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WETTING AT THE SOLID-SOLUTION INTERFACE AS A FUNCTION OF SOLUTE ADSORPTION

by

Richard Julius Ruch

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Dean of Graduate College

Iowa State College
Ames, Iowa
1959

TABLE OF CONTENTS

Page

I. INTRODUCTION 1

II. OBJECTIVES 4

III. EXPERIMENTAL 5

A. Materials 5

B. Apparatus 8

C. Procedures 12

IV. RESULTS 17

A. Surface Tension 17

B. Adsorption Isotherms 30

C. Contact Angles 47

V. THEORY 64

A. Adsorption 64

B. Wetting 66

VI. DISCUSSION 75

A. Adsorption 75

B. Wetting 79

VII. SUMMARY 83

VIII. LITERATURE CITED 86

IX. ACKNOWLEDGMENTS 88

I. INTRODUCTION

The wetting of solids by aqueous solutions of polar organic molecules plays an important role in many processes. The degree of wetting is most often described in terms of the contact angle of the solution on the solid (see Figure 19). The captive-bubble apparatus introduced by Taggart *et al*. (1) provides a convenient method for measuring contact angles in solution. The method consists of attaching a bubble to the surface of the solid with an immersed tube and viewing the bubble with a microscope.

The wetting properties of these systems are determined to a large extent by the adsorption of solute molecules at the solid-solution interface. Shafrin and Zisman (2) isolated films of certain polar organic molecules from aqueous solution and showed that the films were monomolecular in nature. The wetting behavior of the films was found to be a function of the pH, the concentration of the solute, and the chain length of the adsorbing molecules.

In another study it was shown that adsorption of polar organic molecules from solutions may reach multimolecular coverage at high concentrations. Fu *et al*. (3) found this to be the case in the study of the adsorption of butyric acid from aqueous solution on graphite. Adsorption was determined interferometrically and surface areas were determined by the gas adsorption technique of Brunauer *et al*. (4).

The methods available for determining adsorption from aqueous solution have in the past hindered concurrent measurements of wetting; consequently, studies have involved separate determinations of adsorption and of wetting. Many such studies have been carried out in connection with the flotation of minerals. Gaudin and coworkers (5, 6) studied the adsorption of carbon fourteen tagged dodecylammonium acetate from aqueous solution on crushed quartz and hematite. Surface areas were determined by using gas adsorption. Contact angles were determined on separate samples of polished quartz and hematite. The work of adhesion, which is a function of the contact angle, was found to be a maximum at thirty-five per cent surface coverage. No theory, however, was advanced relating the contact angles to surface coverage.

Sasaki *et al*. (7) discuss various theories previously proposed to relate contact angles to surface coverage and point out that the theories have often been empirical in nature or have failed to be generally applicable. They present a theory designed to explain wetting for aqueous systems of polar-non-polar molecules in which the contact angle decreases as adsorption increases and for systems in which the contact angle increases as adsorption increases. Although the theory considers aspects fundamental in wetting, many of the basic assumptions appear to be unsound.

Recently Trurnit (8, 9) reported a study of the action of an enzyme on a protein in aqueous solution. The removal of protein or the adsorption of enzyme was detected by using a recording ellipsometer, the principle of which is based on the pioneer work of Drude (10, 11, 12). Trurnit suggested that this method would be of great value in adsorption studies on plane smooth surfaces. The method has the further advantage that wetting measurements may be carried out in the same system used for adsorption measurements. Thus, the method appeared to offer the long-sought solution to the problem of studying adsorption and wetting simultaneously on flat well-characterized surfaces.

II. OBJECTIVES

The present investigation had a two-fold purpose:

First, to develop and utilize the ellipsometer as an instrument for studying adsorption from solution on flat metallic substrates of small surface area;

Second, to correlate the results of adsorption measurements with those of contact angle measurements, with a view to elucidating the structural basis of the wetting of solids by aqueous solutions of long-chain polar organic molecules.

III. EXPERIMENTAL

A. Materials

1. Surfaces

a. Platinum The same piece of platinum, 3/4" x 3/8" x 2 mm., was used for all of the adsorption experiments on platinum. The platinum had a threaded hole near one corner so that a platinum rod could be attached during cleaning procedures to facilitate handling.

The platinum was originally mounted in a bakelite disk and polished on dry Behr-Manning emery polishing paper. Grades 2 through 4/0 were used in the initial polishing. The platinum was then polished on a polishing wheel with silicon carbide 400 and Linde B alumina. Buehler Ltd. finest quality microcloth, consisting of synthetic rayon fibers bound to a cotton back, was used in all cloth polishing procedures. The platinum was removed from the bakelite with concentrated nitric acid.

In subsequent polishings the platinum was glued to a threaded brass cylinder with Ducco cement. The brass cylinder fit into a threaded stainless steel ring. It was possible to advance the platinum to any desired position for polishing. The steel ring prevented rounding of the platinum edges during polishing. The use of this holder and wet emery paper greatly decreased the time required for polishing.

The use of Linde A alone in the wheel polishing step was found to cause less pitting of the surface and to remove scratches as effectively as the silicon carbide-Linde B treatment.

The platinum was cleaned before each trial by hand polishing on microcloth with Linde A or Linde B, flushing in a stream of distilled water, and wiping dry with a benzene dampened Kleenex. Before placing the platinum in the adsorption medium, it was flamed to a bright red glow in a Meker burner and cooled for two minutes after the disappearance of the red glow. The slide was still warm at this time as evidenced by a slight sizzle on entering the medium.

It was possible to use the platinum for as many as six to eight adsorption trials before it was necessary to repolish with emery paper. Scratches on the surface and heterogeneous adsorption necessitated repolishing. Scratches running parallel to the incident light of the ellipsometer were not as troublesome as others. As a result, polishing with emery paper was arranged so that 4/0 scratches ran parallel to the incident light.

b. Chromium   Chromium plated steel slides were cut from commercial ferrotype plates to fit the adsorption cell. The slides were diamond-shaped, 4 cm. long and 1 cm. wide, with an area of about 2 cm^2. Prior to use the slides were cleaned by hand polishing with Linde A or Linde B, flushing in a stream of distilled water, and wiping dry with a benzene dampened Kleenex. Before immersing in the adsorption medium, the slide was passed through the flame of a Meker burner six times and cooled thirty-five seconds. No attempts were made to use a given piece of chromium for more than one adsorption trial.

2. Water

The water used in all experiments was doubly distilled. Laboratory supply distilled water was re-distilled with a small quantity of potassium hydroxide and potassium permanganate.

The water did not have any adsorbable impurities that could be detected by contact angle measurements. The surface tension obtained for the water was in good agreement with values reported in the literature.

3. Buffers

Reagent grade sodium carbonate and sodium bicarbonate were used in the preparation of buffer systems. No adsorbable impurities producing finite contact angles were detected.

4. Decylamine hydrochloride

Matheson Co. decylamine quoted as having a boiling point of 90-92° C at 10 mm. was used to prepare the hydrochloride.

The amine was dissolved in anhydrous ether and hydrogen chloride was bubbled through the solution. The hydrochloride was isolated and recrystallized from redistilled benzene. The product used for all except one solution was recrystallized four times and had a melting point of 181.5° C. A 0.547 M solution was prepared with a product recrystallized twice and having a melting point of 181-182° C. The melting point is reported as 182-183° C. by Murr and Lester (13).

B. Apparatus

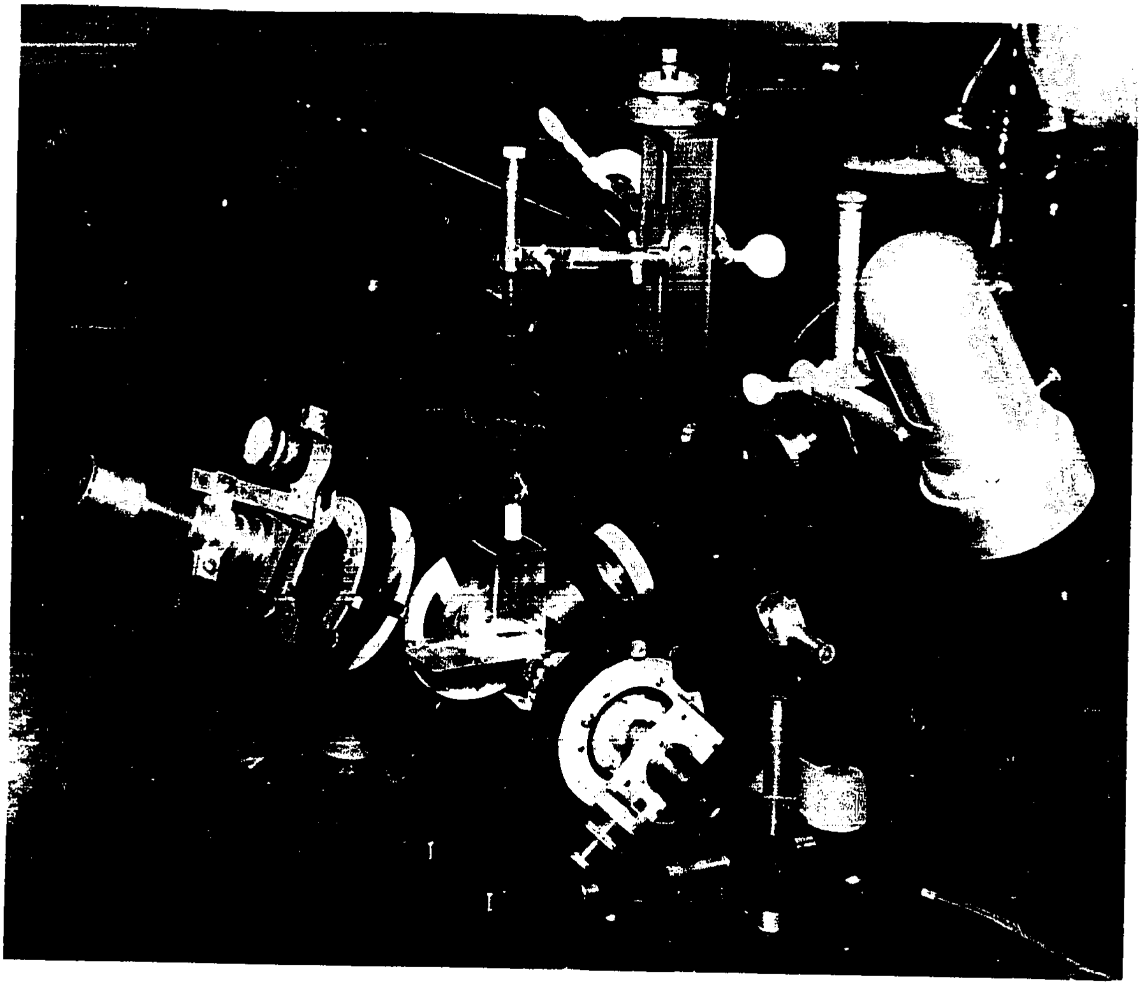
1. Tensiometer

A Cenco-DuNouy tensiometer was employed for all surface tension measurements. The platinum ring had a mean circumference of 4.00 cm. and a R/r value of 38.5.

