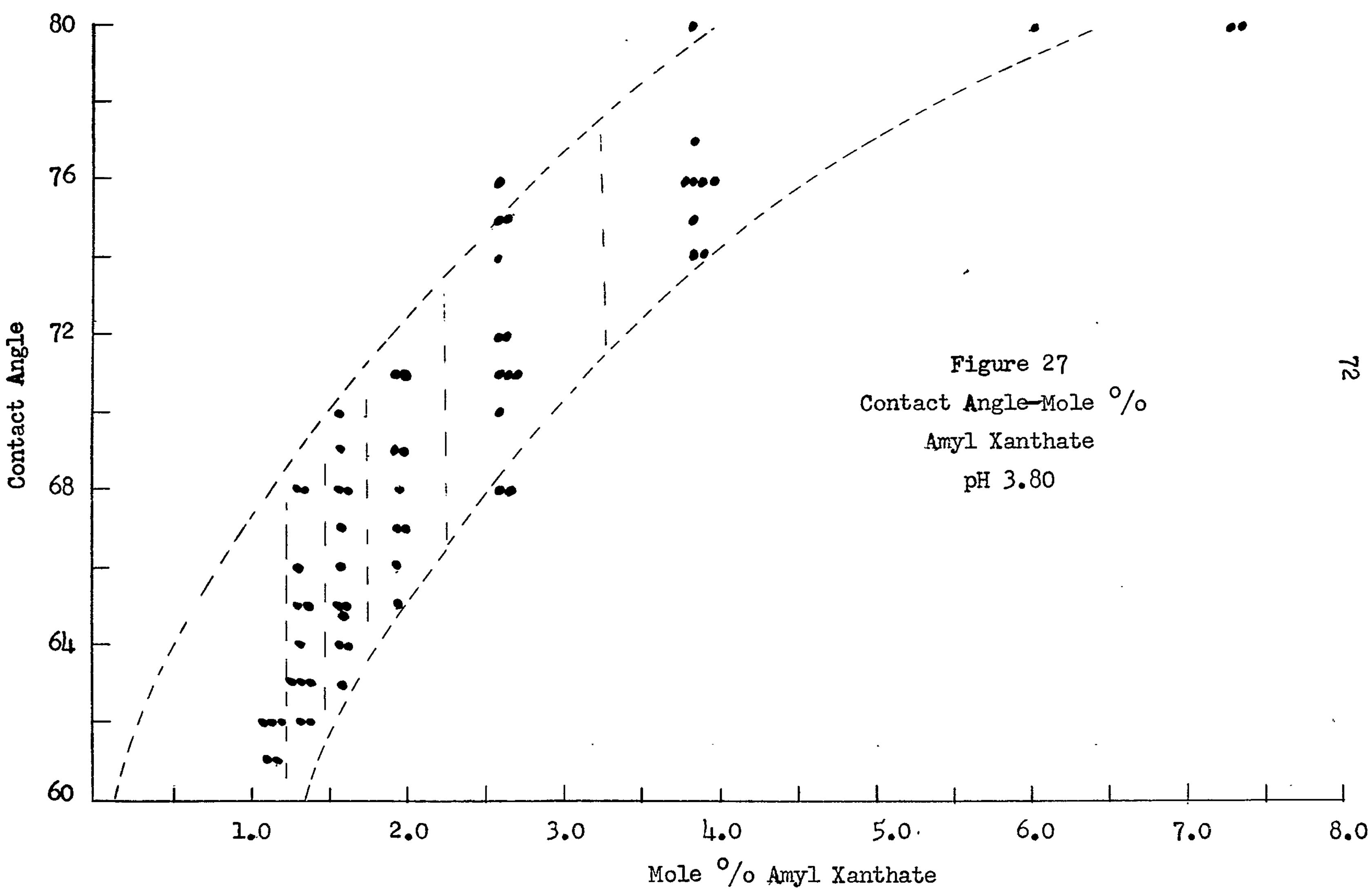


Figure 27
Contact Angle–Mole °/o
Amyl Xanthate
pH 3.80

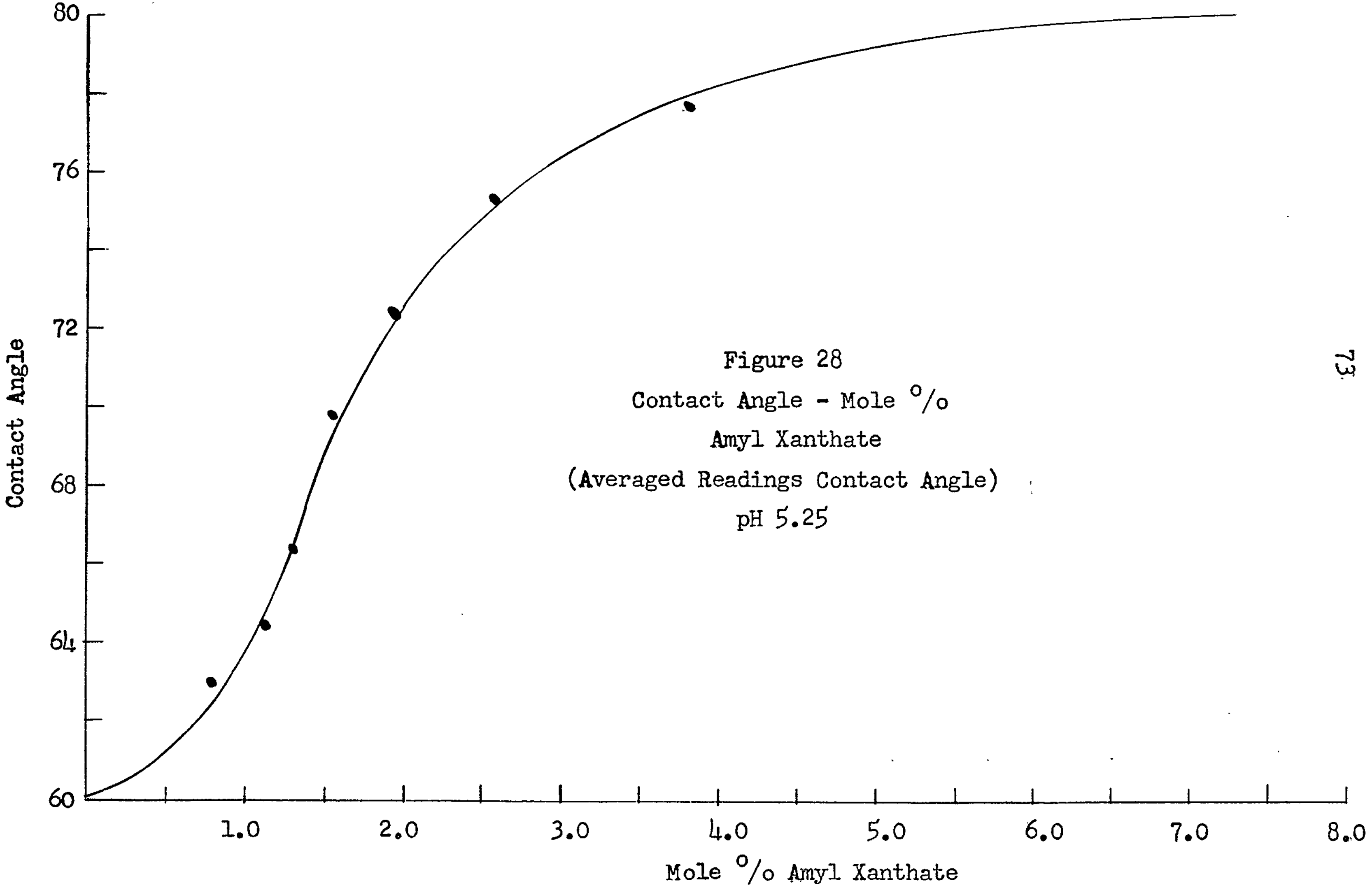


Figure 28
Contact Angle - Mole °/o
Amyl Xanthate
(Averaged Readings Contact Angle)
pH 5.25