2. Ellipsometer

The ellipsometer used for the study is shown in Figure 1. A sodium vapor lamp used for illumination is shown at the right. The light enters a lens and slit system and is focused on a Polaroid disk set to transmit plane polarized light at an angle of 45° to the plane of incidence. Near the stage for the adsorption cell is a phase-shifting piece of mica about 0.04 mm. thick. The mica is glued to a piece of brass which may be rotated through 360°. The stage may be lowered or raised as well as rotated to bring the specimen to the op-

Figure 1. Ellipsometer, captive-bubble apparatus and adsorption cell.



tical center of the instrument. A quarter-wave plate mounted in a graduated disk follows next in the light path and is adjusted to convert the elliptically polarized light reflected from the specimen surface to approximately plane polarized light. During a given adsorption experiment, the quarter-wave plate setting is fixed. A rotating object-holder with attached Polaroid serves as an analyzer to determine the plane of polarization of the light from the quarter-wave plate. A spectrum measuring magnifier is attached to the object-holder to enable readings to be estimated to the one one-hundredth of a degree. An adjustable ocular system permits focusing on the specimen.

3. Captive-bubble apparatus

The apparatus used for measuring contact angles is shown with the ellipsometer in Figure 1. Air bubbles are produced with the pipette and micro-syringe attached above the ellipsometer stage. The tip of the 0.1 ml. pipette with 1 mm. bore is cut flat and covered with a flat teflon tip. The air bubbles adhered to the teflon better than to glass. The bubble-holder is attached to a screw-type device which allows fine control of the motion of the bubble.

The bubbles are viewed with the low-power microscope which has a filar micrometer eyepiece. A light attached to the barrel of the microscope illuminates the bubble. The entire assembly is mounted in a rotating object-holder graduated in degrees.

4. Adsorption cell

The adsorption cell shown on the ellipsometer stage in Figure 1 is a pyrex turbidity cell obtained from Phoenix Precision Instrument Company. The cell is 30 x 30 x 60 mm. with a refractive index of 1.474 and 91% light transmission. A quarter-inch teflon block was cut to fit the adsorption cell and to hold the platinum in the optical path. Enough of the teflon was removed to prevent obstruction of the optical path.

C. Procedures

1. Surface tension measurements

A crystallizing dish 7.5 cm. in diameter and 4.0 cm. deep was used to contain the solutions being measured. The dish and all other glassware were cleaned in a 1:8 solution of nitric and sulphuric acid before each trial.

The platinum ring was cleaned in the acid solution, rinsed with distilled water, dried with Kleenex and flamed briefly before each trial. The ring was not removed during measurements and was dried by touching with Kleenex before calibration of the tensiometer with known weights.

The solutions were stirred with a platinum stirrer three minutes after the addition of amine hydrochloride. Measurements were then taken over a ten to twenty minute period until the drift of the readings had fallen to a point where the average deviation of the last five to seven readings was 0.1 to 0.2 dynes/cm. In one series of measurements in which the solutions were not stirred, the readings drifted considerably and it was at least fifteen minutes before the readings became constant.

2. Ellipsometer measurements

The ellipsometer was adjusted for an angle of incidence of 63^o in air to obtain an angle of incidence of 70^o at the solution-metal interface. The value at the solution interface can be calculated from $n_1 \cos \theta_1 = n_2 \cos \theta_2$, where n_1 is 1.0 for air and n_2 is 1.333 for water. θ_1 and θ_2 are the angles in air and in water between the light rays and a line perpendicular to the specimen being studied.

The platinum slide was placed in a reproducible position in the cell by using the teflon guide described before. The chromium slides were cut so that they fit in a reproducible position in the cell. The cell was moved prior to each reading to help prevent systematic errors produced in positioning of the cell. The cell was frequently tapped to ensure that the platinum or the chromium was resting on the bottom of the cell. The cell was positioned by placing it against a right-angle guide on the stage of the ellipsometer.

Fourteen readings were taken for each point on adsorption curves. The two highest and the two lowest were discarded and the average of the remaining ten was used for the point. In order to achieve conditions of equilibrium, initial readings were taken one-half to several hours after the addition of the decylamine hydrochloride. Subsequent readings were taken after contact angle measurements. This allowed at least fifteen minutes for equilibrium to be reached. Frequently, readings were taken at later periods of time to see if adsorption had changed significantly.

3. Contact angle measurements

The teflon tip and glass rod of the bubble-holder was cleaned before each trial with acid. They were flushed with doubly distilled water and drained on Kleenex before being placed in the adsorption medium.

Bubbles in the range of 3-5 mm. in diameter were usually used for making measurements. The bubbles were placed on the surface by lowering the bubble-holder. The bubble-holder was raised after the attachment of the bubble and the medium advanced over the surface. Direct measurement of the contact angle provided an advancing angle. Similarly, lowering the bubble-holder provided a receding angle. Measurement at three different areas of the surface provided three advancing and three receding angles.

The shape of the teflon holder for the platinum necessitated moving the platinum onto the top of the teflon for contact angle measurements. The contact angles on chromium could be measured without moving the chromium.

The surfaces were assumed suitable for adsorption studies when there were no traces of attachment of air bubbles. Angles less than 15° were difficult to measure by this technique. Slight but noticeable attachment of the bubble to the surface was denoted as a "cling", indicating a contact angle between 0° and 15°. For a contact angle of 0°, there was no attachment or cling of the air bubble to the surface.

4. Solution preparations

a. Adsorption media   Buffer systems were prepared by adding sodium carbonate and sodium bicarbonate to doubly distilled water. Varying amounts of carbon dioxide necessitated slight changes in molar ratios to produce desired pH values.

Doubly distilled water at its pH value from the still was used for isotherms in the region around pH of 6.0. For one isotherm at pH of 10.63, 0.1 N KOH was added to the system periodically with a Radiometer Model TTT 1a automatic titrator. In this manner the pH was kept fairly constant without the addition of large quantities of salt as in the case of the buffered systems.

b. Decylamine hydrochloride Stock solutions of the hydrochloride were prepared by weighing the appropriate amount of the compound on an analytical balance and dissolving it in volumetric flasks with doubly distilled water. Quantities of these solutions were pipetted to the adsorption cell or surface tension dish containing a known quantity of adsorption medium. Volumetric pipettes were used for quantities larger than 1 ml. and measuring pipettes for quantities less than 1 ml. Concentrations were calculated directly from these measurements. No corrections were made for adsorption of the compound on container walls or for errors introduced by not drying equipment. The errors introduced by adsorption on containers may be estimated assuming a roughness factor of one for the glass and monolayer adsorption. In the case of the concentrated stock solutions, the error would be less than one-tenth per cent. For the most dilute solutions used in adsorption, the error could be as much as ten per cent.

Solutions used for adsorption were stirred for approximately five minutes after the addition of the hydrochloride. A platinum stirrer which was cleaned by flaming was used for stirring the solutions.

IV. RESULTS

A. Surface Tension

Figures 2 through 6 represent the surface tension results for the five systems used in adsorption and wetting studies. Tables 1 through 5 list the mass of the liquid from the calibration curve and the correction factor, $F(R^3/V,R/r)$, of Harkins and Jordan (14). The final surface tension values were found by taking the product of the mass of the liquid, $F(R^3/V,R/r)$, the gravity constant and dividing by 8 cm. which is twice the mean circumference of the platinum ring.

All five surface tension curves have a linear segment indicating that the surface active species was approaching a limiting area per molecule at the solution-air interface. Application of the Gibbs adsorption equation to the linear segments of Figures 2, 3, 4, 5 and 6 give respective areas per molecule of: 34.8 Å^2, 31.4 Å^2, 31.2 Å^2, 30.4 Å^2, and 29.4 Å^2.

Surface tension depression in the alkaline region was greater in the system without buffer, Figure 5, than in the buffered system, Figure 4. The break in the surface tension curve of Figure 6 at 0.047 M is due to the critical micelle concentration of decylamine hydrochloride being reached. The critical micelle concentration is reported as 0.048 M by refractometry measurements by Klevens (15) and as 0.042 M by

Figure 2. Surface tension of aqueous solutions of decylamine at pH of 9.28 to 9.32 and 27.5-28.0° C. System was buffered with 0.01 M sodium carbonate and 0.06 M sodium bicarbonate.

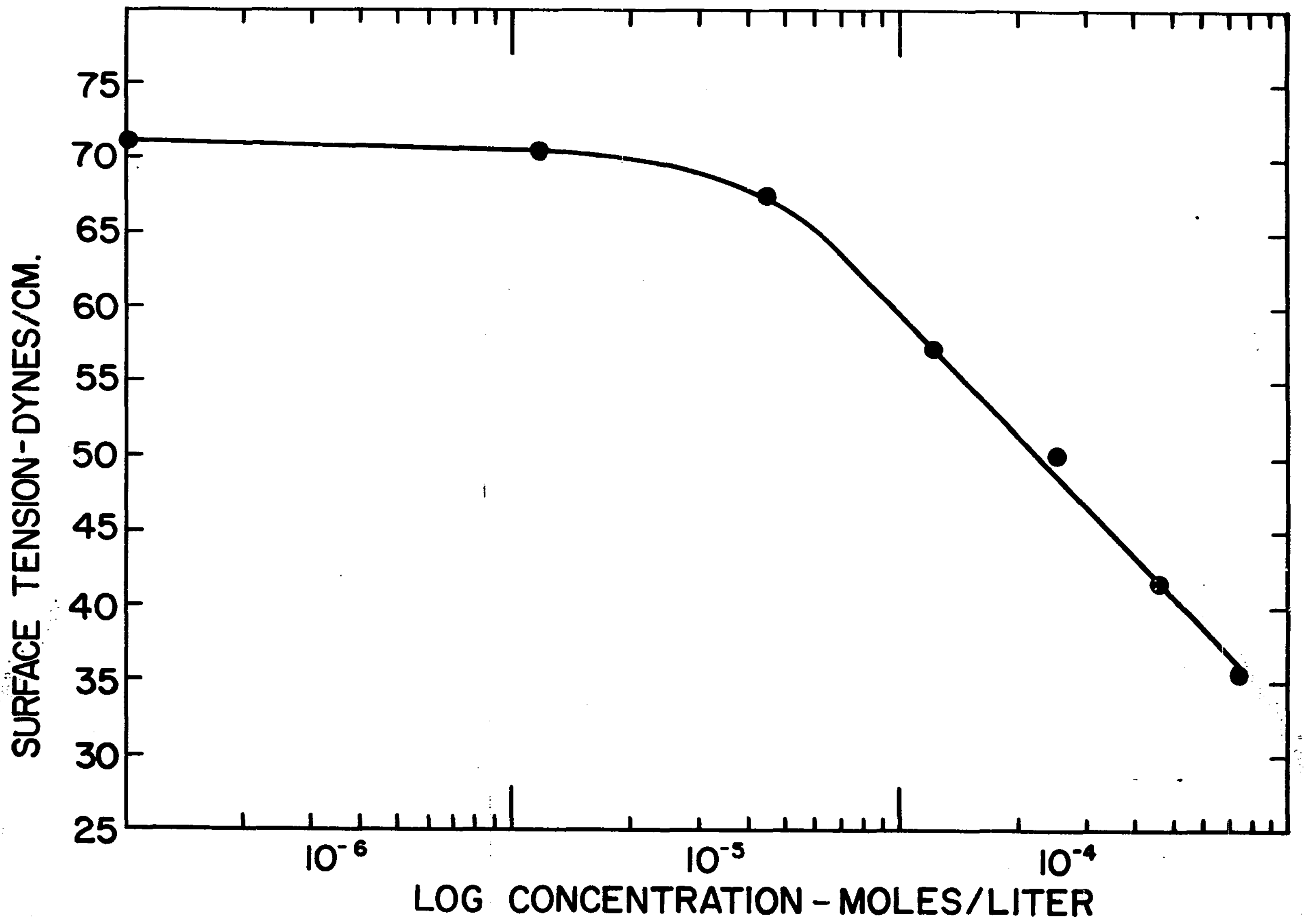

SURFACE TENSION-DYNES/CM.
75
70
65
60
55
50
45
40
35
30
25
10^-6
10^-5
10^-4
LOG CONCENTRATION - MOLES/LITER

Figure 3. Surface tension of aqueous solutions of decylamine at pH of 10.2 and 28° C. System was buffered with 0.05 M sodium carbonate and 0.05 M sodium bicarbonate.

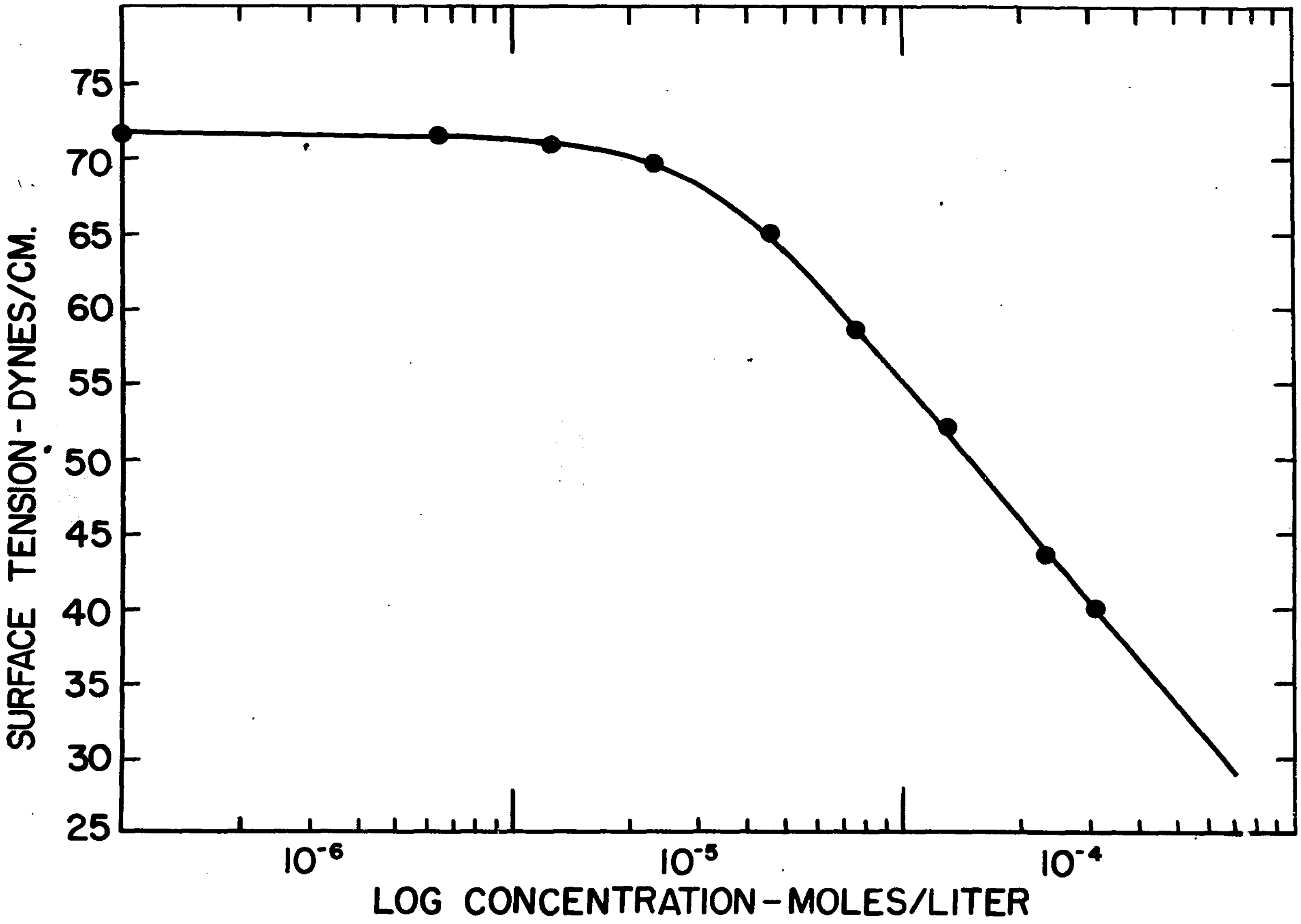

SURFACE TENSION - DYNES/CM.
75
70
65
60
55
50
45
40
35
30
25
10^-6
10^-5
10^-4
LOG CONCENTRATION - MOLES/LITER

Figure 4. Surface tension of aqueous solutions of decylamine at pH of 10.53 to 10.68 and 25.0-26.0° C. System was buffered with 0.06 M sodium carbonate and 0.01 M sodium bicarbonate.

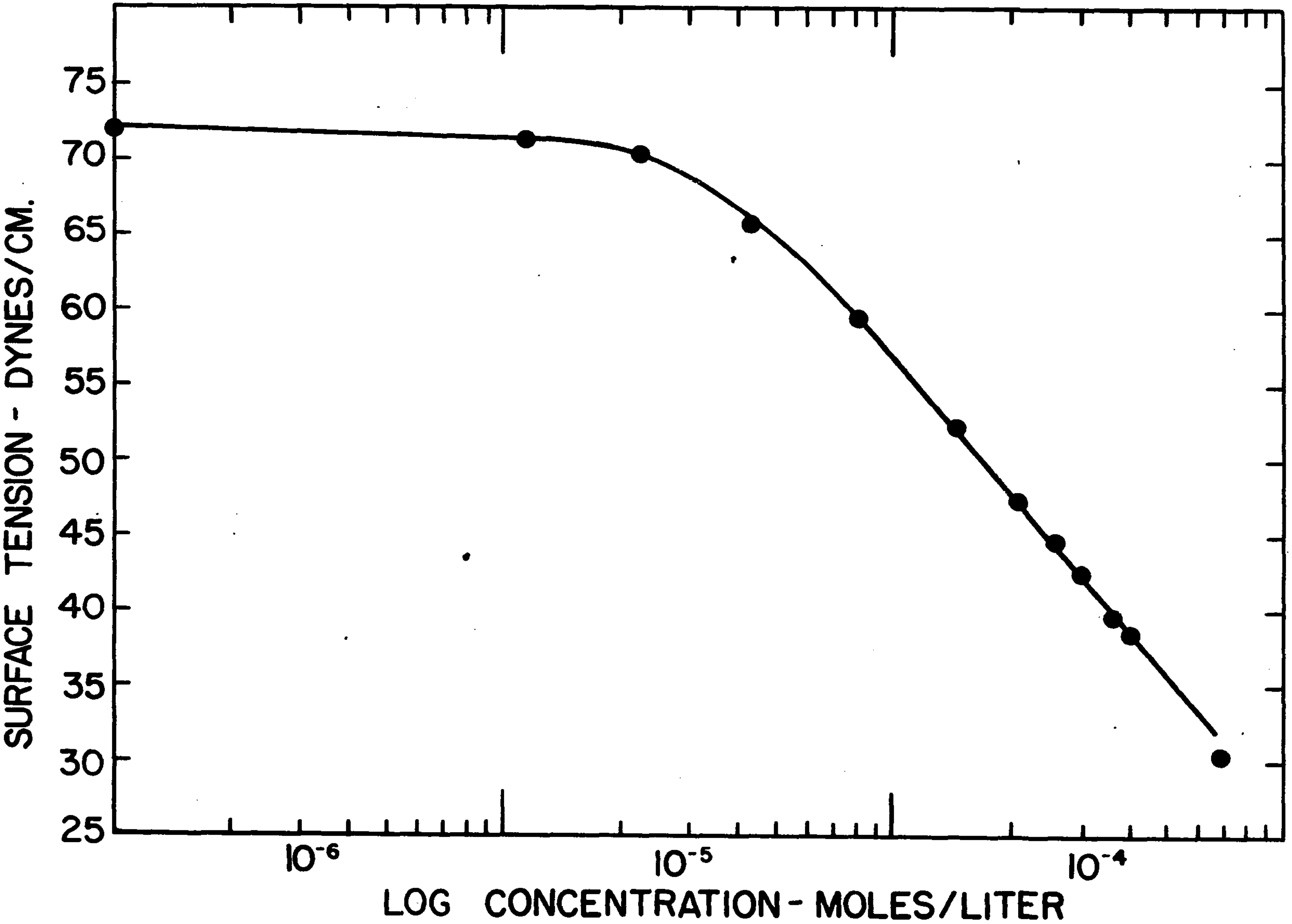

SURFACE TENSION - DYNES/CM.
75
70
65
60
55
50
45
40
35
30
25
10^{-6}
10^{-5}
10^{-4}
LOG CONCENTRATION - MOLES/LITER

Figure 5. Surface tension of aqueous solutions of decylamine at pH of 10.63 and 27.0-28.0° C. pH was maintained at 10.63 with 0.1 N potassium hydroxide added to the system with an automatic titrator.