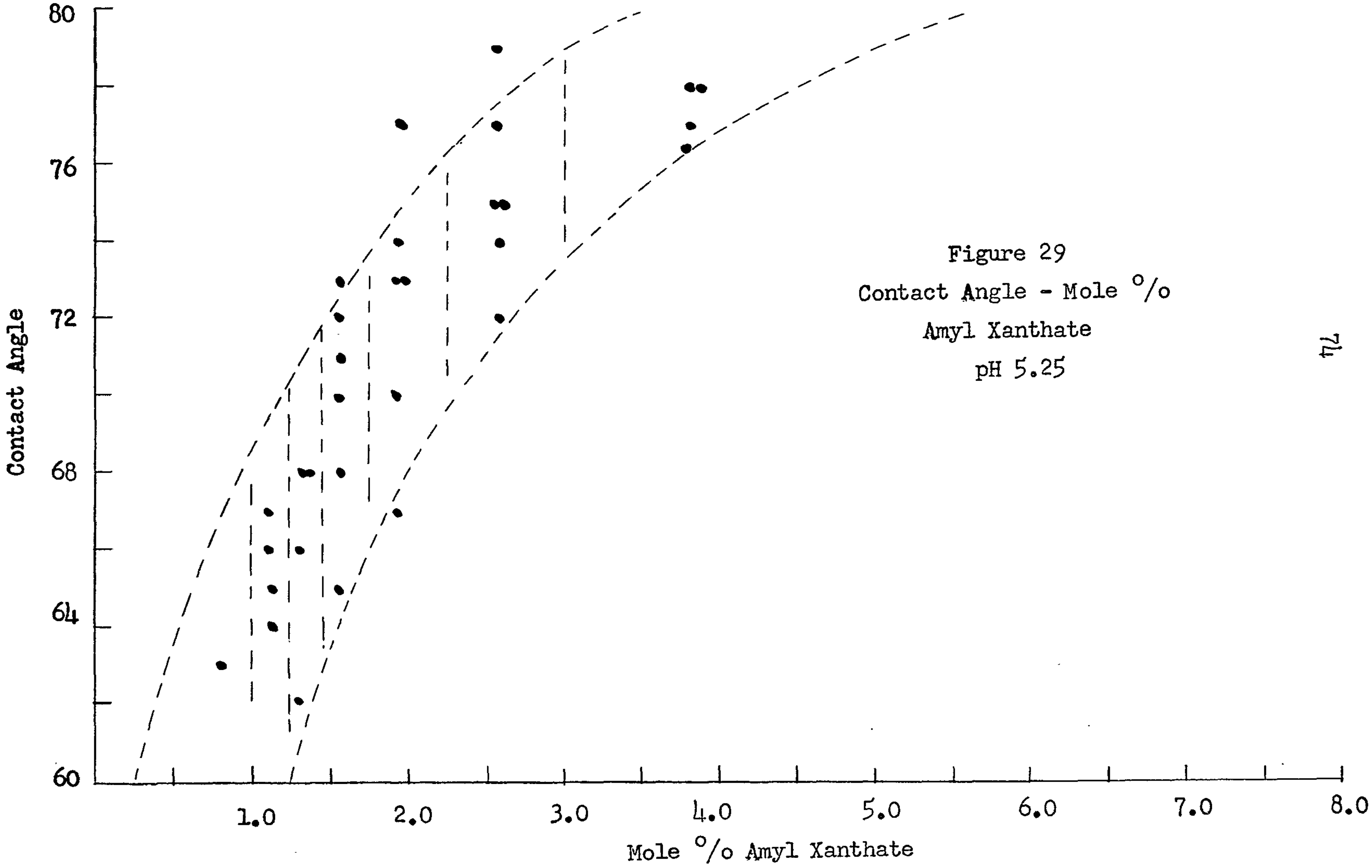


Figure 29
Contact Angle - Mole °/o
Amyl Xanthate
pH 5.25

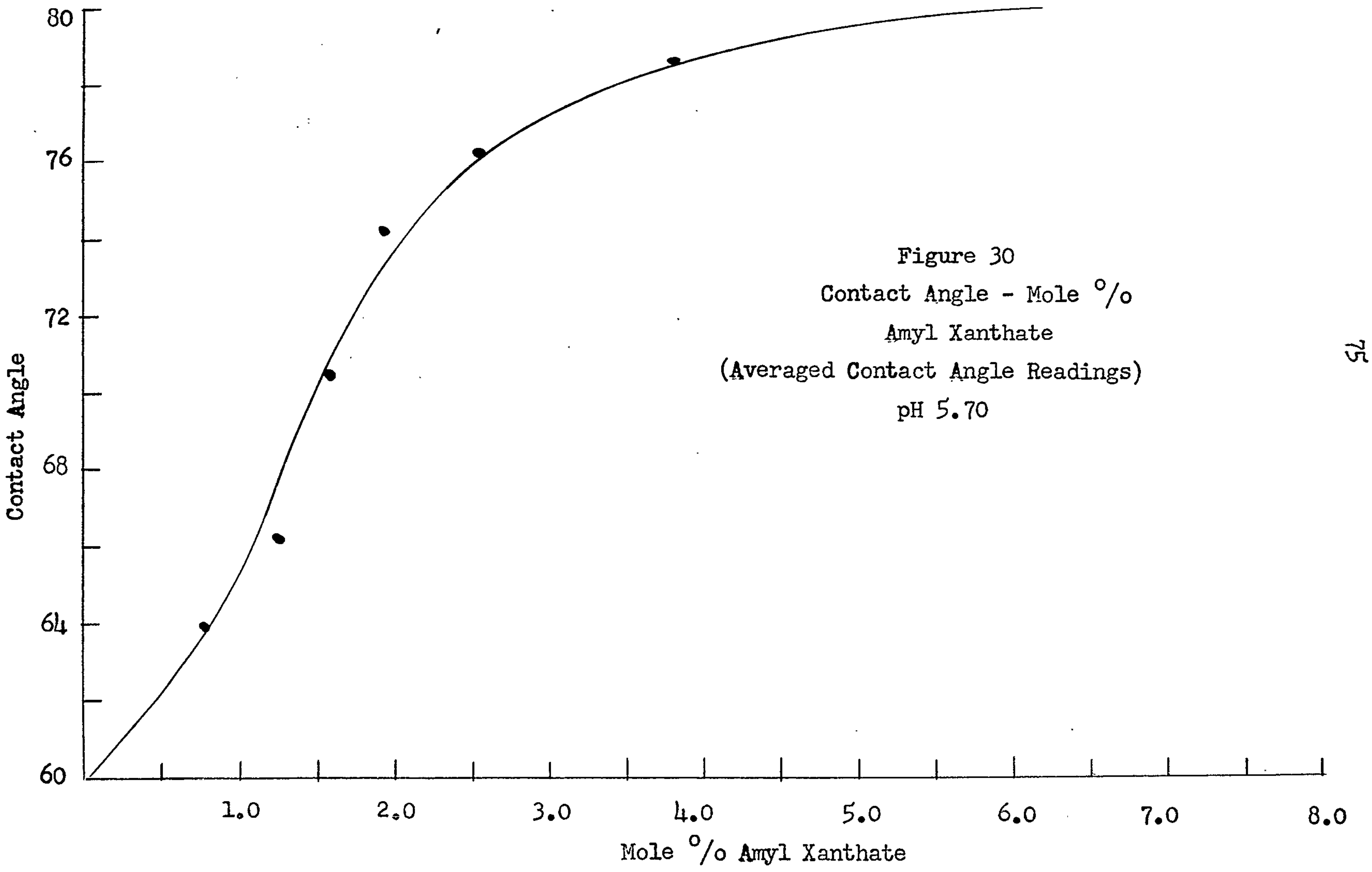


Figure 30
Contact Angle - Mole °/o
Amyl Xanthate
(Averaged Contact Angle Readings)
pH 5.70

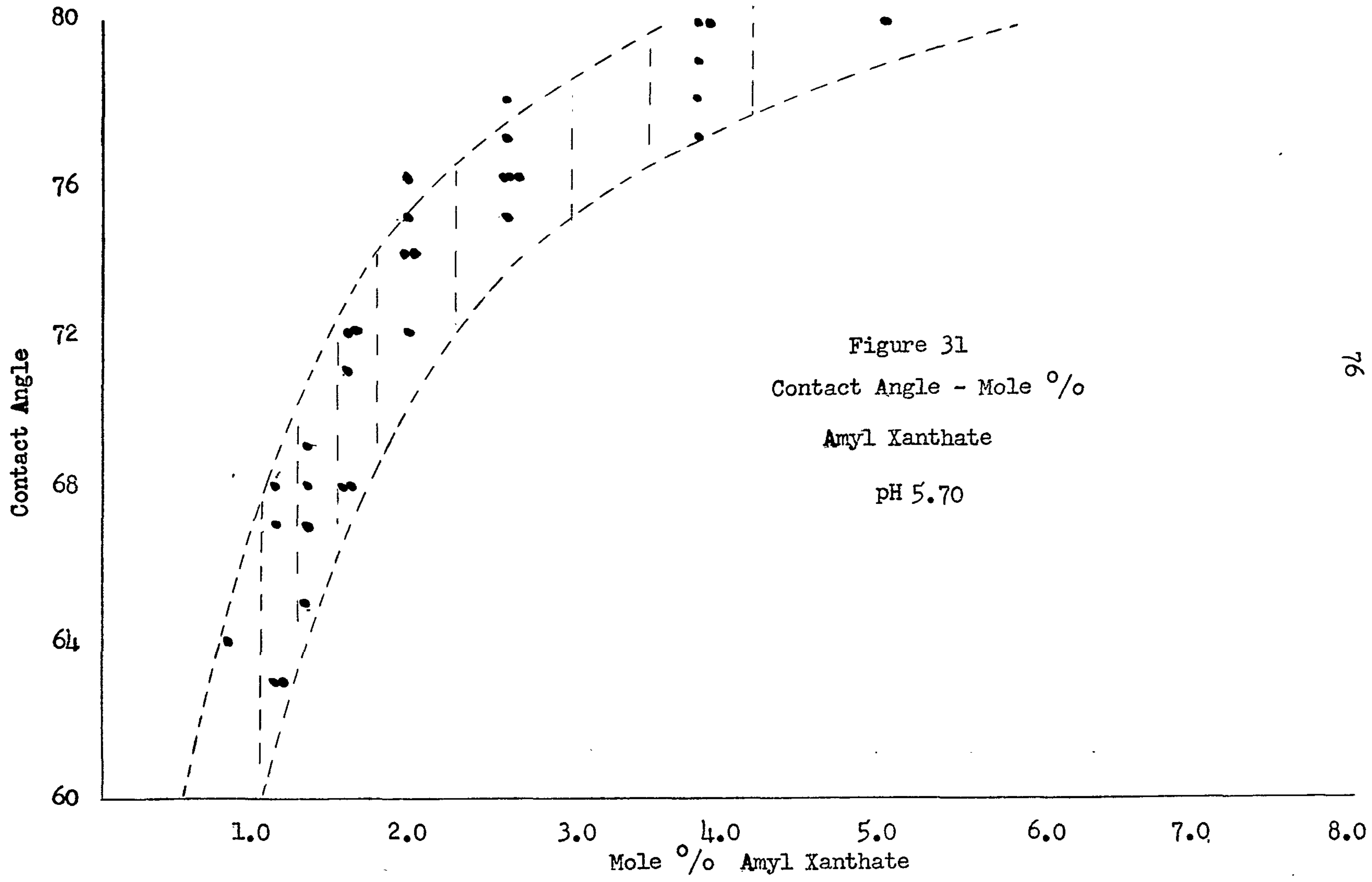


Figure 31

Contact Angle - Mole °/o

Amyl Xanthate

pH 5.70

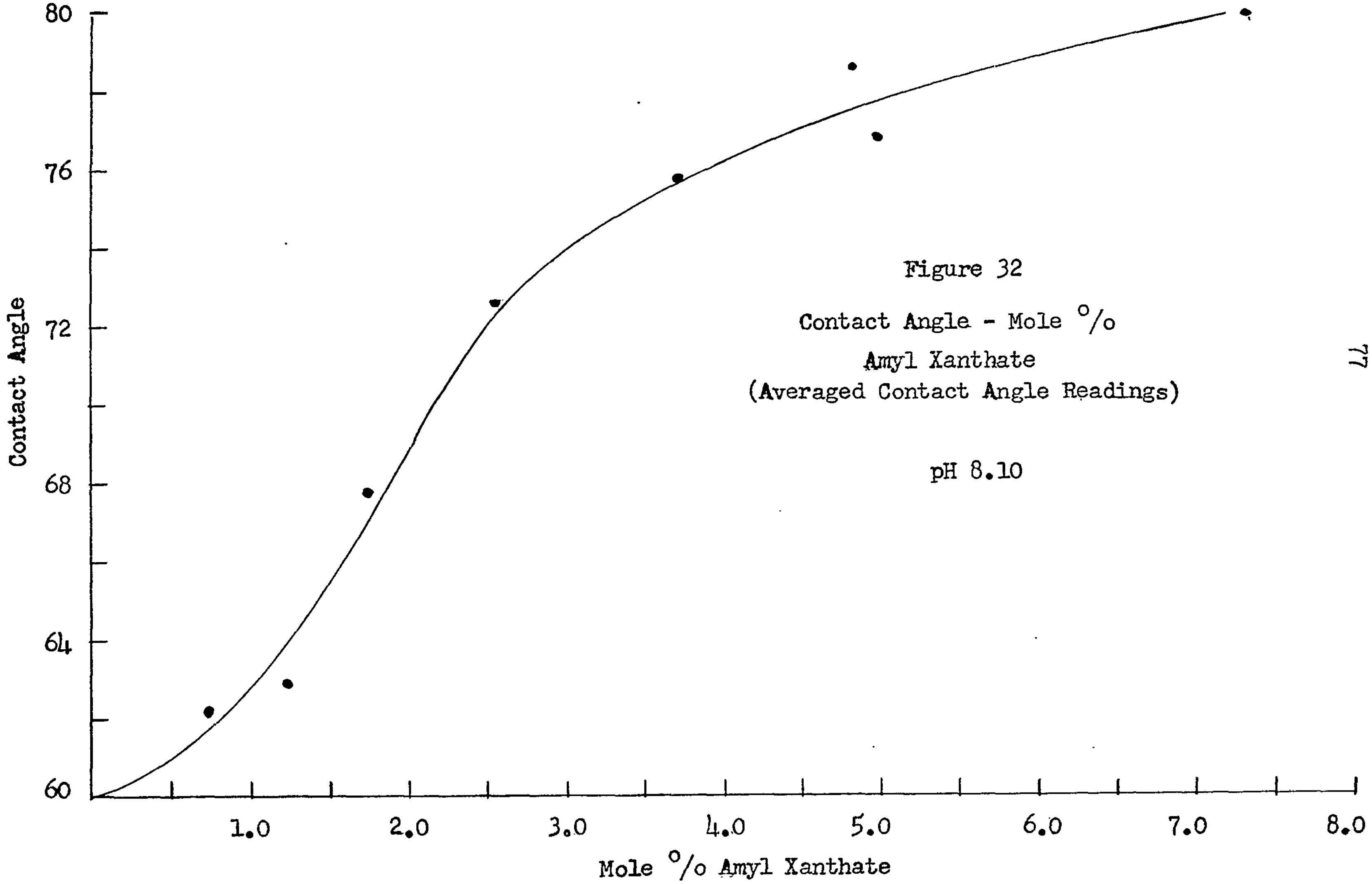


Figure 32

Contact Angle - Mole °/o
Amyl Xanthate
(Averaged Contact Angle Readings)

pH 8.10

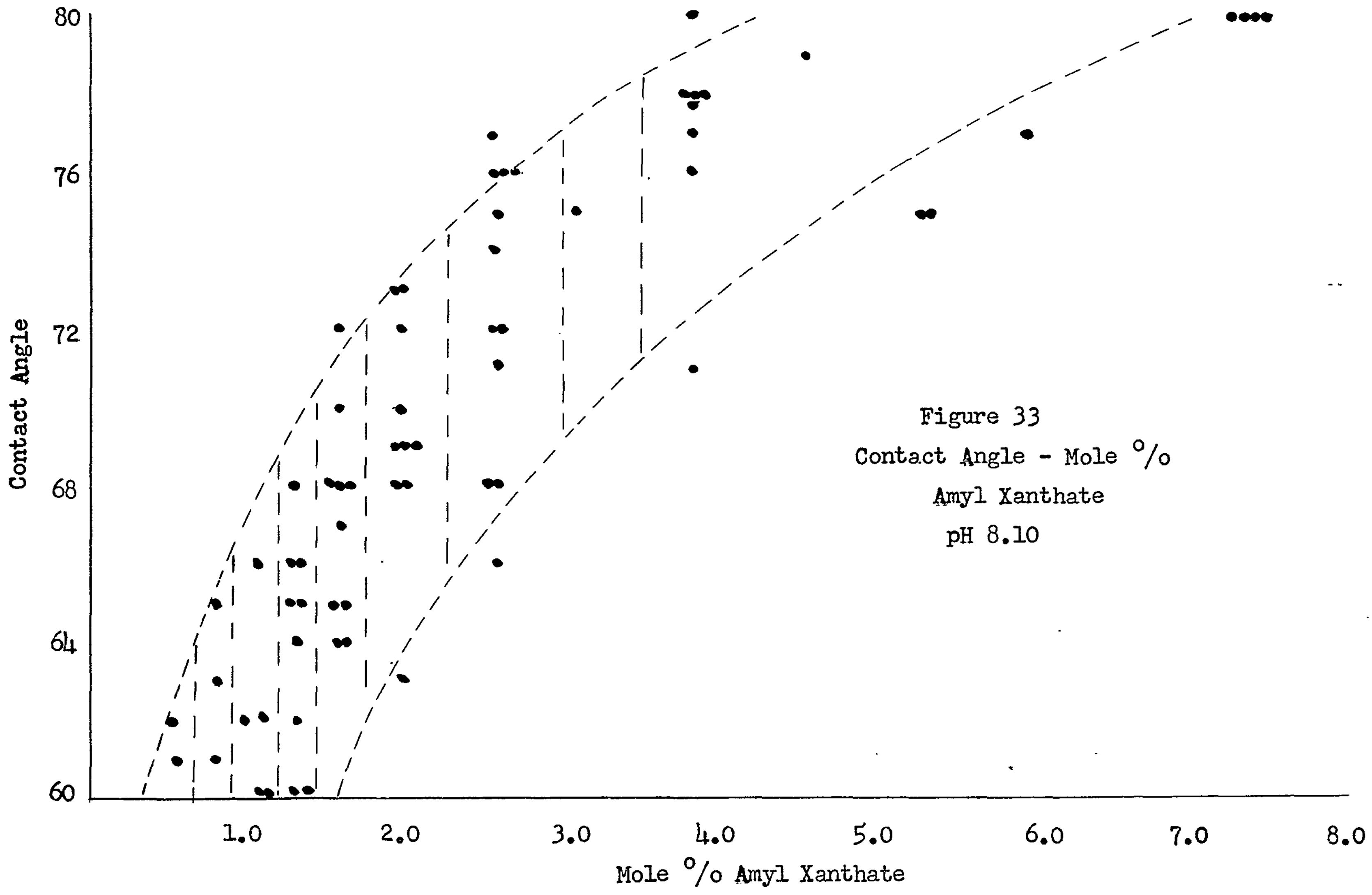


Figure 33
Contact Angle - Mole °/o
Amyl Xanthate
pH 8.10

aged values of these points.