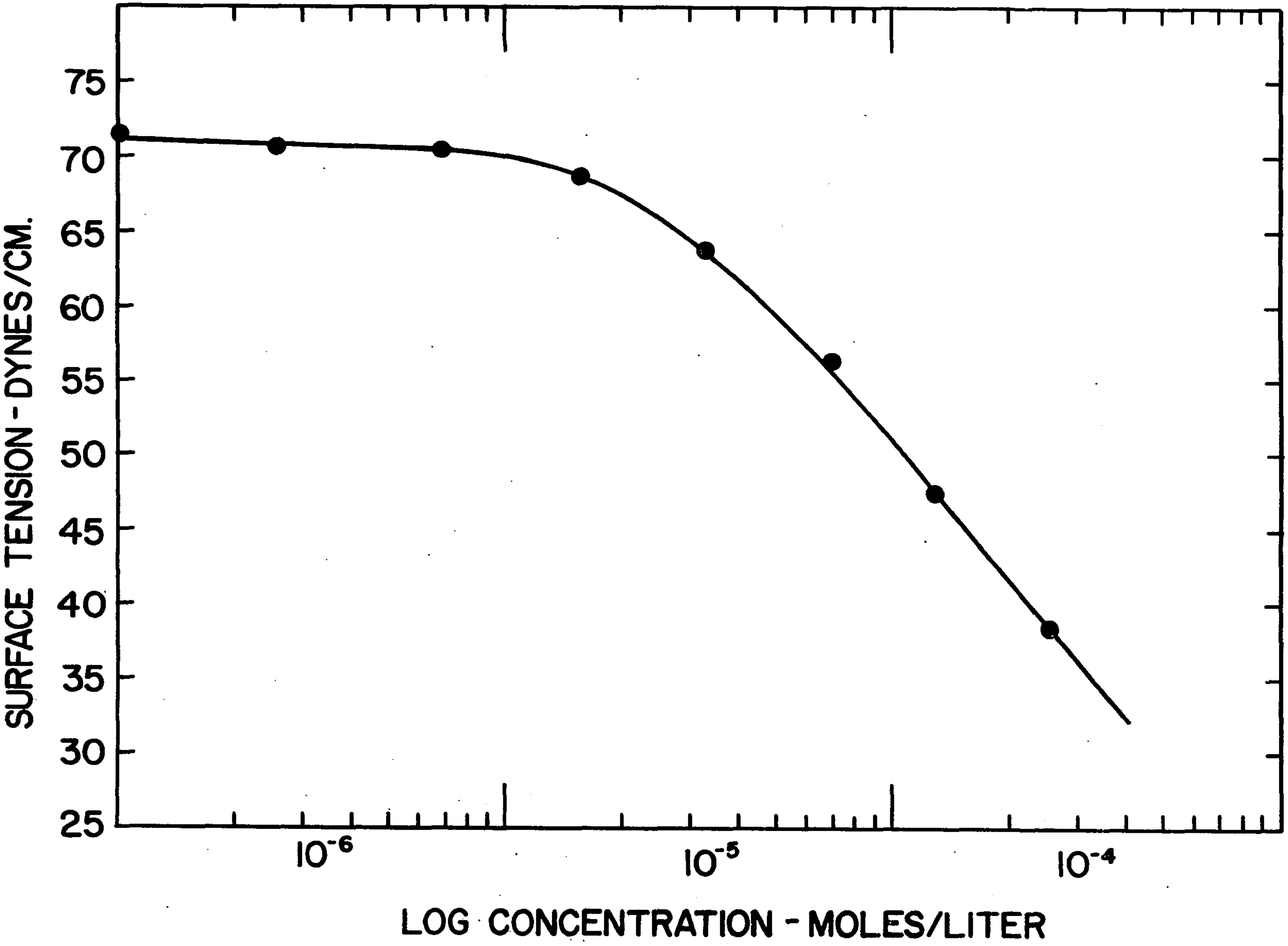

75
70
65
60
55
50
45
40
35
30
25
SURFACE TENSION - DYNES/CM.
10^{-6}
10^{-5}
10^{-4}
LOG CONCENTRATION - MOLES/LITER

Figure 6. Surface tension of aqueous solutions of decylamine hydrochloride at pH of 5.95 to 6.20 and 28.5° C. No buffer, acid or base was added to the system. C.M.C. refers to the critical micelle concentration.

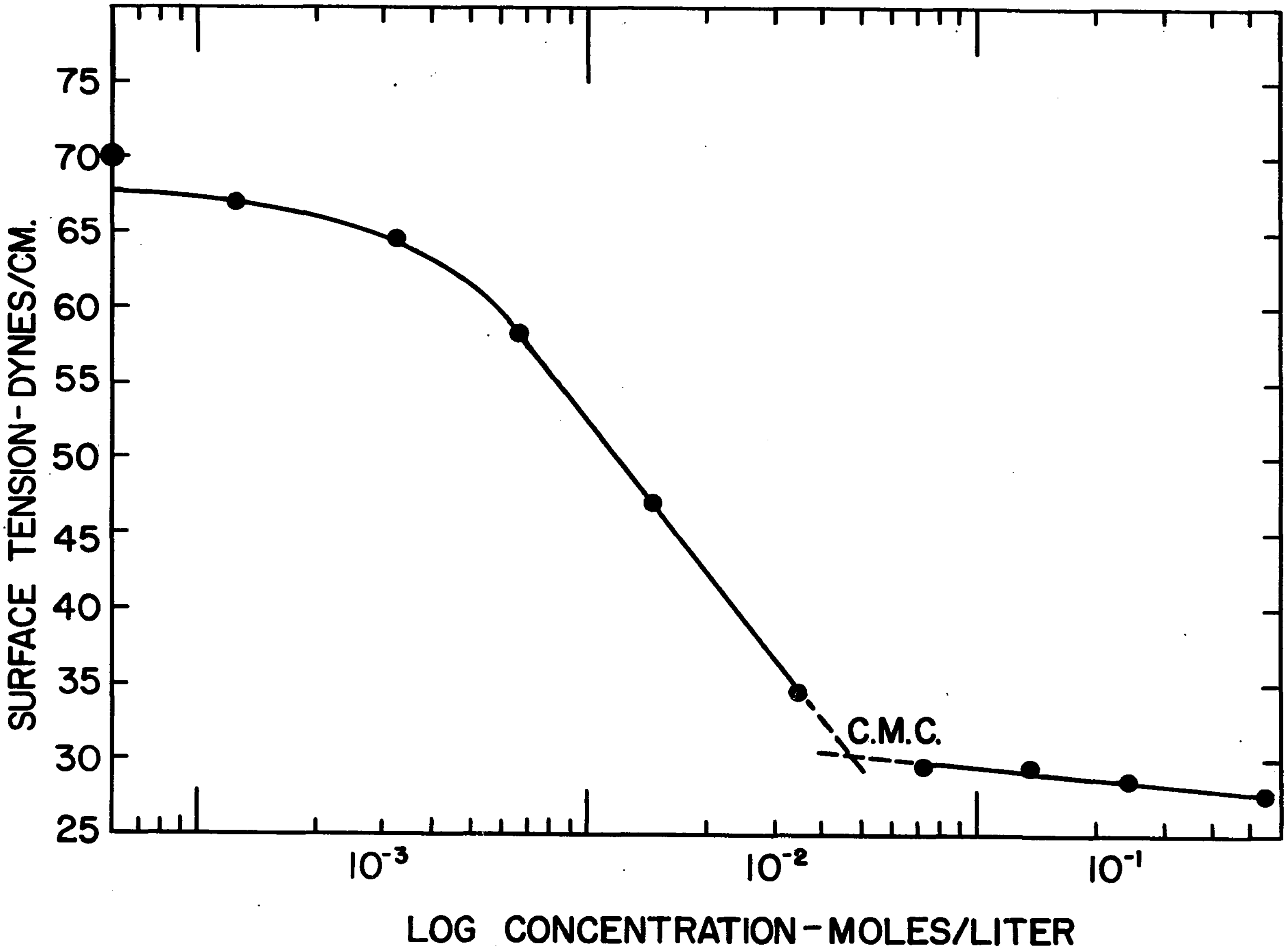

SURFACE TENSION - DYNES/CM.
75
70
65
60
55
50
45
40
35
30
25
C.M.C.
10^{-3}
10^{-2}
10^{-1}
LOG CONCENTRATION - MOLES/LITER

Table 1. Surface tension data for decylamine at pH of 9.28 to 9.32 and 27.5-28° C. System was buffered with 0.01 M sodium carbonate and 0.06 M sodium bicarbonate.

Molarity x 10^5	Mass in grams	$F(R^3/V,R/r)$	Surface tension dynes/cm.
Buffer	.591	.981	71.1
1.17	.587	.980	70.5
4.40	.566	.975	67.7
12.1	.488	.959	57.4
25.4	.432	.946	50.1
46.3	.366	.931	41.8
65.2	.316	.917	35.5

Table 2. Surface tension data for decylamine at pH of 10.2 and 28° C. System was buffered with 0.05 M sodium carbonate and 0.05 M sodium bicarbonate.

Molarity x 10^6	Mass in grams	$F(R^3/V,R/r)$	Surface tension dynes/cm.
Buffer	.596	.981	71.7
6.53	.595	.981	71.6
12.6	.590	.980	70.9
23.0	.582	.979	69.9
46.0	.546	.972	65.1
75.8	.498	.961	58.7
130	.448	.949	52.1
232	.382	.934	43.7
306	.352	.926	40.0
732	.229	.890	25.0[a]

[a] pH of 9.8.

Table 3. Surface tension data for decylamine at pH of 10.53 to 10.68 and 25-26° C. System was buffered with 0.06 M sodium carbonate and 0.01 M sodium bicarbonate.

Molarity x 10^5	Mass in grams	$F(R^3/V, R/r)$	Surface tension dynes/cm.
Buffer	.599	.982	72.1
1.15	.593	.980	71.3
2.24	.584	.980	70.2
4.33	.553	.972	65.9
8.15	.503	.962	59.3
14.6	.448	.949	52.1
20.9	.412	.940	47.5
25.9	.390	.937	44.8
30.0	.372	.931	42.5
36.2	.349	.926	39.6
40.7	.341	.923	38.6
69.1	.273	.905	30.3[a]

[a] pH of 9.85.

Table 4. Surface tension data for decylamine at pH of 10.63 and 27-28° C. pH was adjusted with 0.1 N potassium hydroxide.

Molarity x 10^6	Mass in grams	$F(R^3/V, R/r)$	Surface tension dynes/cm.
Water	.594	.981	71.5
2.55	.589	.980	70.8
6.91	.585	.980	70.3
15.8	.575	.977	68.9
33.1	.537	.969	63.8
70.0	.479	.956	56.1
130	.412	.941	47.5
253	.340	.924	38.5

Table 5. Surface tension data for decylamine hydrochloride at pH of 5.95 to 6.20 and 28.5° C. No buffer, acid or base was added to the system.

Molarity x 10^5	Mass in grams	$F(R^3/V,R/r)$	Surface tension dynes/cm.
Water	.584	.981	70.2
9.05	.564	.975	67.4
19.2	.570	.976	68.2
53.5	.561	.974	67.0
125	.561	.974	67.0
322	.543	.970	64.6
663	.495	.961	58.3
1470	.408	.940	47.0
3460	.307	.915	34.4
7240	.270	.903	29.9
13700	.265	.902	29.3
24100	.259	.900	28.6
54700	.252	.898	27.7

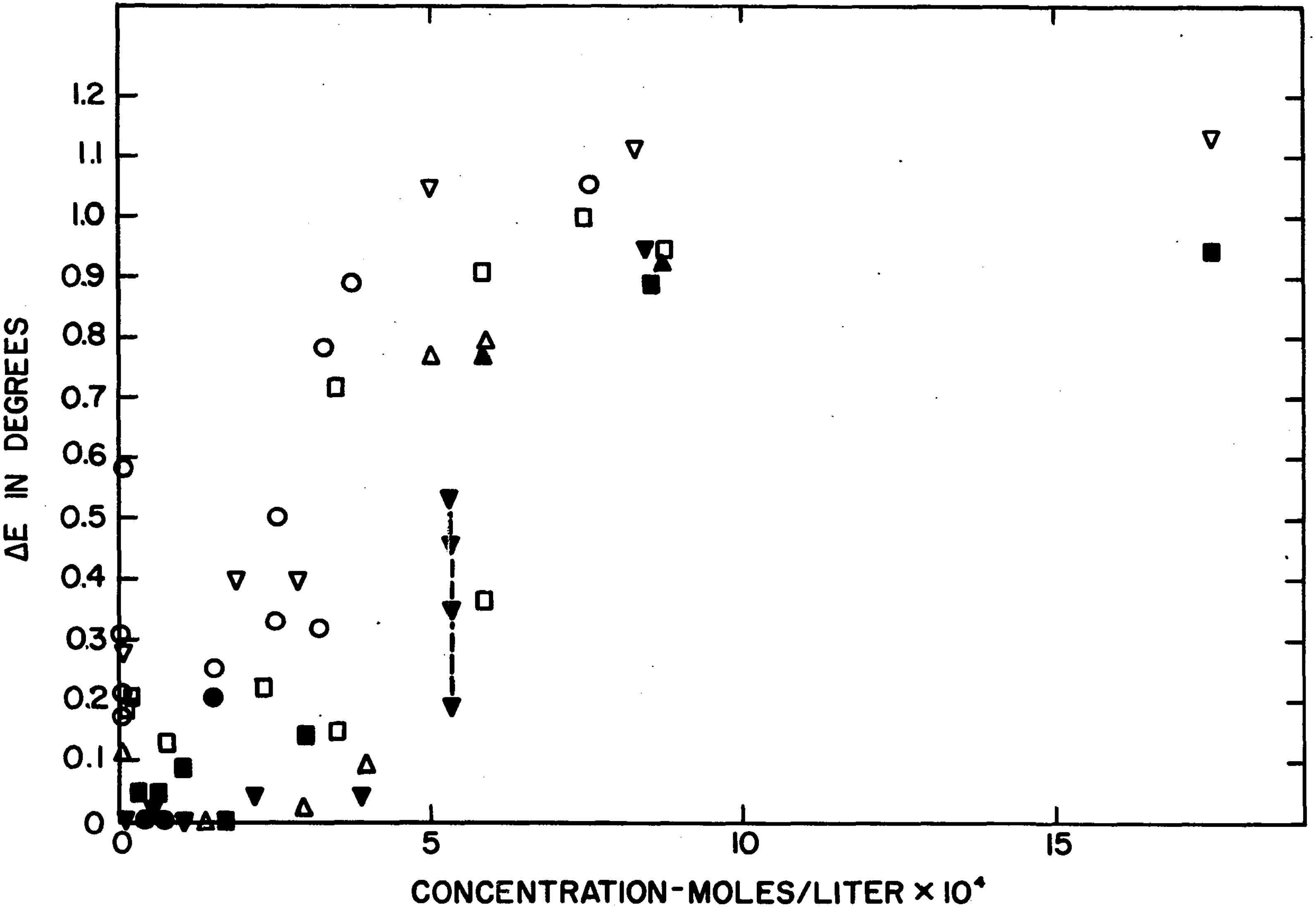
conductivity measurements by Ralston and Hoerr (16).