These plots at first seem inconsistent since a higher concentration of collector is necessary at lower pH values. It should be emphasized that the total change in contact angle is twenty degrees and that contact angle is quite sensitive to changes in amyl xanthate concentration, especially at very low concentrations of amyl xanthate. A glance at the actual experimental results shows that the data are not as precise as those obtained with the single collector systems. Nevertheless, all experimental data have been included and have been averaged in accordance with the procedure outlined in the section on Potassium Ethyl Xanthate on Galena "Experimental Results," page 28.

Determination of Ka Values

Neglecting collector decomposition, the HX dissociation may be represented by

$$HX_1 = H^+ + X_1^- \qquad (1)$$

$$HX_2 = H^+ + X_2^- \qquad (2)$$

HX_1 represents ethyl xanthic acid, HX_2 is amyl xanthic acid,

$$Ka_1 = \frac{[H^+][X_1]}{[HX_1]} \qquad (3)$$

$$Ka_2 = \frac{[H^+][X_2]}{[HX_2]} \qquad (4)$$

where Ka_1 and Ka_2 are the dissociation constants for HX_1 and HX_2 respectively. Since

$$m_1 = HX_1 + X_1^- \tag{5}$$

and

$$m_2 = HX_2 + X_2^- \tag{6}$$

Substituting for X_1^- and X_2^- in equations 3 and 4 and solving for Ka_1 and Ka_2:

$$Ka_1 = \frac{[H^+]\,[m_1 - HX_1]}{HX_1} \tag{7}$$

$$Ka_2 = \frac{[H^+][m_2 - [HX_2]}{HX_2} \tag{8}$$

Solving equations 7 and 8 for HX_1 and HX_2

$$HX_1 = \frac{[m_1]\,[H^+]}{Ka_1 + H^+} \tag{9}$$

$$HX_2 \quad \frac{[m_2]\,[H^+]}{Ka_2 + H^+} \tag{10}$$

Dividing equation 9 by equation 10 gives

$$\frac{HX_1}{HX_2} \quad \frac{m_1\,(Ka_2 + H^+)}{m_2\,(Ka_1 + H^+)} \tag{11}$$

Assuming that, for a constant value of contact angle, HX_1/HX_2 is a constant, the values of Ka's can be determined.

$$\frac{Ka_2 + H^+}{Ka_1 + H^+} = \frac{m_2}{m_1} \times \text{const.} \tag{12}$$

Since the abscissa in Figure 25 is $m_2/(m_1 + m_2)$

$$\frac{m_2}{m_1} = \frac{N}{1-N} \tag{13}$$

where N = mole fraction of amyl xanthate. Knowing values of pH and m_2/m_1 from Figure 25, the values of Ka_1 and Ka_2 were adjusted to superimpose all the experimental curves. See Figure 34, which is plotted in terms of HX_2/HX_1.

This method gives a value of $Ka_1 = 8.6 \times 10^{-7}$ and a value of $K_2 = 9.3 \times 10^{-7}$.

Cook and Nixon(3) have determined these values and have reported values of 2.5×10^{-5} for amyl xanthic acid and 3×10^{-3} for ethyl xanthic acid. Last and Cook(22) have shown by bubble pick-up method that the dissociation of amyl xanthic acid is 1×10^{-6}.

Contact Angle - Surface Coverage Relationship

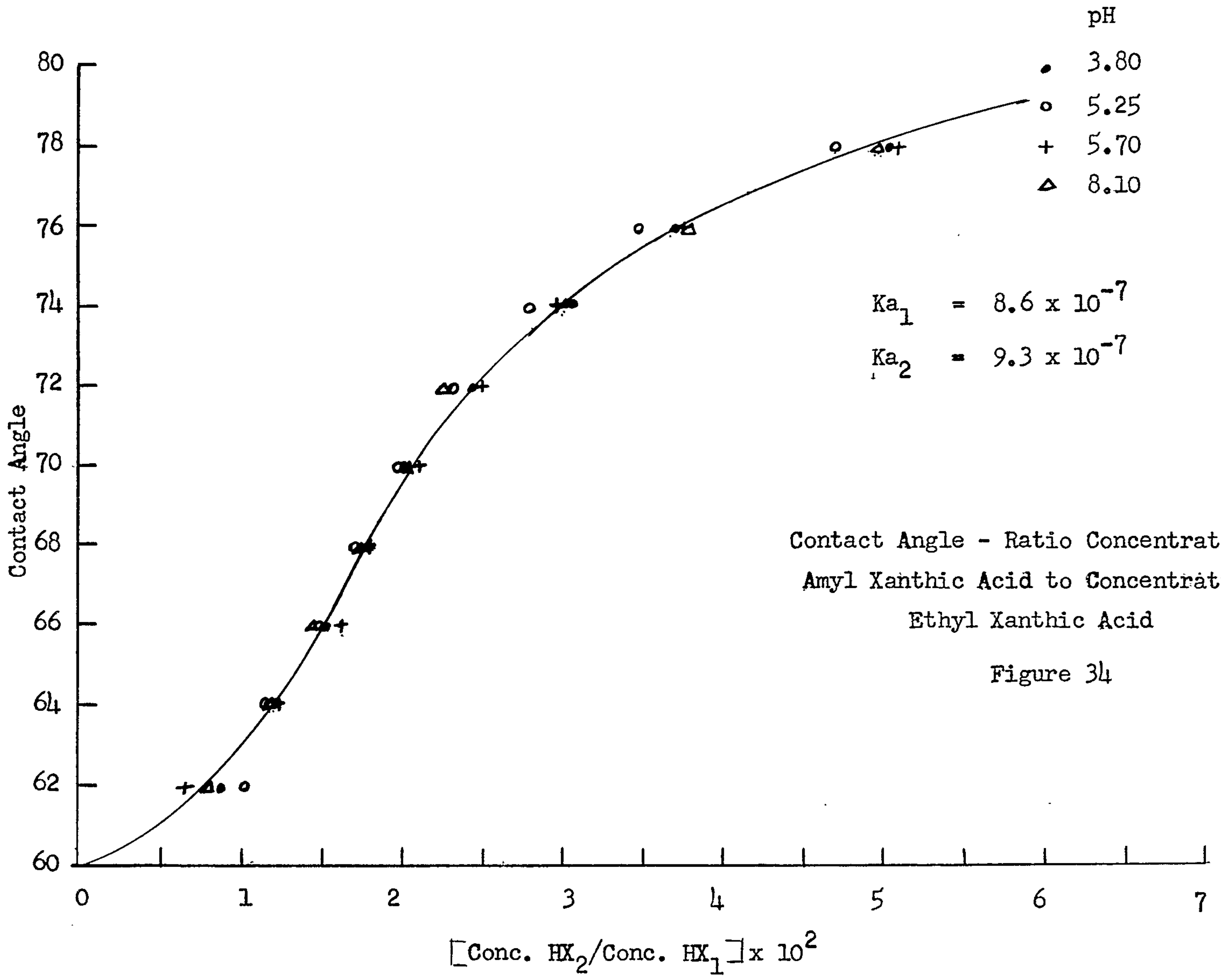
Competitive adsorption of two collectors on a single mineral can be represented as follows:

$$S + HX_1 \rightleftharpoons SHX_1 \tag{14}$$

and

$$S + HX_2 \rightleftharpoons SHX_2 \tag{15}$$

where S represents the concentration of unoccupied surface sites, HX_1 represents the concentration of ethyl xanthic acid, HX_2 is the concentration of amyl xanthic acid. SHX_1 and SHX_2 represent the concentration of surface sites occupied by HX_1 and HX_2 respectively. The equilibrium constants may be



Contact Angle - Ratio Concentration
Amyl Xanthic Acid to Concentration
Ethyl Xanthic Acid

Figure 34

written as follows:

$$K_1 = \frac{[SHX_1]}{[S][HX_1]} \tag{16}$$

$$K_2 \quad \frac{[SHX_2]}{[S]\ [HX_2]} \tag{17}$$

Dividing equation 16 by equation 17 gives:

$$\frac{K_1}{K_2} = \frac{[SHX_1]\ [HX_2]}{[SHX_2]\ [HX_1]} = \frac{\theta_1}{\theta_2}\ \frac{[HX_2]}{[HX_1]} \tag{18}$$

where θ_1 = fraction surface covered by HX_1 and θ_2 is the fraction of the surface covered by HX_2.

It may be shown that the relationship between contact angle and surface coverage for two collector systems is non linear. Rewriting equation 18

$$\frac{K_1}{K_2} = \frac{\theta_1}{\theta_2}\ \frac{[HX_2]}{[HX_1]} \tag{19}$$

Knowing the values of K_1 and K_2, HX_1 and HX_2 can be calculated. K_1 and K_2 were determined independently from work on single collectors. From data in Figure 25

$$\frac{\theta_2}{\theta_1} = \frac{8.9 \times 10^8}{3.3 \times 10^8}\ \frac{m_2}{m_1}\ \frac{[8.6 \times 10^{-7} + H^+]}{[9.3 \times 10^{-7} + H^+]} \tag{20}$$

or from Figure 34, taking a value of HX_2/HX_1 corresponding to a given contact angle the relationship between contact angle and θ_2/θ_1 is obtained from

$$\frac{\theta_2}{\theta_1} = \frac{8.9 \times 10^8}{3.3 \times 10^8}\ \frac{[HX_2]}{[HX_1]} \tag{21}$$

A plot of contact angle ϕ versus θ_2/θ_1 is shown in Figure 35. Equation 21 was used in making this plot.

Discussion

Obviously there are insufficient data to calculate the dissociation constants as precisely as may be obtained from other experimental methods.

It can only be concluded that the dissociation constants are of the same order of magnitude, i.e., 1×10^{-6}. More experimental data are required to determine definitely the relative values of dissociation constants. The data are also inadequate to rule out the possibility of a linear relationship between contact angle and surface coverage for the two collector system.

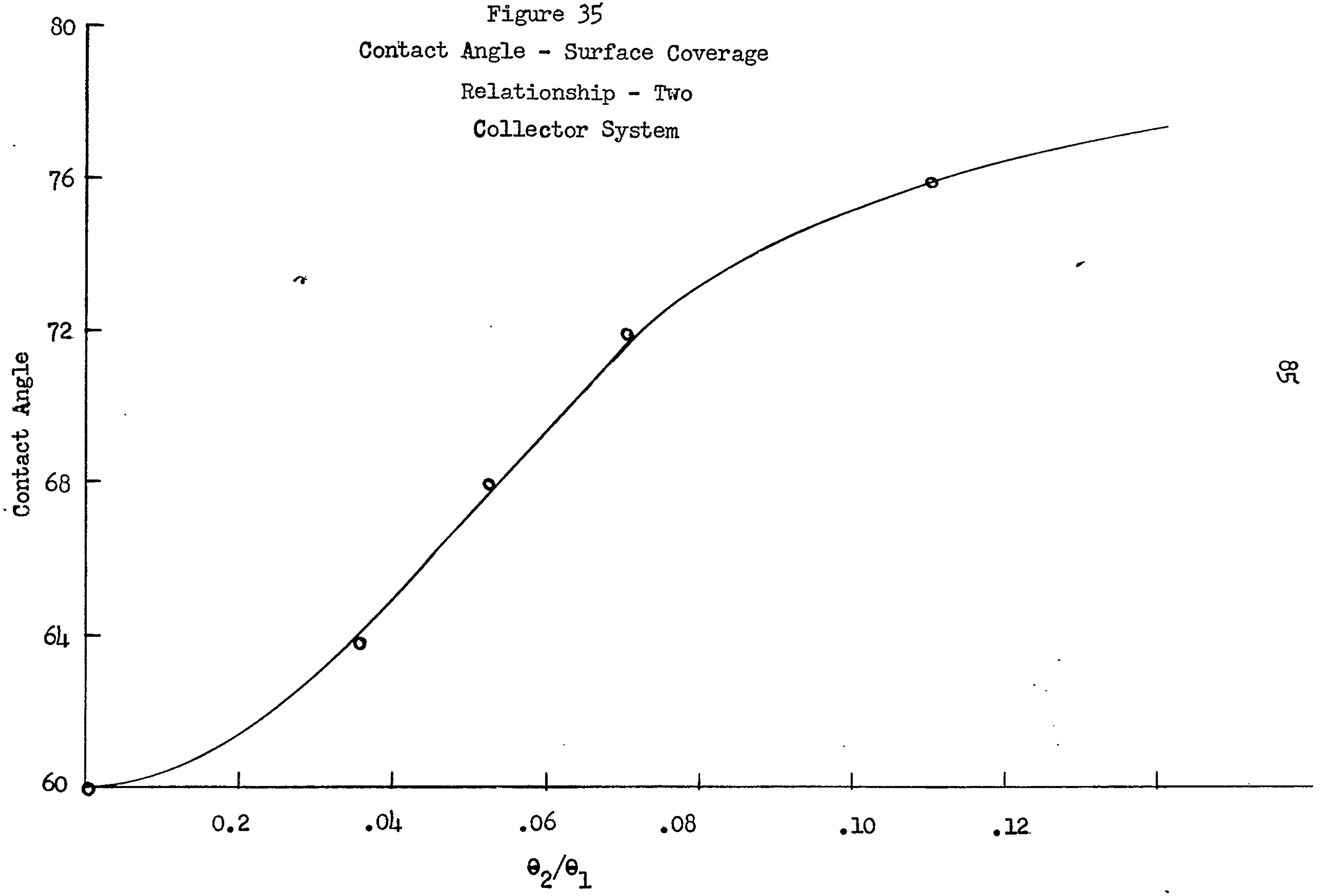


Figure 35
Contact Angle - Surface Coverage
Relationship - Two
Collector System

COLLECTOR-DEPRESSANT STUDIES

A theory of collector-depressant-mineral equilibria based upon adsorption of free acids of these compounds has been proposed by Last and Cook(22). The object of the present study is to obtain experimental data with which to more completely validate the above theory. Evidence concerning the relationship between surface coverage and contact angle as presented in the section on "Single Collector Systems" has been found to be applicable to collector-depressant systems. This allows calculation of all necessary constants including K_1, the value of which had previously been determined(22) after making an assumption of the critical concentration of collector, i.e., the amount of surface coverage at "bubble pick up."