B. Adsorption Isotherms

Adsorption isotherms of decylamine hydrochloride on platinum and chromium are shown in Figures 7 through 12. Adsorption is expressed as ΔE, which is the difference in ellipsometer readings between the bare metal in water or buffer and the reading at any particular solution concentration. The base reading of platinum was quite reproducible between trials if the platinum was not completely repolished in the cleaning procedure.

Figure 7 contains data for four adsorption trials on

Figure 7. Four adsorption trials of decylamine on chromium. All of the systems were buffered with sodium carbonate and sodium bicarbonate. The pH varied from trial to trial from 9.8 to 10.3 and the temperature ranged from 24.5-28.5° C. Solid symbols refer to initial adsorption measurements taken while increasing the concentration of the system. Open symbols refer to adsorption measurements taken after replacing the solution by buffer and again increasing the concentration of the system. The initial measurements were not always taken to a maximum concentration before replacing the solution by buffer.


ΔE IN DEGREES
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
0
5
10
15
CONCENTRATION-MOLES/LITER × 10⁴

chromium. Adsorption was generally low and erratic at low concentrations. As the concentration was increased, adsorption suddenly became high, usually within a short period of time. In one case, however, denoted in Figure 7 by a dashed line, adsorption took place over a long period of time. The last three points are at times of 16, 27, and 58 minutes from the first point. The reproducibility and adsorption on chromium did not seem to be improved by varying the time of flaming and cooling of the slides, removing the buffer and dissolved gases from the adsorption medium, or by lowering the temperature for adsorption.

Results on platinum were more consistent than results on chromium and adsorption proceeded in a smooth manner. Adsorption was time dependent but much less so than in the case of chromium. The data for Figures 8 through 12 are in Tables 6 through 10. The average deviations of the ten readings given in the Tables was usually around $\pm 0.03^{\circ}$.

Ellipsometer readings of rubbed paraffin films in air and in water indicated that the sensitivity (analyzer rotation/Angstrom) of the ellipsometer at an angle of incidence of 70° was very nearly the same in the two media. Equal sensitivities in air and in water were also found for adsorbed films. This comparison of sensitivities was obscured for films thicker than monolayers since some of the molecules in multilayers in solution were left in the solution on withdrawing the film.

The concentration range of the adsorption trials in the alkaline region was limited by the formation of a precipitate. Using the ionization constant of decylamine of 4.4×10^{-4} as determined by Hoerr et al. (17) and the solubility of decylamine as 5.2×10^{-4} moles/liter as determined by Brown (18), one may calculate the allowable hydrochloride concentration at any pH. These values are for curves 8 through 11, 0.012 M, 0.002 M, 0.001 M, and 0.001 M. The calculated molarities are considerably higher than the molarities reached in the adsorption trials. The most concentrated solution of hydrochloride prepared was 0.547 M and Figure 12 indicates results to this molarity. Ralston and Hoerr (16) used the hydrochloride to a concentration of 0.9 M in conductivity studies, so a higher concentration could have been used for the study at pH of 6.0.

A larger amount of adsorbed material remained on platinum than on chromium when the films remained in contact with water or buffer for one to many hours. The average amount remaining on chromium was 0.22°; the average amount remaining on platinum was 0.33°. These averages disregard two extreme values of 0.58° and 0.76° on chromium and platinum respectively.

Figure 8. Adsorption of decylamine on platinum at a pH of 9.28 to 9.32 and 28.5-29.0° C. The system was buffered with 0.01 M sodium carbonate and 0.06 M sodium bicarbonate. The round points refer to the initial adsorption isotherm. The triangular points refer to the desorption isotherm. The dashed line refers to the BET calculated curve for $n = 2$. The adsorption of molecules in the first layer as postulated for the calculation of contact angles is represented by the dotted line.

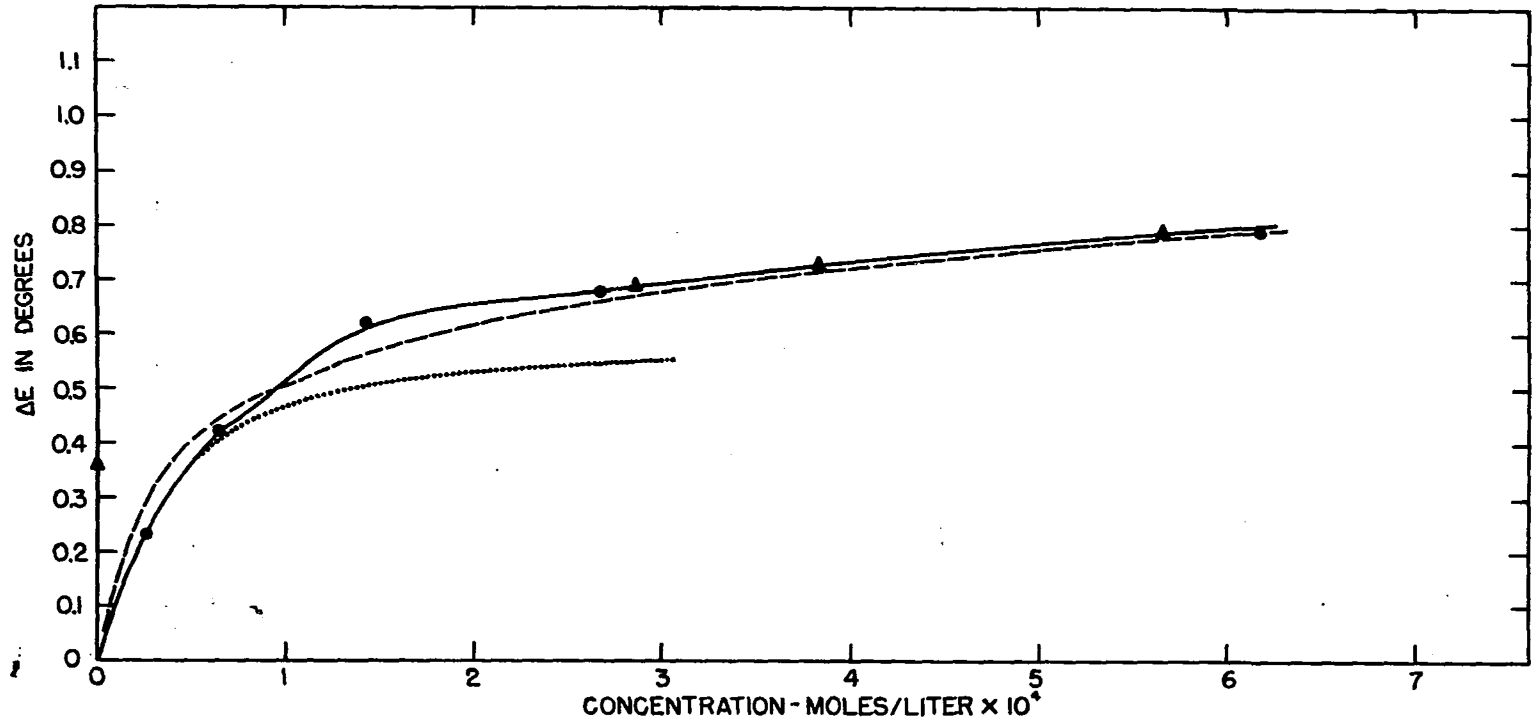

ΔE IN DEGREES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
7
CONCENTRATION - MOLES/LITER × 10⁴

Figure 9. Adsorption of decylamine on platinum at a pH of 10.08 to 10.10 and 26.0-27.0° C. The system was buffered with 0.07 M sodium carbonate and 0.05 M sodium bicarbonate. The round points refer to the initial adsorption isotherm. The triangular points refer to the adsorption obtained after replacing the solution of maximum concentration by buffer and repeating the isotherm. The dashed line refers to the BET calculated curve for n = 2. The adsorption of molecules in the first layer as postulated for the calculation of contact angles is represented by the dotted line.