Experimental Procedure

The experimental procedure for the collector-depressant system was similar to that used in the case of single collectors, with only one exception. A covered cell must be used to condition the minerals, because of the possibility of concentration changes caused by the liberation of hydrogen sulphide in the acid solutions. 60 mm. weighing bottles were convenient for use as conditioning bottles. Contact angle measurements for various concentrations of potassium amyl xanthate and $Na_2S + 9H_2O$ at pH values of 5.50, 6.05, 7.45, 7.90, and 8.60 have been taken. Figures 37 through 45 are plots of the actual experimental data whereas Figure 36 shows a composite of the averaged values. The data are also tabulated in Appendix I.

Interpretation of Data

Briefly, Last and Cook's(22) interpretation of collector-depressant equilibria is as follows: assuming a single site adsorption of both collector

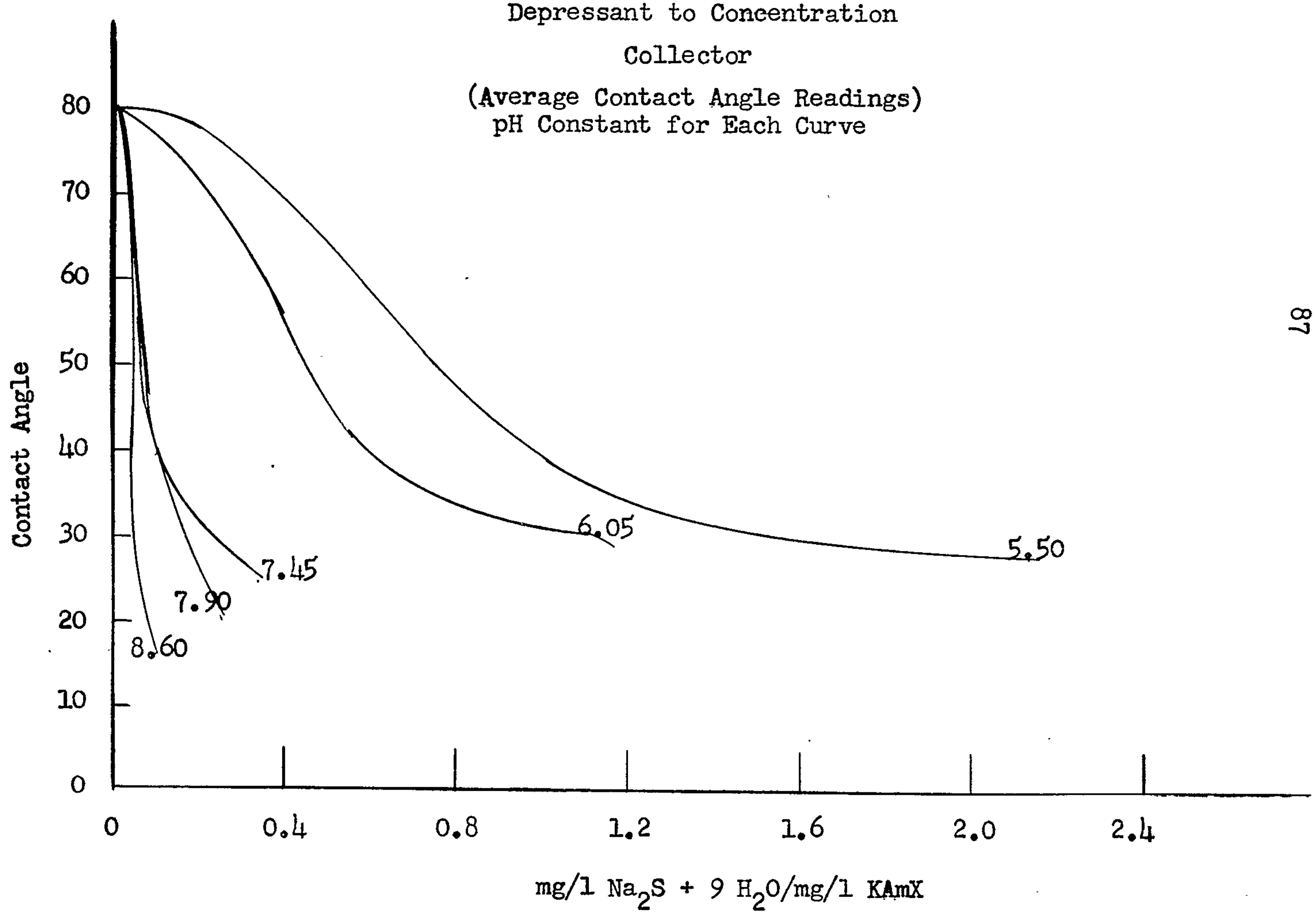


Figure 36

Contact Angle-- Ratio Concentration
Depressant to Concentration
Collector
(Average Contact Angle Readings)
pH Constant for Each Curve

Figure 37
Contact Angle - Ratio Concentration
Depressant to Concentration
Collector

pH 5.50

(Average Contact Angle Readings)

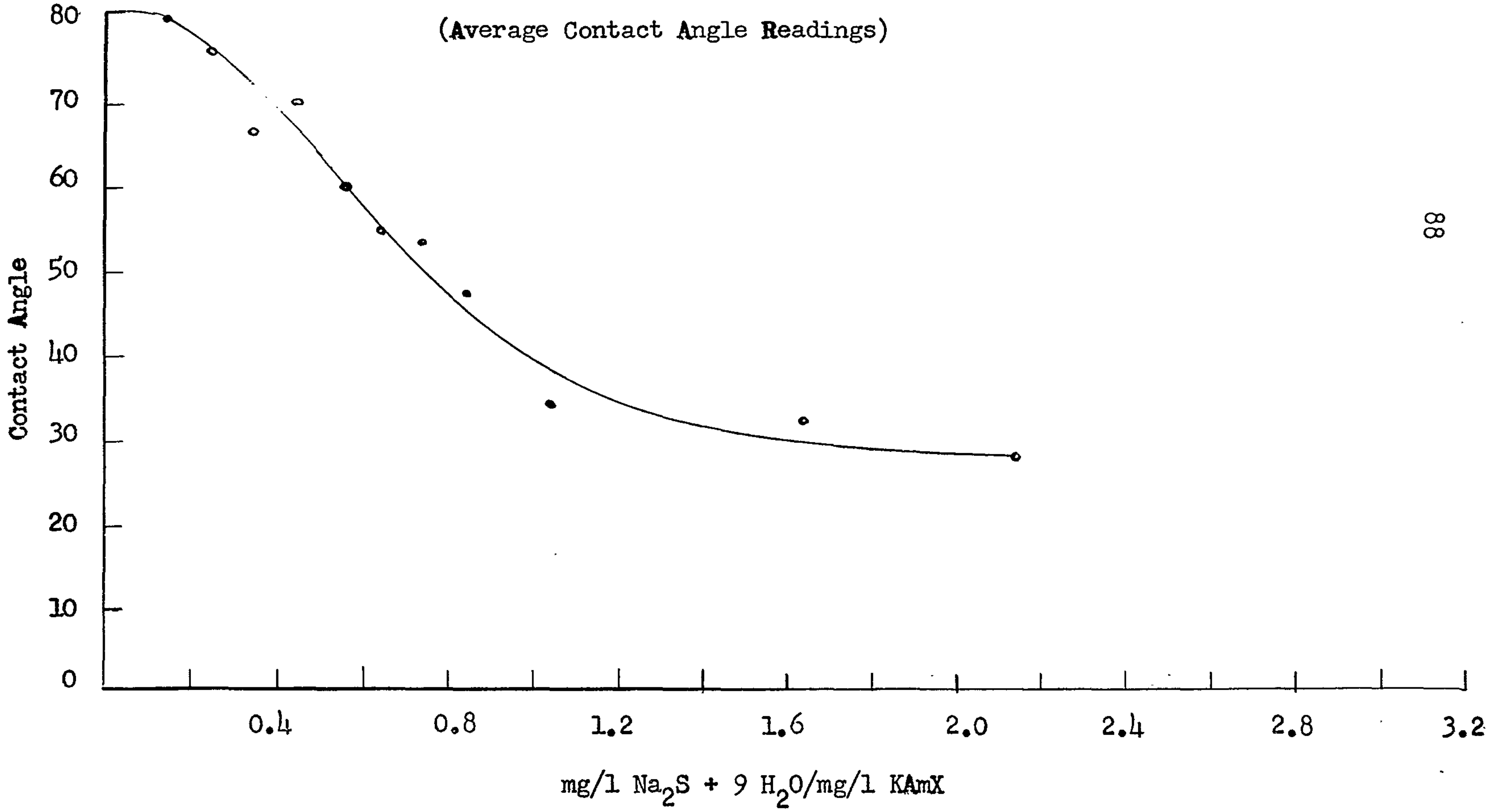


Figure 38

Contact Angle - Ratio Concentration Depressant
to Concentration Collector
pH 5.50

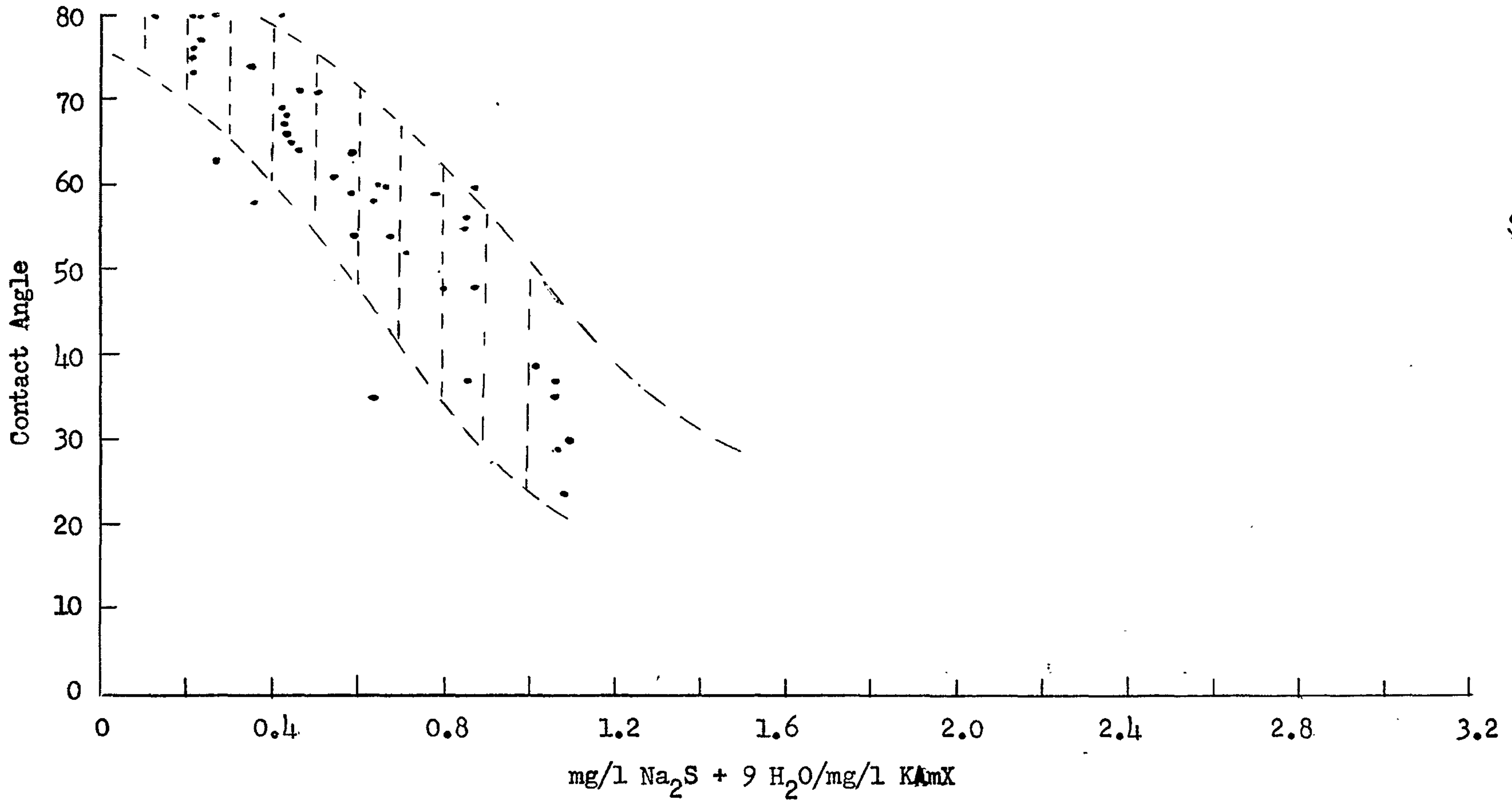


Figure 39
Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 6.05

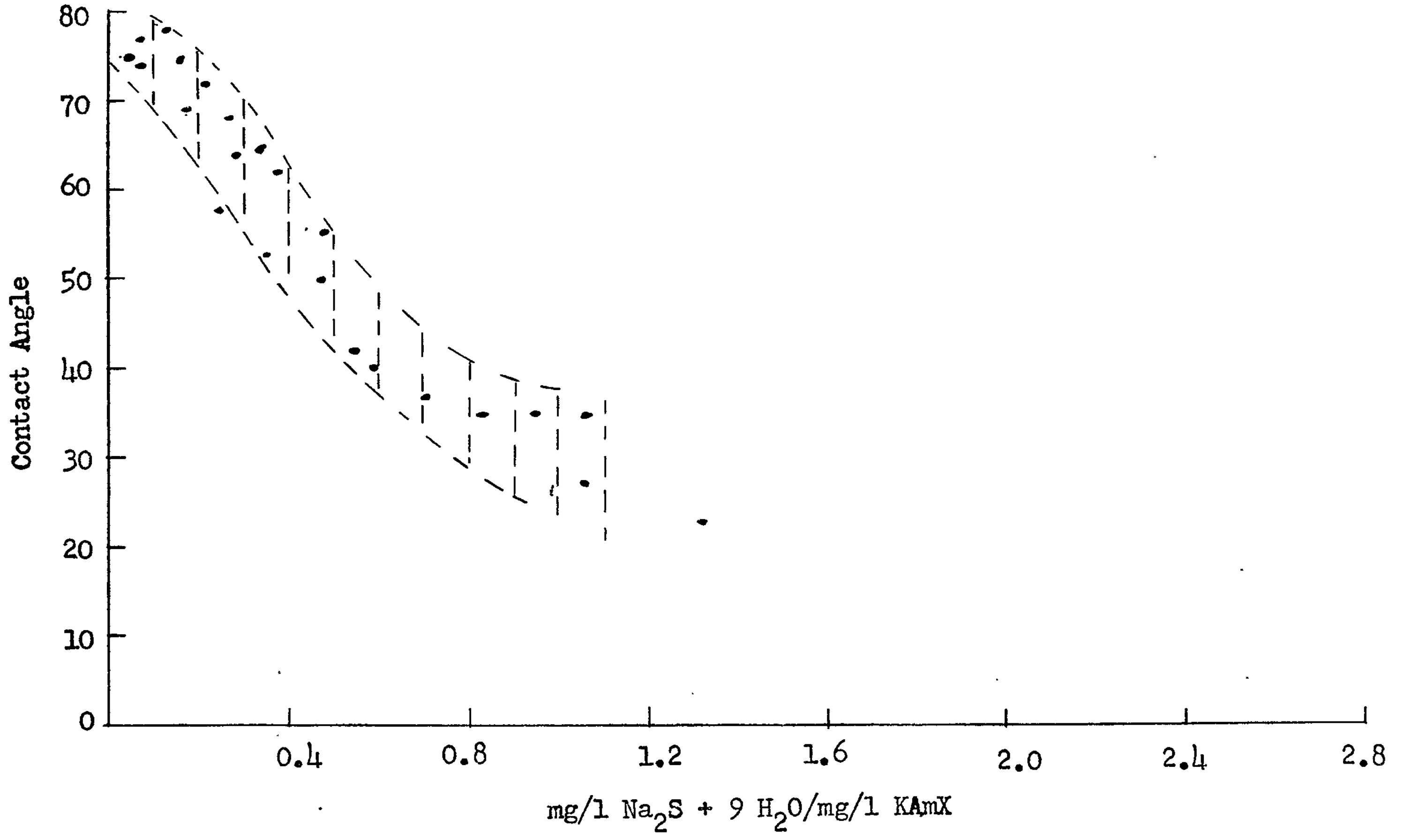


Figure 40
Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 6.05
(Average Contact Angle Readings)

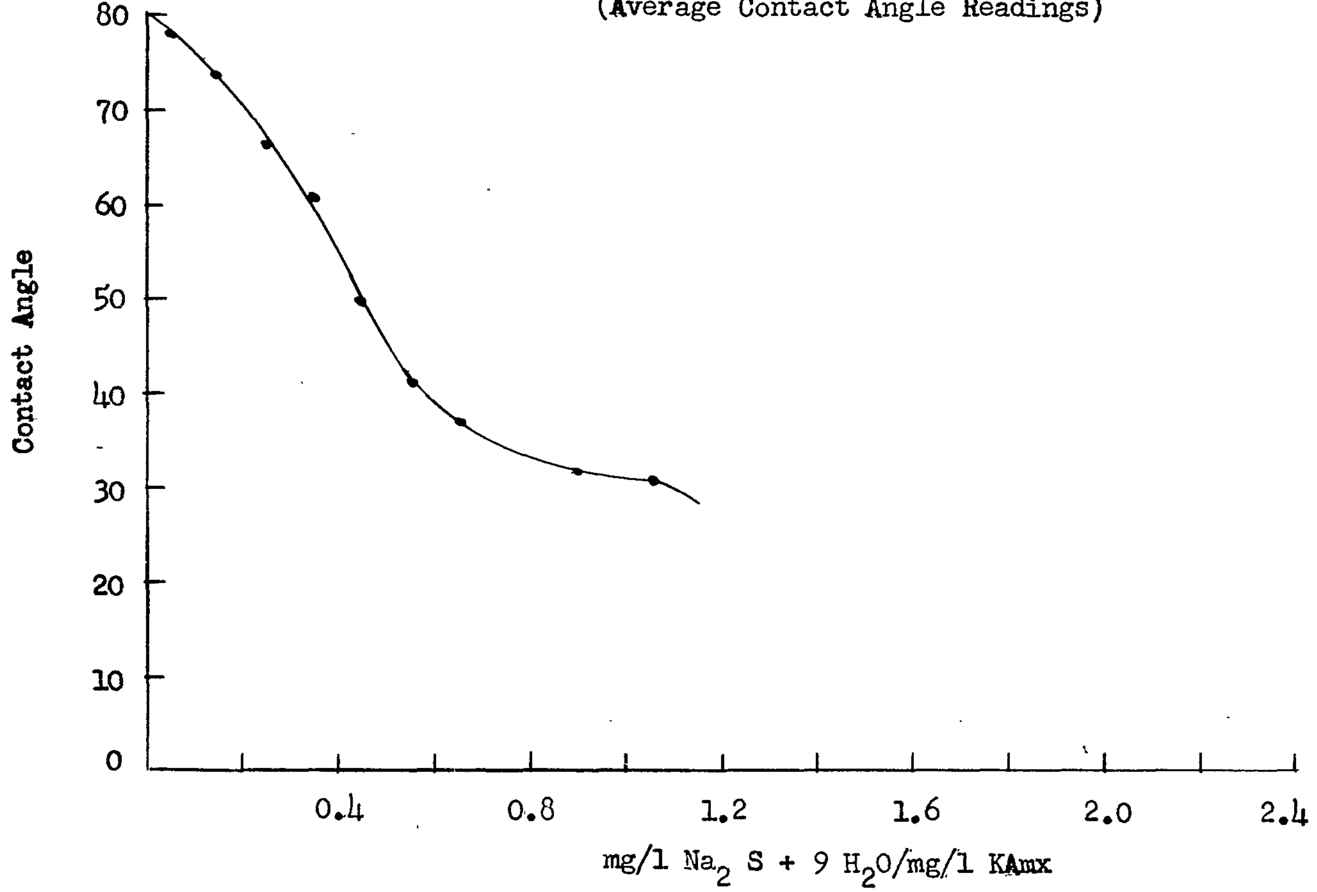
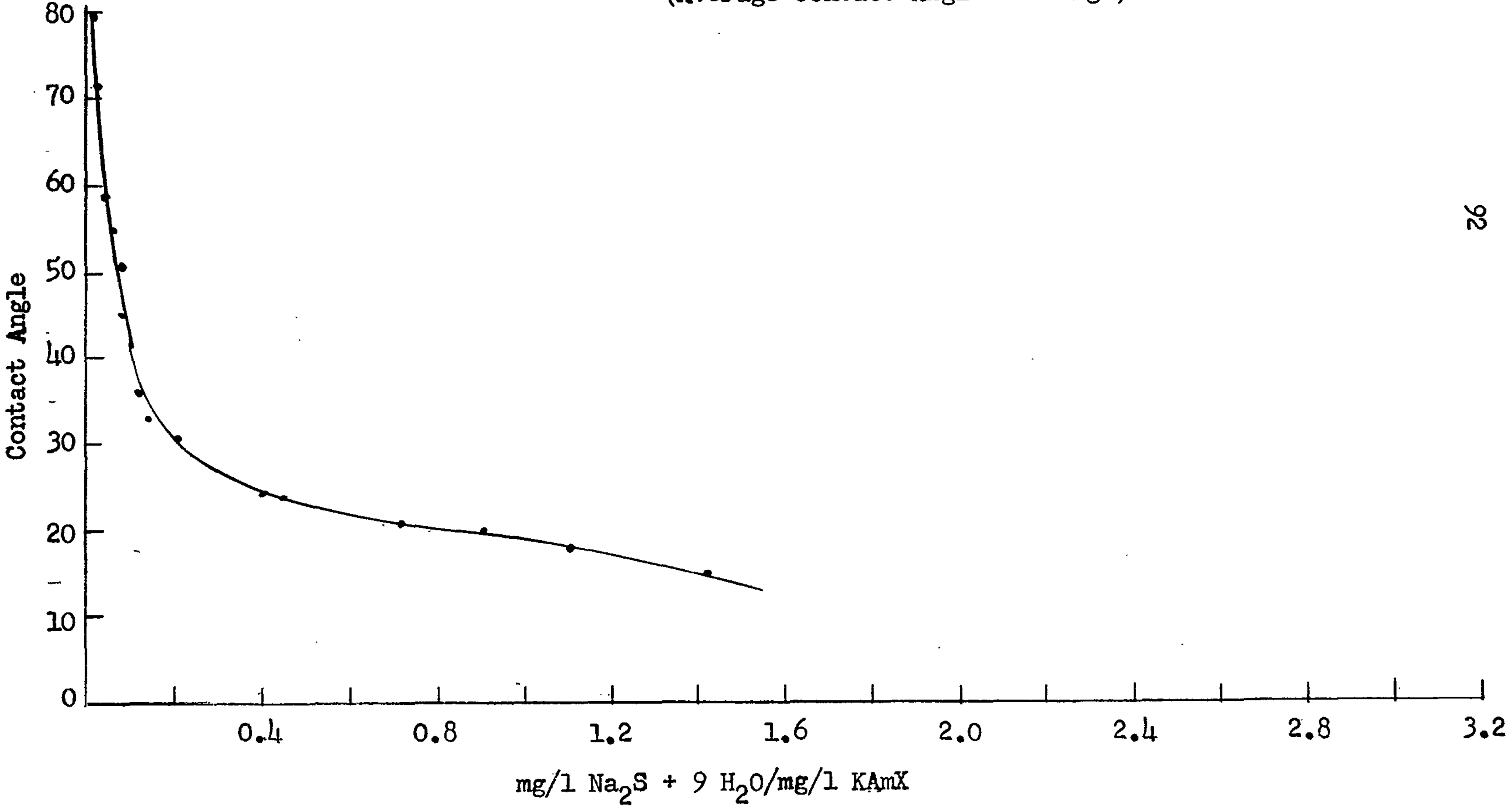


Figure 41
Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH.7.45
(Average Contact Angle Readings)