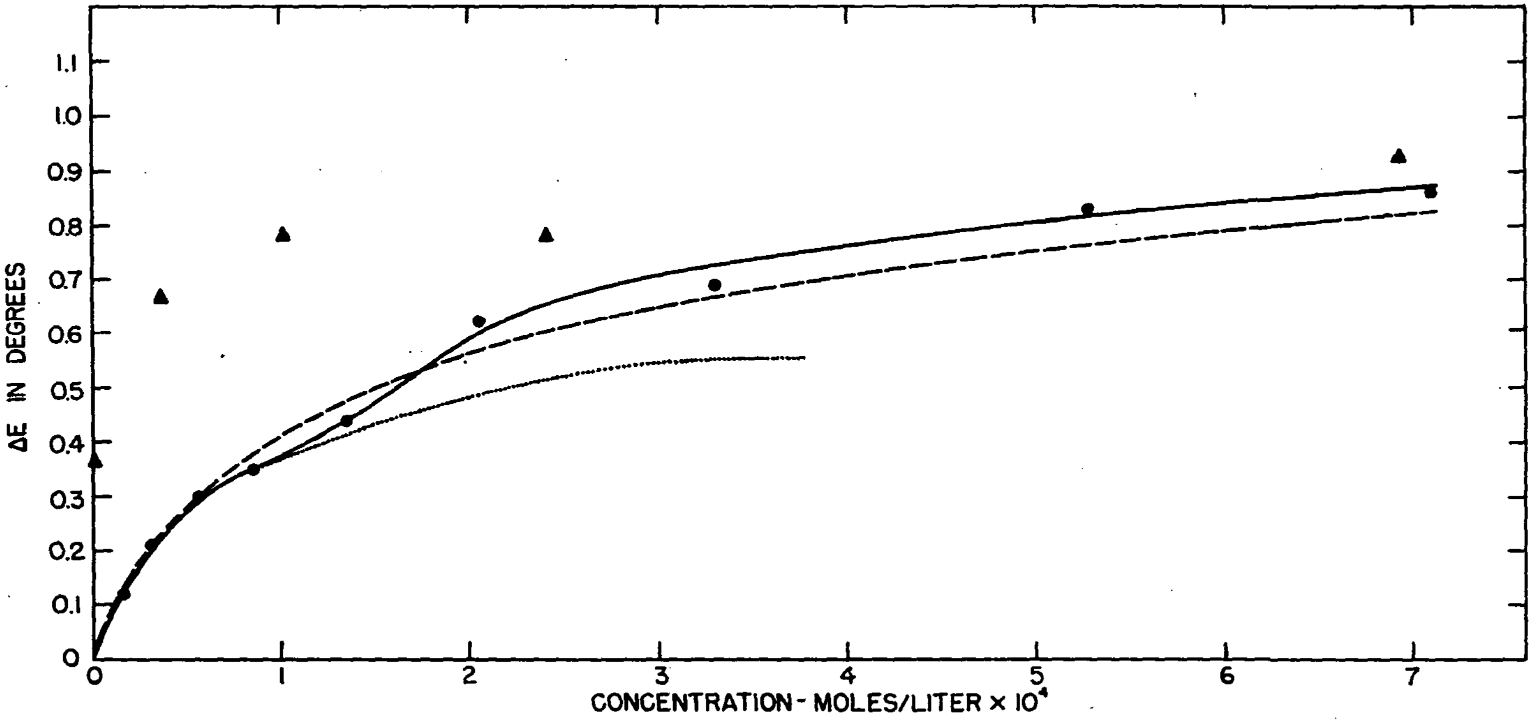

ΔE IN DEGREES
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0
1
2
3
4
5
6
7
CONCENTRATION - MOLES/LITER × 10^4

Figure 10. Adsorption of decylamine on platinum at a pH of 10.58 to 10.71 and 27.0-28.5° C. The system was buffered with 0.06 M sodium carbonate and 0.01 M sodium bicarbonate. The round points refer to the initial adsorption isotherm. The triangular points refer to the adsorption obtained after replacing the solution of maximum concentration by the buffer and repeating the isotherm. The dashed line refers to the BET calculated curve for n=2. The adsorption of molecules in the first layer as postulated for the calculation of contact angles is represented by the dotted line.

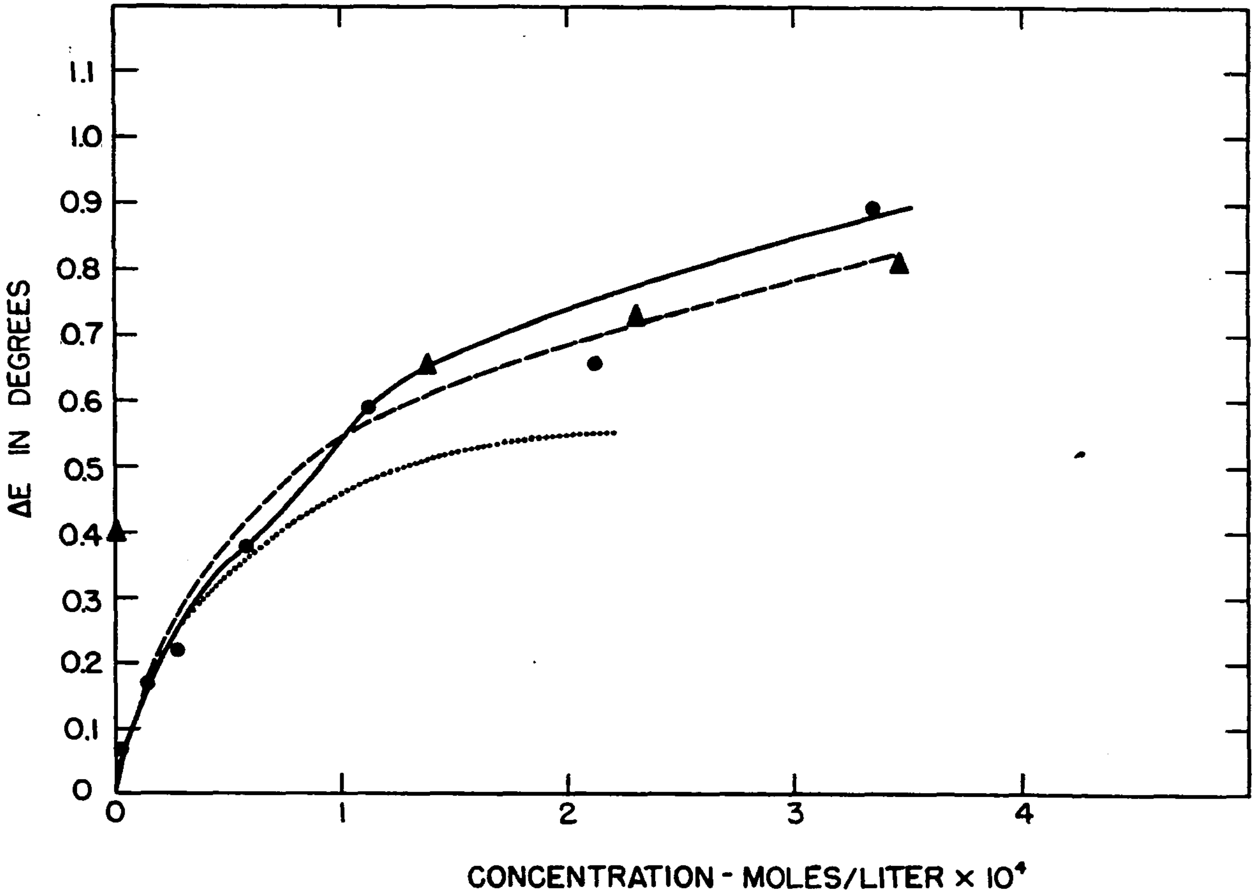

ΔE IN DEGREES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
CONCENTRATION - MOLES/LITER × 10⁴

Figure 11. Adsorption of decylamine on platinum at a pH of 10.63 and 28.0-28.5° C. The system was kept at a pH of 10.63 with 0.1 N potassium hydroxide added to system with an automatic titrator. The round points refer to the initial adsorption isotherm. The triangular points refer to the adsorption obtained after replacing the solution of maximum concentration by buffer and repeating the isotherm. The dashed line refers to the BET calculated curve for n=2. Two different representations for the adsorption of molecules in the first layer as postulated for the calculation of contact angles are represented by the dotted line and the dot-dashed line.

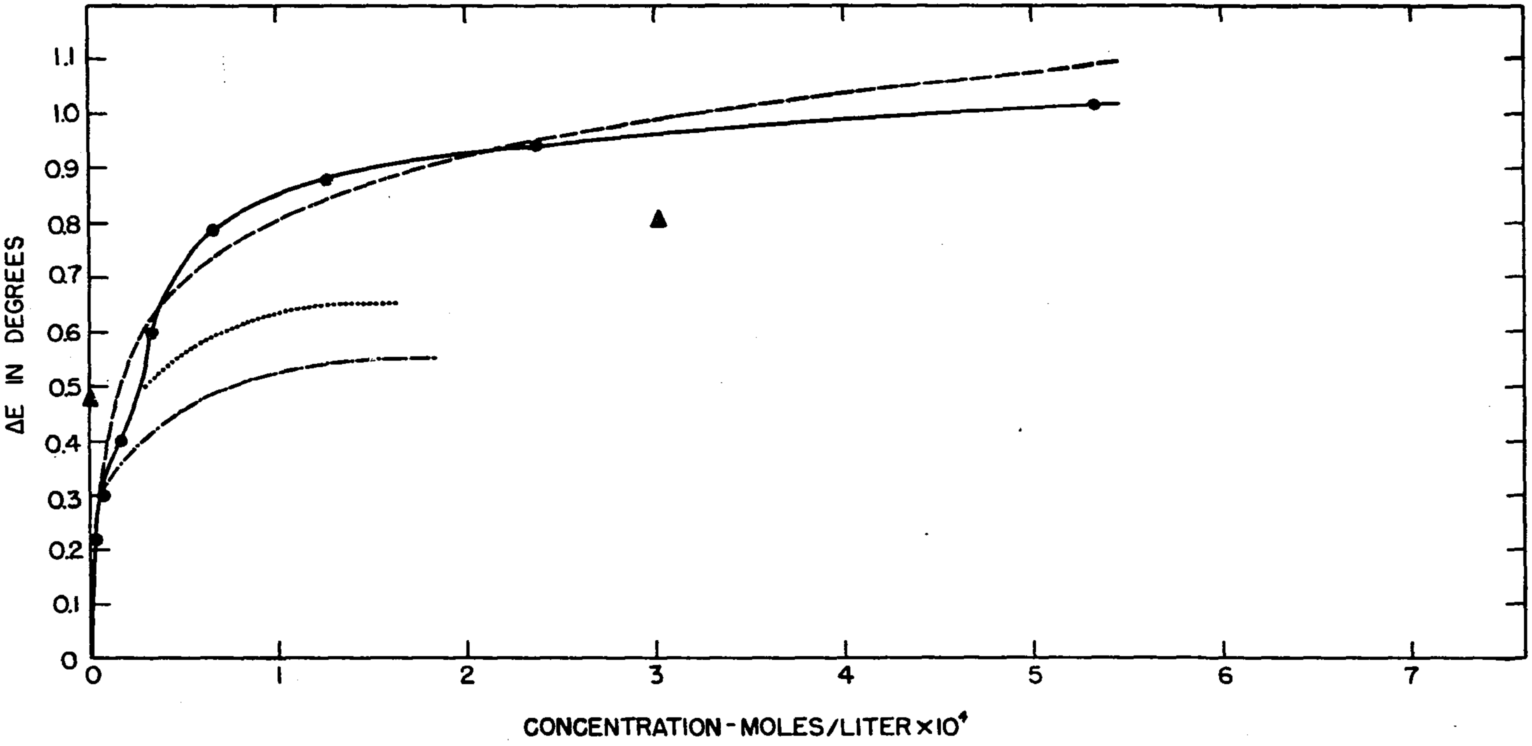

ΔE IN DEGREES
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0
1
2
3
4
5
6
7
CONCENTRATION - MOLES/LITER × 10⁴

Figure 12. Adsorption of decylamine hydrochloride on platinum at a pH of 5.9 to 6.2 and 27.0° C. No buffer, acid or base was added to the system. The round points refer to the initial adsorption isotherm. The triangular points refer to adsorption obtained after replacing the solution of maximum concentration by buffer and repeating the isotherm. The dashed line refers to the BET calculated curve for $n=3$. The adsorption of molecules in the first layer as postulated for the calculation of contact angles is represented by the dotted line. C.M.C. refers to the critical micelle concentration.

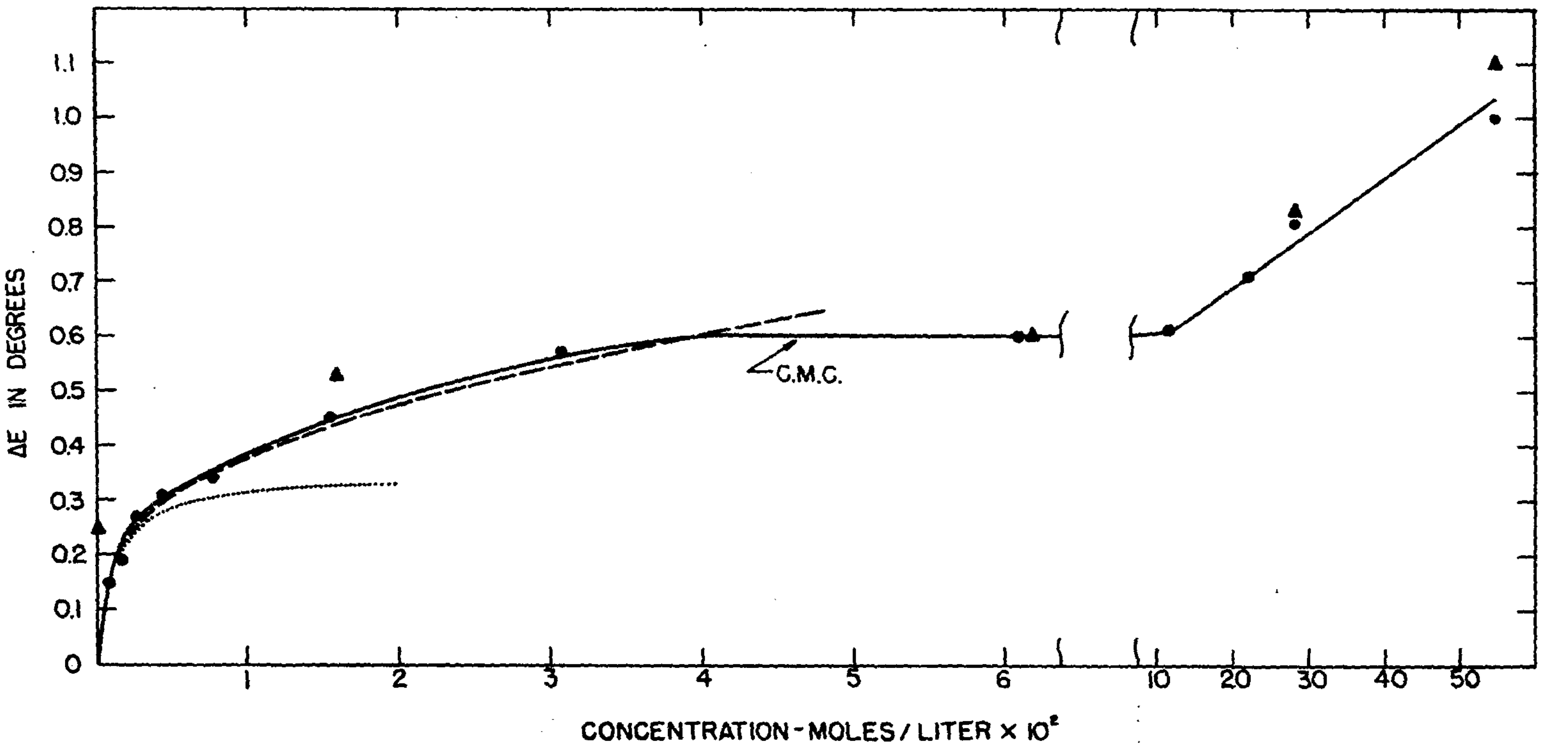

ΔE IN DEGREES
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C.M.C.
1
2
3
4
5
6
10
20
30
40
50
CONCENTRATION - MOLES / LITER × 10²

Table 6. Adsorption data for decylamine on platinum at pH of 9.28-9.32 and 28.5-29.0° C. The system was buffered with 0.01 M sodium carbonate and 0.06 M sodium bicarbonate.

Molarity x 10^5	ΔE Observed in degrees	$x=c/c_0$	$x+x^2$	$x+2x^2$	$x+2x^2/\Delta E$	ΔE Calculated
2.6	.23 ± .03	.0289	.0297	.0306	.1330	.31
6.5	.42 ± .01	.0722	.0774	.0286	.1967	.45
14.2	.62 ± .04	.1578	.1827	.2076	.3348	.57
26.8	.68 ± .03	.2978	.3865	.4752	.6988	.66
61.8	.79 ± .04	.6867	1.1583	1.6298	2.0630	.79
56.6	.79 ± .04	.6289	1.0244	1.4199	1.7973	.78
38.2	.73 ± .02	.4244	.6045	.7846	1.0748	.72
28.9	.69 ± .04	.3211	.4242	.5273	.7642	.67
Buffer	.36 ± .03					

Table 7. Adsorption data for decylamine on platinum at pH of 10.08-10.1 and 26.0-27.0° C. The system was buffered with 0.07 M sodium carbonate and 0.05 M sodium bicarbonate.

Molarity x 10^5	ΔE Observed in degrees	$x=c/c_0$	$x+x^2$	$x+2x^2$	$x+2x^2/\Delta E$	ΔE Calculated
1.65	.12 ± .04	.0206	.0210	.0234	.1950	.13
3.17	.21 ± .04	.0396	.0412	.0427	.2033	.20
5.66	.30 ± .03	.0708	.0758	.0808	.2693	.30
8.48	.35 ± .04	.1060	.1172	.1285	.3671	.38
13.5	.44 ± .04	.1688	.1973	.2258	.5132	.48
20.5	.62 ± .03	.2563	.3220	.3877	.6253	.57
33.0	.69 ± .03	.4125	.5827	.7528	1.0910	.67
52.8	.83 ± .05					
70.9	.86 ± .02					
Buffer	.37 ± .04					
3.59	.67 ± .03					
10.2	.78 ± .06					
24.2	.78 ± .02					
69.5	.93 ± .03					

Table 8. Adsorption data for decylamine on platinum at pH of 10.58-10.71 and 27.0-28.5° C. The system was buffered with 0.06 M sodium carbonate and 0.01 M sodium bicarbonate.

Molarity $\times 10^5$	ΔE Observed in degrees	$x=c/c_0$	$x+x^2$	$x+2x^2$	$x+2x^2/\Delta E$	ΔE calculated
.344	.07 ± .05	.0086	.0086	.0087	.1243	.05
1.45	.17 ± .02	.0363	.0376	.0389	.2288	.16
2.82	.22 ± .02	.0705	.0755	.0804	.3655	.27
5.85	.38 ± .03	.1463	.1677	.1891	.4976	.42
11.2	.59 ± .01	.2800	.3584	.4368	.7403	.57
21.2	.69 ± .01					
33.5	.89 ± .03					
Buffer	.40 ± .03					
13.8	.65 ± .02					
23.0	.73 ± .05					
34.6	.81 ± .04					

Table 9. Adsorption data for decylamine on platinum at pH of 10.63 and 28.0-28.5° C. The pH of the system was adjusted with 0.1 N potassium hydroxide.

Molarity $\times 10^6$	ΔE Observed in degrees	$x=c/c_0$	$x+x^2$	$x+2x^2$	$x+2x^2/\Delta E$	ΔE calculated
2.73	.22 ± .04	.0046	.0046	.0046	.0209	.17
7.08	.30 ± .03	.0118	.0119	.0121	.0403	.34
16.4	.40 ± .04	.0273	.0281	.0288	.0720	.50
33.0	.60 ± .02	.0550	.0580	.0610	.1017	.63
66.5	.79 ± .02	.1108	.1231	.1354	.1714	.74
126	.88 ± .04	.2100	.2541	.2982	.3389	.84
238	.94 ± .02	.3967	.5548	.7128	.7583	.95
533	1.02 ± .03					
Water	.48 ± .02					
302	.80 ± .04					

Table 10. Adsorption data for decylamine hydrochloride on platinum at pH of 5.9-6.2 and 27.0-29.0° C. No buffer, acid or base was added to the system.

Molarity x 10^4	ΔE Observed in degrees	$x=c/c_0$	$x+x^2$ $+x^3$	$x+2x^2$ $+3x^3$	$x+2x^2/\Delta E$ $+3x^3$	ΔE Calculated
8.85	.15 ± .03	.0184	.0187	.0191	.1273	.15
17.4	.19 ± .03	.0363	.0377	.0391	.2058	.21
25.9	.27 ± .01	.0540	.0571	.0603	.2233	.25
43.2	.31 ± .03	.0900	.0988	.1084	.3497	.29
77.5	.34 ± .02	.1615	.1918	.2263	.6656	.35
154	.45 ± .02					
307	.57 ± .02					
608	.60 ± .03					
1180	.61 ± .03					
2210	.71 ± .03					
2840	.81 ± .02					
5470	1.00 ± .06					
Water	.25 ± .03					
159	.53 ± .02					
617	.60 ± .04					
2840	.83 ± .03					
5470	1.10 ± .06					

C. Contact Angles

The contact angles for several trials with adsorption on chromium are illustrated in Figure 13. Each contact angle is the average of three values at different portions of the surface. In many instances it was necessary for the air bubble to remain in contact with the surface for a minute or longer before the bubble became attached. The maximum contact angles were usually from 70° to 80°.

Adhesion of the air bubble to the surface in the case of platinum usually took place in seconds. The contact angle data are given in Tables 11 through 15 and illustrated in Figures 14 through 18. The contact angles increased to a maximum and then decreased, sometimes to zero, as adsorption proceeded. The maximum values reached were usually around 90°. The difference between advancing and receding contact angles or hysteresis was usually around 30° at early stages of adsorption and approached 15° as adsorption increased.

Figure 13. Contact angles for two adsorption trials on chromium. Solid circles represent advancing angles and open circles represent receding angles. Both systems were buffered. Upper points were at a pH of 10.3 and 26.0-28.0° C. Lower points were at a pH of 9.78 to 9.98 and 27.5-28.5° C.