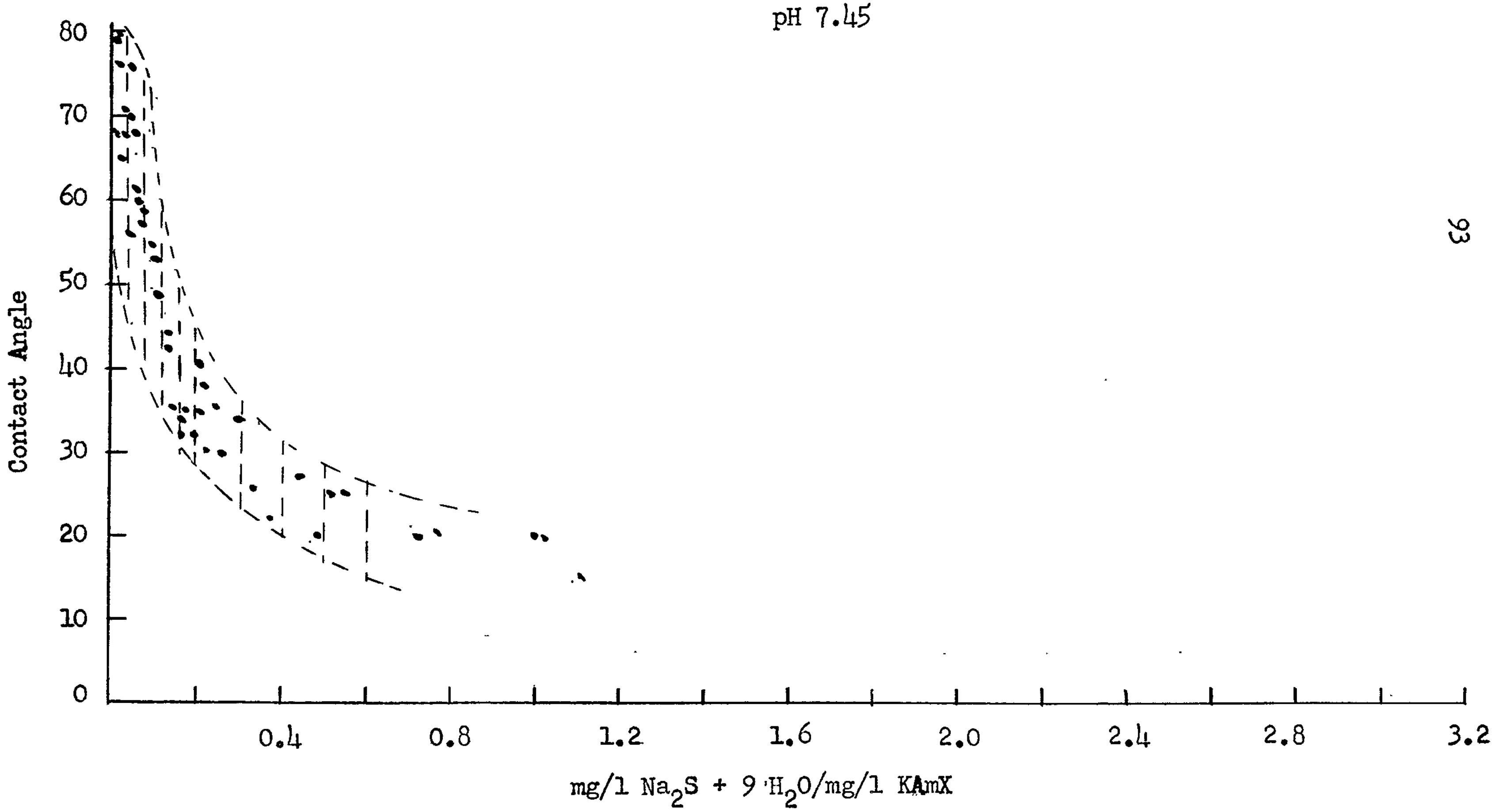


Figure 42
Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 7.45

Figure 43

Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 7.90
(Average Contact Angle Readings)

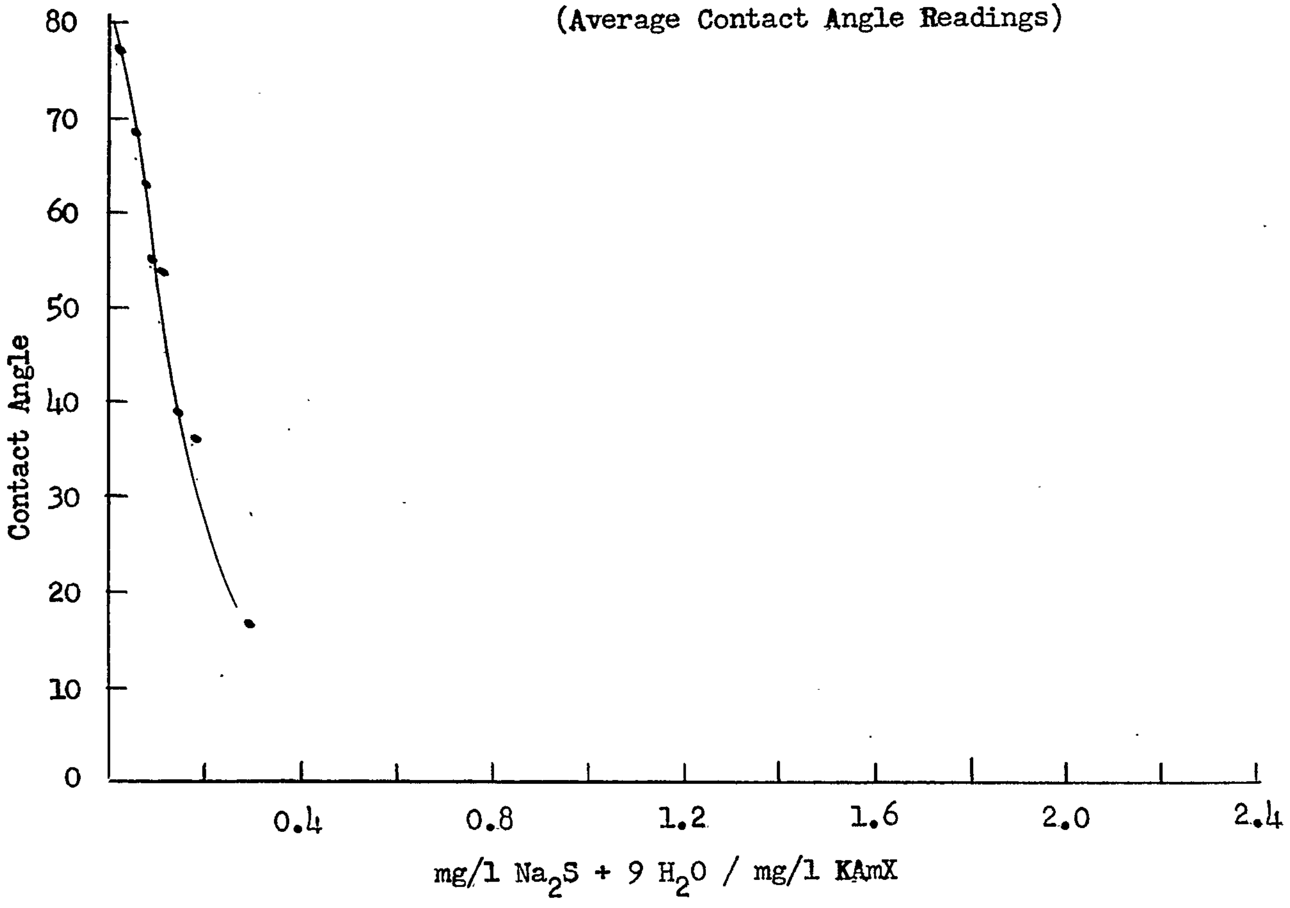


Figure 44
Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 7.90

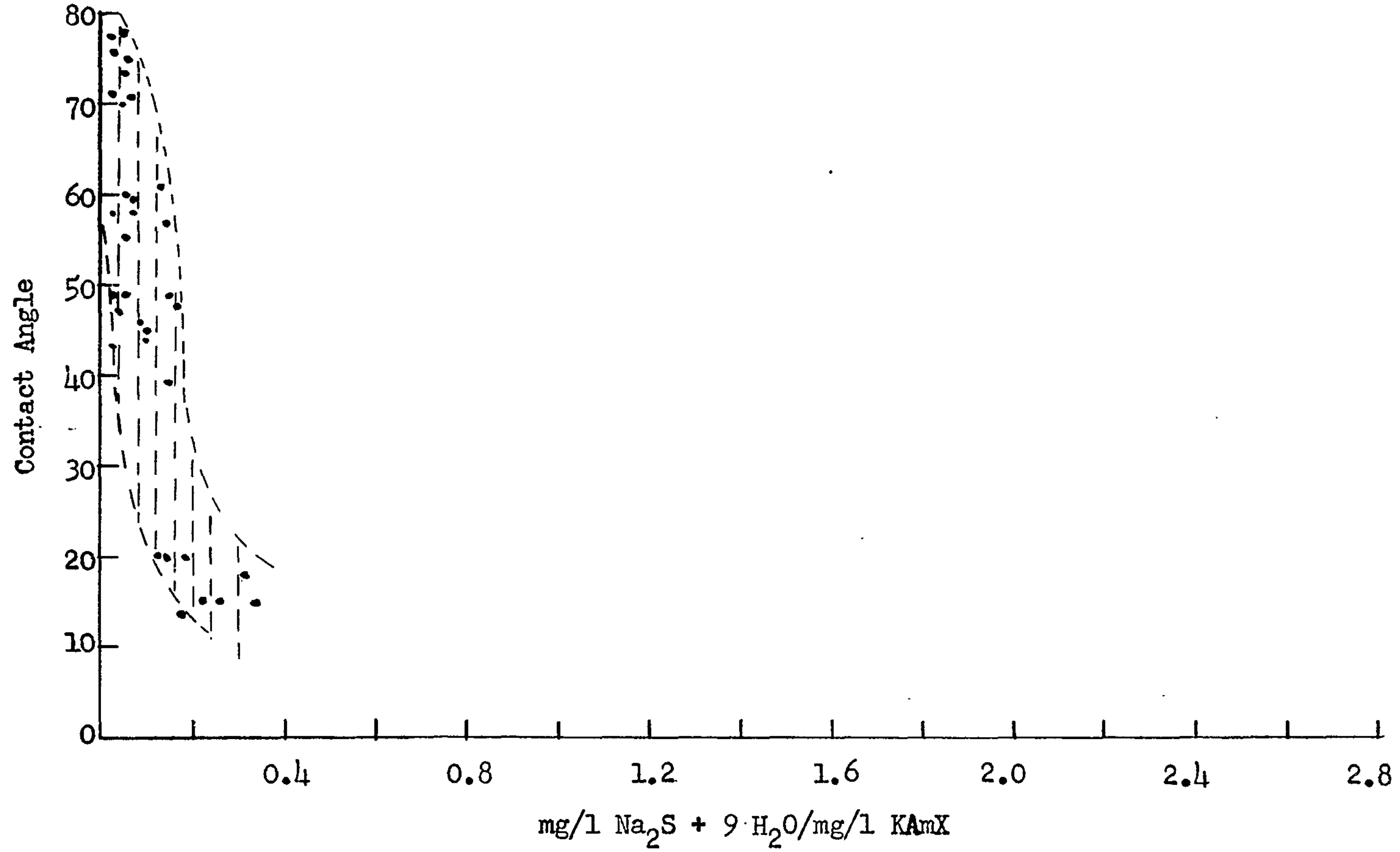
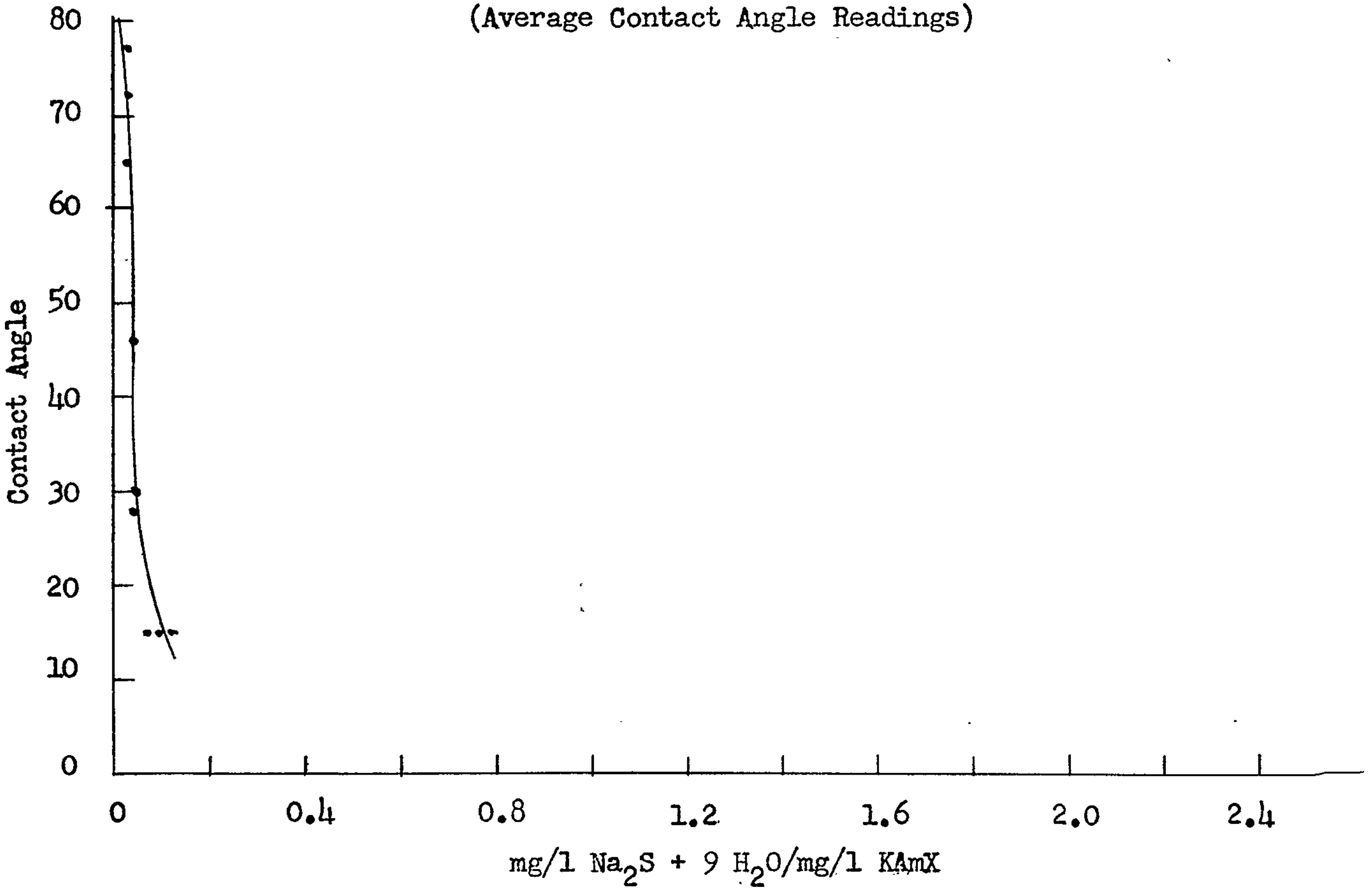


Figure 45

Contact Angle - Ratio Concentration
Depressant to Concentration
of Collector
pH 8.60
(Average Contact Angle Readings)



and depressant

$$S + HX \rightleftharpoons SHX \tag{1}$$

$$S + HD \rightleftharpoons SHD \tag{2}$$

$$K_1 = \frac{[SHX]}{[S][HX]} = \frac{\theta_{HX}}{\sigma} \frac{1}{[HX]} \tag{3}$$

$$K_2 = \frac{[SHD]}{[S][HD]} = \frac{\theta_{HD}}{\sigma} \frac{1}{[HD]} \tag{4}$$

or, in terms of equilibrium constants, where θ_{HX} is the fraction of surface sites covered by HX, θ_{HD} is the fraction of surface sites covered by HD, and σ is the fraction of uncovered surface sites. The mass balance is represented by

$$\sigma = 1 - \theta_{HX} - \theta_{HD} \tag{5}$$

where

σ = unoccupied surface sites.

Solving for θ_{HD} and substituting into equation 4 gives

$$\sigma = \frac{1 - \theta_{HX}}{1 + K_2 [HD]} \tag{6}$$

Substituting this value of σ into equation 3 gives

$$K_1 = \frac{\theta_{HX}}{1-\theta_{HX}} \cdot \frac{1 + K_2 [HD]}{[HX]} = \frac{K'(1 + K_2 HD)}{[HX]} \tag{7}$$

where,

$$K' = \frac{\theta_{HX}}{1-\theta_{HX}} \tag{8}$$

rewriting the above equation, thus

$$K_1 [HX] = K' + K' K_2[HD] \tag{9}$$

By making the assumption that when HD = 0, HX = HX_o they simplify the above equation to

$$K_1 HX_o = K' \tag{10}$$

or rewriting equation

$$HX = HX_o + \frac{K'K_2\ [HD]}{K_1} \qquad (11)$$

which is their final statement of the proposed mechanism of collector-depressant equilibria.

Values of K' may be determined using the linear relationship between surface coverage and contact angle which had been determined for amyl xanthate in a study of single collector system:

$$\theta = .009\ \phi + .27 \qquad (12)$$

Since HX_o is the value of collector required when HD is equal to zero, HX_o may be taken directly from the m-pH plots of section on "Potassium Amyl Xanthate on Galena." This allows calculation of the K_1.

By substituting the value of K' into equation 11 the value of K_2 was determined thus:

$$K_2 = \frac{[HX - HX_o]}{[HD]\ [HX_o]} \qquad (13)$$

All terms in the above equation can be evaluated from contact angle data. Evaluating all of the contact angle data according to the above interpretation gives constant values of K_2, the constancy of which aids in validating the proposed mechanism. (See Table 5, page 101).

Using the relationship shown in equation 11, a theoretical contact angle curve was calculated. The value of K_2 was the average value obtained from the above calculations. The value of K_1 used in calculating the curve was adjusted to give the best fit of the data. This value was 1.35×10^9 as compared to an average value of 1.20×10^9 which is the average of the calculated K_1 values of Table 5. This difference is well within the limits of experimental error. Figure 46 shows the calculated curve together with the superimposed ϕ - HD/HX curves. Calculated values of K_1 and K_2 are given in the accompanying Table No. 5.

The agreement between experimental and calculated curve of Figure 46 further substantiates the proposed mechanism involved in collector-depressant equilibria. The constancy of calculated K_2 values shows that the adsorption of depressant is independent of the concentration of amyl xanthate.

The fact that the previously established relationship between contact angle and surface coverage was used in calculating K' values indicates that this relationship is approximately correct.

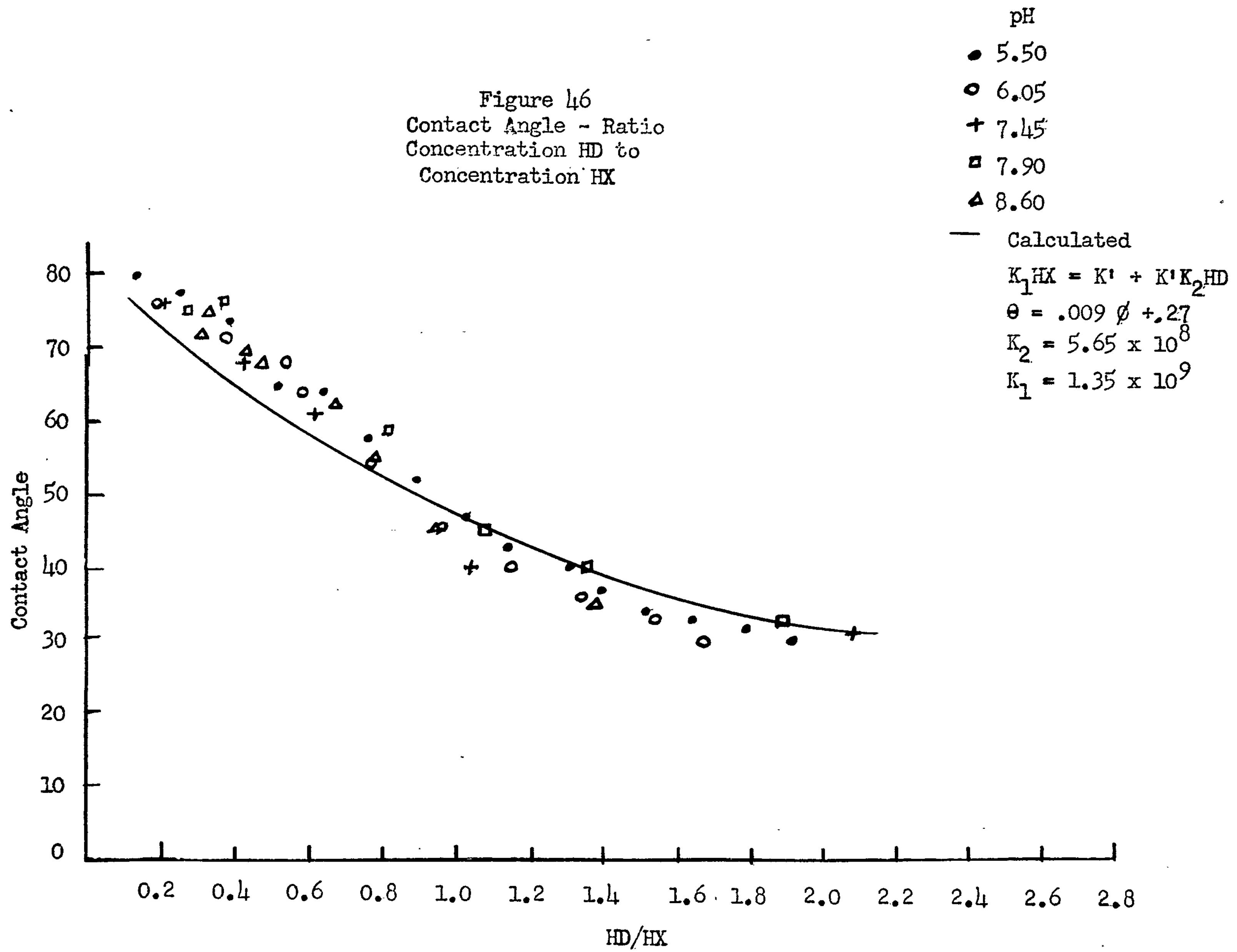


Figure 46
Contact Angle - Ratio
Concentration HD to
Concentration HX

Table 5

Calculated values of Constants Involved in Collector-Depressant Equilibria.

pH	M_X	M_D	θ	ϕ	HD	HX	HX_o	K'	K_1	K_2
5.50	95.2	9.5	1.0	80	4.86×10^{-5}	3.73×10^{-4}				
	91.1	8.2	.98	78	8.95×10^{-5}	3.57×10^{-4}	6.3×10^{-9}	.49	7.8×10^{9}	6.4×10^{8}
	87.5	26.2	.94	74	1.30×10^{-4}	3.43×10^{-4}	4.5×10^{-9}	15.7	3.5×10^{9}	5.8×10^{8}
	84.0	33.6	.90	69	1.68×10^{-4}	3.29×10^{-4}	3.7×10^{-9}	9.0	2.4×10^{9}	5.3×10^{8}
	80.7	40.4	.85	64	2.02×10^{-4}	3.16×10^{-4}	3.2×10^{-9}	5.7	1.8×10^{9}	4.9×10^{8}
	78.0	46.7	.80	58	2.32×10^{-4}	3.06×10^{-4}	2.8×10^{-9}	4.0	1.4×10^{9}	4.7×10^{8}
	75.0	52.5	.74	52	2.62×10^{-4}	2.94×10^{-4}	2.3×10^{-9}	2.8	1.2×10^{9}	4.8×10^{8}
	72.5	58.0	.70	47	2.90×10^{-4}	2.84×10^{-4}	2.0×10^{-9}	2.3	1.15×10^{9}	4.9×10^{8}
	70.2	63.1	.66	43	3.14×10^{-4}	2.75×10^{-4}	1.8×10^{-9}	1.8	1×10^{9}	4.9×10^{8}
	67.8	67.8	.62	39	3.38×10^{-4}	2.66×10^{-4}	1.5×10^{-9}	1.6	1.07×10^{9}	5.2×10^{8}
	65.8	72.4	.61	37	3.61×10^{-4}	2.58×10^{-4}	1.4×10^{-9}	1.56	1.1×10^{9}	5.0×10^{8}
	63.8	76.5	.58	34	3.80×10^{-4}	2.50×10^{-4}	1.3×10^{-9}	1.4	1.08×10^{9}	5.1×10^{8}
	61.9	80.4	.57	33	4.01×10^{-4}	2.43×10^{-4}	1.1×10^{-9}	1.3	1.18×10^{9}	5.5×10^{8}
	60.2	84.1	.56	32	4.20×10^{-4}	2.36×10^{-4}	1.1×10^{-9}	1.25	1.1×10^{9}	5.1×10^{8}
6.05	96.5	1.87	.96	76	8.1×10^{-5}	2.34×10^{-4}	5.4×10^{-9}	24.0	4.5×10^{9}	5.3×10^{8}
	93.0	3.74	.92	71	8.55×10^{-5}	2.25×10^{-4}	3.6×10^{-9}	11.5	3.2×10^{9}	7.2×10^{8}
	90.0	5.61	.85	64	1.26×10^{-4}	2.18×10^{-4}	3.2×10^{-9}	5.7	1.8×10^{9}	5.5×10^{8}
	87.0	7.49	.76	54	1.68×10^{-4}	2.11×10^{-4}	2.5×10^{-9}	3.2	1.3×10^{9}	5.0×10^{8}
	84.2	9.35	.68	45	1.96×10^{-4}	2.04×10^{-4}	1.9×10^{-9}	2.12	1.1×10^{9}	5.5×10^{8}
	81.7	11.2	.63	40	2.28×10^{-4}	1.98×10^{-4}	1.6×10^{-9}	1.70	1.06×10^{9}	5.5×10^{8}
	79.2	13.1	.60	36	2.57×10^{-4}	1.92×10^{-4}	1.3×10^{-9}	1.50	1.15×10^{9}	5.8×10^{8}
	77.1	14.9	.57	33	2.88×10^{-4}	1.87×10^{-4}	1.1×10^{-9}	1.33	1.2×10^{9}	5.8×10^{8}
	74.9	16.8	.55	31	3.13×10^{-4}	1.81×10^{-4}	1.0×10^{-9}	1.21	1.2×10^{9}	5.8×10^{8}
7.45	99.1	1.98	.96	76	3.78×10^{-6}	1.80×10^{-5}	5.4×10^{-9}	24.0	4.5×10^{9}	9.0×10^{8}
	98.5	3.9	.89	68	7.52×10^{-6}	1.79×10^{-5}	3.7×10^{-9}	8.1	2.2×10^{9}	6.2×10^{8}
	97.9	5.9	.82	61	1.1×10^{-5}	1.78×10^{-5}	3.0×10^{-9}	4.6	1.5×10^{9}	5.4×10^{8}
	96.5	9.7	.63	40	1.83×10^{-5}	1.76×10^{-5}	1.6×10^{-9}	1.70	1.05×10^{9}	6.1×10^{8}
	93.1	18.6	.55	31	3.52×10^{-5}	1.69×10^{-5}	1.0×10^{-9}	1.2	1.2×10^{9}	4.8×10^{8}
	90.5	27.2		27	5.15×10^{-5}	1.65×10^{-5}				
	87.1	34.8		24		1.59×10^{-5}				

Table 5 (Continued)

pH	M_X	M_D	θ	ϕ	HD	HX	H_o	K'	K_1	K_2
7.90	99.0	1.98	.95	75	1.78×10^{-6}	6.58×10^{-6}	4.8×10^{-9}	19.0	4.0×10^{9}	7.8×10^{8}
	97.7	3.9	.89	68	2.97×10^{-6}	6.50×10^{-6}	3.7×10^{-9}	8.1	2.2×10^{9}	5.9×10^{8}
	96.6	5.8	.81	59	5.20×10^{-6}	6.42×10^{-6}	2.8×10^{-9}	4.3	1.5×10^{9}	4.3×10^{8}
	95.5	7.6	.68	45	6.85×10^{-6}	6.35×10^{-6}	1.9×10^{-9}	2.12	1.1×10^{9}	4.9×10^{8}
	94.2	9.4	.63	40	8.45×10^{-6}	6.26×10^{-6}	1.6×10^{-9}	1.70	1.06×10^{9}	4.6×10^{8}
	92.1	12.9	.57	33	1.16×10^{-5}	6.12×10^{-6}	1.1×10^{-9}	1.3	1.2×10^{9}	4.8×10^{8}
8.60	96.5	1.93	.92	72	4.0×10^{-7}	1.29×10^{-6}	4.3×10^{-9}	11.5	4.7×10^{9}	7.5×10^{8}
	94.5	2.8	.89	68	5.97×10^{-7}	1.27×10^{-6}	3.7×10^{-9}	8.1	2.2×10^{9}	5.8×10^{8}
	93.0	3.7	.88	67	7.75×10^{-7}	1.25×10^{-6}	3.5×10^{-9}	7.3	2.1×10^{9}	4.7×10^{8}
	91.3	4.6	.77	55	9.5×10^{-7}	1.22×10^{-6}	2.6×10^{-9}	3.3	1.3×10^{9}	4.9×10^{8}
	89.6	5.4	.68	45	1.13×10^{-6}	1.20×10^{-6}	1.9×10^{-9}	2.12	1.1×10^{9}	8.9×10^{8}

APPENDIX I

Experimental Contact Angle Readings for Potassium Amyl Xanthate - $Na_2S + 9H_2O$ - Galena System

pH: 5.50

Buffer $HPO_4^{=} - H_2PO_4^{-}$

Ionic Strength 0.10

Potassium Amyl Xanthate (mg/l)	$Na_2S + 9H_2O$ (mg/l)	Contact Angle
50.0	145.3	35
66.7	64.9	25
71.5	59.8	25
77.0	48.2	35
83.4	34.8	80
90.8	19.0	80
74.7	52.9	52
75.9	50.6	54
78.2	45.6	59
79.5	43.2	54
80.7	40.4	71
82.0	37.6	71
50.0	109.7	30
66.7	73.0	30
71.5	62.5	48
77.0	50.5	60
83.4	36.6	65
91.0	19.9	77
68.5	69.0	39
73.6	58.0	48
78.8	46.6	54
86.2	30.2	58
89.2	23.5	63
94.4	12.5	80
50.0	108.5	32
50.0	106.6	25
66.7	71.0	37
71.5	60.7	56
77.0	49.1	56
83.4	35.6	68
91.0	19.4	75
50.0	106.6	25
66.7	71.0	35
71.5	60.7	55
77.0	49.1	57
83.4	35.6	67
91.0	19.4	73

pH: 6.05

Buffer $HPO_4^{=}$ - $H_2PO_4^{-}$

Ionic Strength 0.10

Potassium Amyl Xanthate (mg/l)	$Na_2S + 9H_2O$ (mg/l)	Contact Angle
50.0	117.6	15
66.7	78.3	15
71.5	67.0	35
77.0	54.2	37
83.4	39.2	50
91.0	21.4	58
68.9	72.8	35
74.1	61.0	35
80.0	47.0	40
87.0	30.7	53
93.5	15.4	69
97.1	6.8	77
66.7	89.0	23
71.5	76.1	27
77.0	61.6	32
83.4	44.6	42
94.3	15.1	75
89.2	28.6	63
92.6	19.8	72
95.3	12.7	78
96.1	32.8	65
97.1	36.8	62
62.5	80.2	73
66.7	71.4	80

pH: 7.45

Buffer $HPO_4^{=}$ - $H_2PO_4^{-}$

Ionic Strength 0.10

Potassium Amyl Xanthate (mg/l)	$Na_2S + 9H_2O$ (mg/l)	Contact Angle
77.0	59.7	20
83.4	43.3	25
91.0	23.6	35
92.7	19.2	35
94.5	14.7	35
96.1	9.9	55
97.2	7.5	60
98.1	5.1	76
99.0	2.6	80
71.5	80.0	15
77.0	64.6	20
83.4	46.7	25
91.0	25.4	30
62.5	105.0	10
98.0	5.3	70
92.6	20.2	30
93.5	17.8	32
99.0	2.8	80
79.4	57.8	20
86.3	38.6	27
94.3	15.9	34
92.6	20.8	27
95.3	13.3	42
96.1	10.8	53
97.1	8.2	57
98.0	5.5	68
99.0	2.8	80
82.0	49.0	15
84.7	41.5	20
87.8	33.4	22
91.0	24.7	28
94.3	15.4	32
95.3	13.0	35
96.1	10.5	49
97.1	7.9	59

pH: 7.90

Buffer $HPO_4^{=}$ - $H_2PO_4^{-}$

Ionic Strength 0.10

Potassium Amyl Xanthate (mg/l)	$Na_2S + 9H_2O$ (mg/l)	Contact Angle
75.0	11.5	39
75.0	5.8	58
75.0	3.9	78
75.0	7.7	54
75.0	4.6	60
25.0	27.2	45
25.0	9.1	47
25.0	5.8	49
25.0	5.1	63
25.0	2.4	70
25.0	1.4	75
75.0	7.7	69
75.0	4.6	75
75.0	11.5	49
75.0	5.8	60
75.0	3.9	74
25.0	13.6	49
25.0	6.8	43
25.0	4.5	57
25.0	3.0	69
25.0	1.8	71
25.0	1.2	78

pH: 8.60

Buffer $CO_3^{=} - HCO_3^{-}$

Ionic Strength 0.1

Potassium Amyl Xanthate (mg/l)	$Na_2S + 9H_2O$ (mg/l)	Contact Angle
94.3	11.6	15
97.1	6.0	15
99.0	2.0	80
98.0	4.0	28
98.4	3.2	65
98.9	2.4	76
96.1	8.9	15
98.0	4.0	28
97.9	4.4	30
98.1	3.6	30
98.6	2.8	72

CONCLUSIONS AND RECOMMENDATIONS

A comprehensive study of equilibria was carried out for the systems:

(a) Potassium ethyl xanthate - galena.

(b) Potassium amyl xanthate - galena.

(c) Potassium ethyl xanthate - potassium amyl xanthate - galena.

(d) Potassium amyl xanthate - sodium sulfide - galena.

The procedure which was followed in the study of potassium ethyl xanthate-galena equilibria has been outlined previously by Wadsworth, Conrady and Cook(38). Contact angle-collector concentration curves, for concentrations of collector less than 50 mg per liter, were obtained for pH values of 5.50, 6.45, 7.35, 8.20, 9.40, 10.00, and 10.50. From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH were constructed. Assuming a single site adsorption of ethyl xanthic acid on galena, and also a linear relationship between contact angle and surface coverage the following equation was obtained:

$$HX = \frac{K^{-1}}{a} \frac{1}{(60-\phi)} - K^{-1}$$

in which, K is the equilibrium constant for the adsorption, ϕ is the contact angle, HX is the concentration of ethyl xanthic acid and a is a constant. A plot of HX vs $\frac{1}{(60-\phi)}$ was made using average values of HX which had been taken from a contact angle - log HX plot. 1/K, taken from the intercept of the HX - vs - $1/(60-\phi)$ plot was equal to 3.0×10^{-9}, giving a value of $K = 3.3 \times 10^{8}$. The slope was 2.33×10^{-7}, giving a value of $a = 0.013$. Substituting this value of a into the equation, $b = 1 - 60a$ gives $b = 0.22$ which is the fraction of the surface covered at zero contact angle. These values of a and b gave $\theta = .013\,\phi + .22$ which checks the relationship of Cook, Conrady, and Wadsworth and demonstrates that their relationship is applicable to systems with collector concentrations less than 50 mg. per liter. Using a dissociation constant of $Ka = 8.7 \times 10^{-7}$ obtained from studies of competitive adsorption of ethyl and amyl xanthates on galena, together with the constants evaluated above, calculated collector concentration - pH curves were constructed for comparison with experimental curves.

An identical procedure was followed to show that a linear relationship between contact angle and surface coverage exists in the case of amyl xanthate on galena. Contact angle-collector concentration curves were obtained for pH values of 5.50, 6.45, 7.35, 8.20, 9.40 and 10.00. From the plots of contact angle versus collector concentration, at constant pH, new plots of collector concentration versus pH were constructed and compared with calculated curves. The calculated curves were obtained by using the following equation:

$$HX = \frac{K^{-1}}{a}\,\frac{1}{80-\phi} - K^{-1}$$

in which K^{-1} and a were evaluated by making a plot of HX vs $1/(80-\phi)$. 9.2×10^{-7} was used for the dissociation constant of amyl xanthic acid. $1/K$, taken from the intercept was equal to 1.12×10^{-9}, giving a value of $K = 8.9 \times 10^{8}$. The value of $a = .009$ was obtained from the slope. Substituting $a = .009$ into the equation, $b = 1 - 80a$, gives $b = 0.27$, which resulted in the following relationship between contact angle and surface coverage for amyl xanthate on galena:

$$\theta = .009\,\phi + 0.27$$

Competitive adsorption data of amyl xanthate and ethyl xanthate on galena were used to evaluate the dissociation constants for amyl xanthic acid and ethyl xanthic acid. The characteristic contact angle for a monolayer of ethyl xanthic acid on galena is sixty degrees. The contact angle for galena covered with a monolayer of amyl xanthic acid is eighty degrees. The contact angle on galena coated with ethyl xanthic acid increased from sixty degrees to eighty degrees, when the specimen was placed in a sufficiently concentrated amyl xanthic acid solution. By adjusting the concentration of amyl xanthic acid intermediate values of contact angle between sixty and eighty degrees were obtained. Contact angle-collector concentration curves were determined at pH values of 3.80, 5.25, 5.70, and 8.10. By interpreting the data in terms of free acid adsorption, the following equation was developed to represent competitive adsorption of the two collectors:

$$\frac{HX_1}{HX_2} = \frac{m_1}{m_2} \frac{(Ka_2 + H^+)}{(Ka_1 + H^+)}$$

HX_1 and HX_2 are free acid concentrations obtained by the addition of amounts of collector m_1 and m_2. Ka_2 and Ka_1 are dissociation constants. Assuming that, for a constant value of contact angle, HX_1/HX_2 is constant, the values of Ka_1 and Ka_2 were determined by adjusting these values to superimpose all experimental data on a contact angle -vs - HX_2/HX_1 curve. This method gave a value of $Ka_1 = 8.6 \times 10^{-7}$ and a value of $Ka_2 = 9.3 \times 10^{-7}$. While this study did not give precisely the absolute values of the equilibrium constants, it can be concluded that the dissociation constants for the two acids are of the same order of magnitude probably around 1×10^{-6}.

The data were inadequate to rule out the possibility of a linear relationship between contact angle and surface coverage for the two collector system.

A contact angle study of the $Na_2S.9H_2O$ - potassium amyl xanthate-galena system was made using experimental procedure similar to that which was used in the study of single collectors. Contact angle measurements were made for various concentrations of collector and depressant at pH values of 5.50, 6.05, 7.45, 7.90, and 8.60. The concentrations of collector and depressant which were required to maintain a given angle were converted to free acid concentrations. By plotting the data, in terms of free acid, curves for different pH values were superimposed. Using contact angle-surface coverage relationships for amyl xanthate, which had been obtained earlier in this work in the constants in the following equation of Last and Cook representing collector-depressant equilibria were evaluated:

$$K_1 \; HX = K' + K'K_2 \; HD$$

Evaluating all of the contact angle data according to the above interpretation gave a constant value for $K_2 = 5.7 \times 10^8$ and a value of $K_1 = 1.35 \times 10^9$. $K' = \theta_{HX}/(1 - \theta_{HX})$ was evaluated from the previously determined contact angle-surface coverage relationship for amyl xanthate, $\theta = .009\ \phi + 0.27$. These constants were used to calculate a contact angle versus ratio of depressant to collector (ϕ vs HD/HX) curve which superimposed the experimental curve. The constancy of K_2, the equilibrium constant for the depressant was particularly evident. Also, the use of the surface coverage-contact angle relationship for amyl xanthate in evaluation of K' validates the linear-relationship.

In this work the ionic strength was maintained at 0.1. Some preliminary investigations indicated that contact angle decreases with increasing ionic strength, however, the work is not conclusive and should be extended. This could be combined with an investigation of the effects of buffers on contact angles.

Further investigation of the use of competitive adsorption of collectors for determining dissociation constants is not jusified, however, investigation of the contact angle-surface coverage relationships for two collector systems would be interesting. Propyl and butyl xanthates could be used, as well as ethyl and amyl xanthates.

An attempt was made to obtain contact angle surface coverage relationships by direct film transfer. Two mineral specimens, one coated with a monolayer of ethyl xanthate, the other polished to zero contact angle were placed in a cell with distilled water and contact angle measurements were taken intermittantly on each sample. It was impossible to obtain conclusive results with ethyl xanthate, however, amyl xanthate because of its greater stability may give more reproducible results.

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