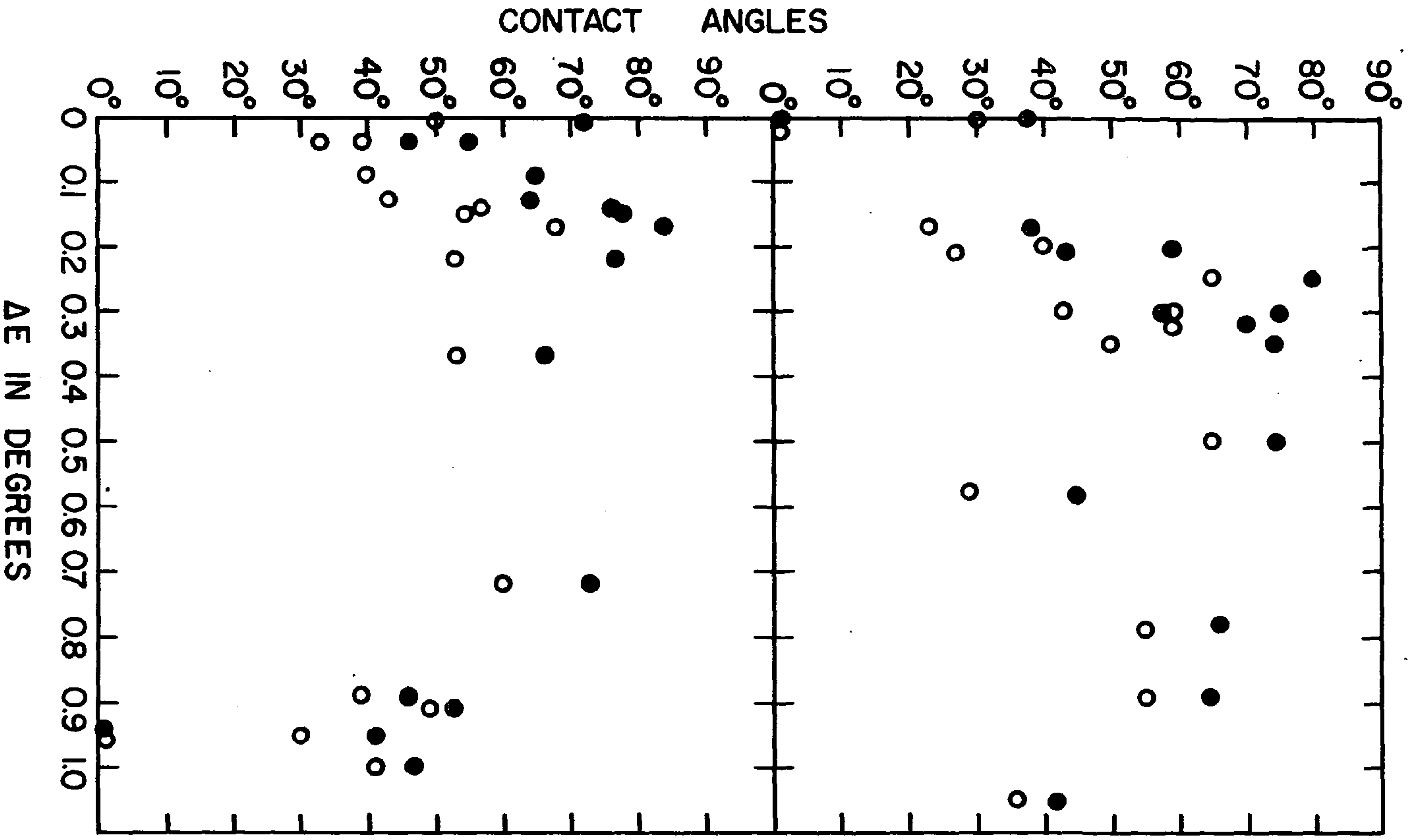

CONTACT ANGLES
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
ΔE IN DEGREES
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 14. Contact angles of aqueous solutions of decylamine on platinum at pH of 9.28 to 9.32. Observed advancing angles are represented by solid symbols and observed receding angles by open symbols. Squares represent contact angles measured at points denoted by triangles on the adsorption isotherms and are not expected in general to follow the smooth curves drawn for the circles corresponding to points on the initial isotherms. The dashed curve for calculated contact angles was plotted using $72.0\ P - 22.3\ R + 72.0\ S = \gamma_{LA} \cos \theta$. The dot-dashed curve was plotted using $72.0\ P - 13.7\ R + 40.0\ S = \gamma_{LA} \cos \theta$. ΔE_m was 0.55° for the calculated curves.

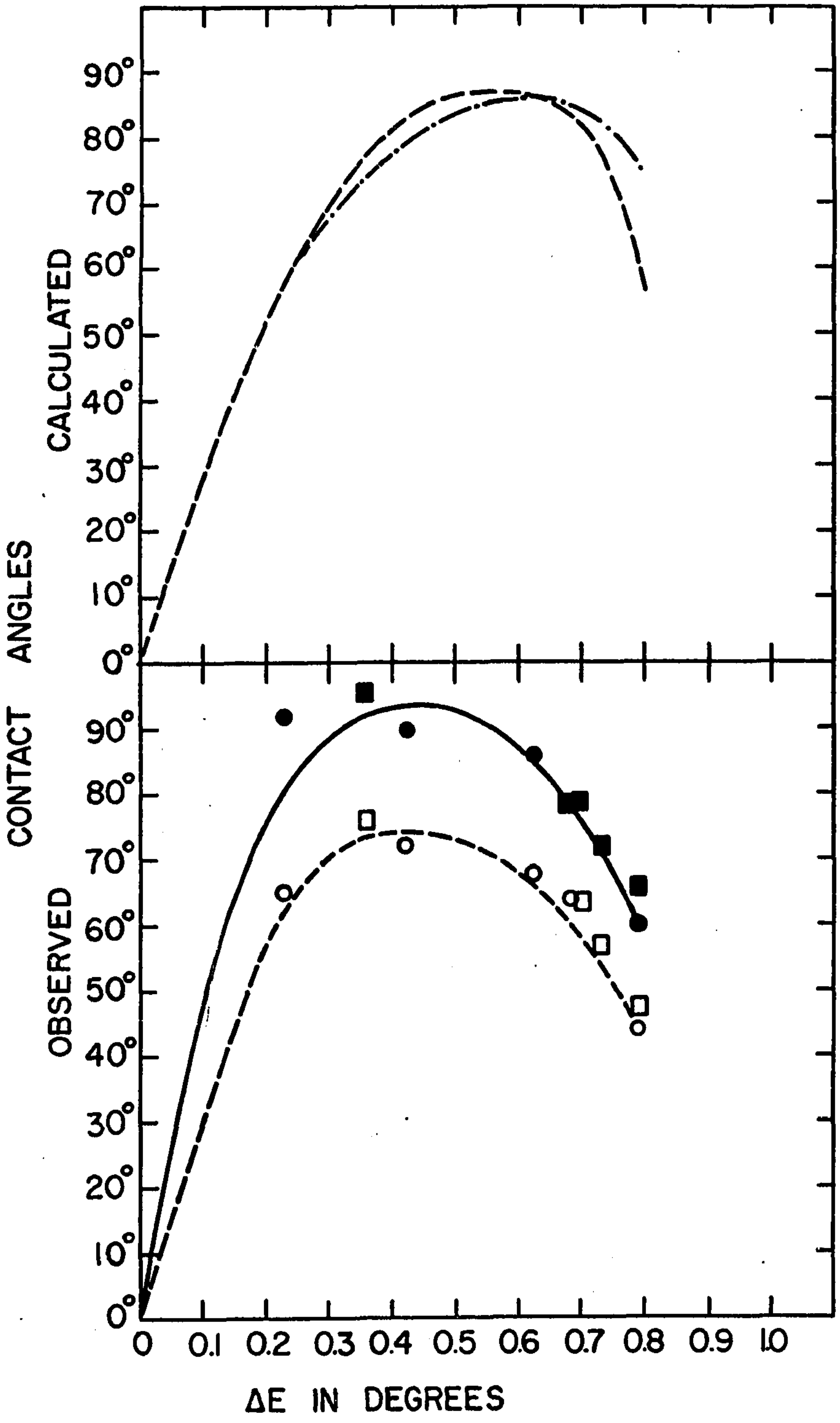

CONTACT ANGLES
CALCULATED
OBSERVED
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
ΔE IN DEGREES

Figure 15. Contact angles of aqueous solutions of decylamine on platinum at pH of 10.08 to 10.10. Observed advancing angles are represented by solid symbols and observed receding angles by open symbols. Squares represent contact angles measured at points denoted by triangles on the adsorption isotherms and are not expected in general to follow the smooth curves drawn for the circles corresponding to points on the initial isotherms. The dashed curve for calculated contact angles was plotted using $72.0\ P - 22.3\ R + 72.0\ S = \gamma_{LA} \cos \Theta$. ΔE_m was 0.55° for the calculated curve.

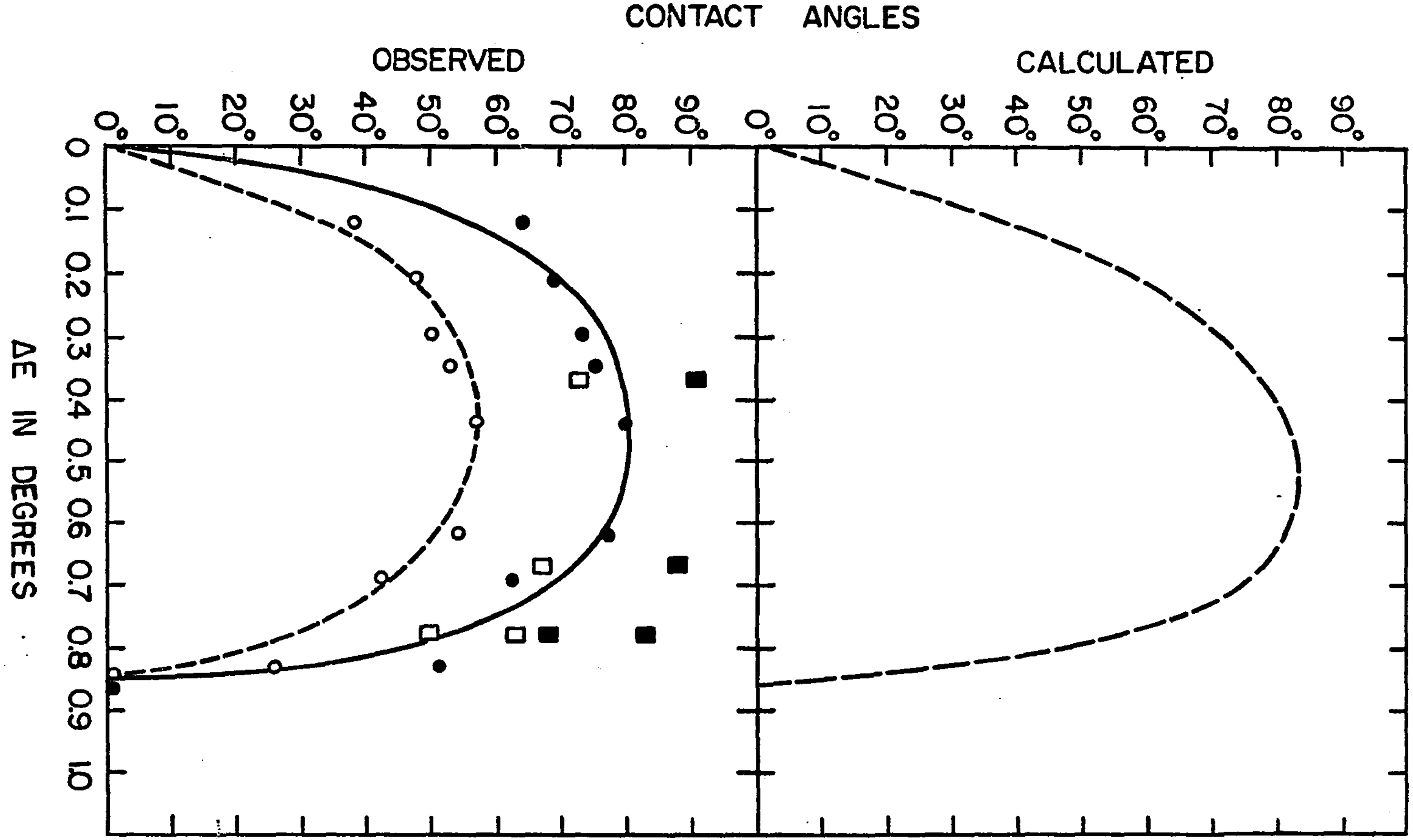

CONTACT ANGLES
OBSERVED
CALCULATED
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
ΔE IN DEGREES

Figure 16. Contact angles of aqueous solutions of decylamine on platinum at pH of 10.58 to 10.71. Observed advancing angles are represented by solid symbols and observed receding angles by open symbols. Squares represent contact angles measured at points denoted by triangles on the adsorption isotherms and are not expected in general to follow the smooth curves drawn for the circles corresponding to points on the initial isotherms. The dashed curve for calculated contact angles was plotted using $72.0\ P - 22.3\ R + 72.0\ S = \gamma_{LA} \cos \theta$. ΔE_m was 0.55° for the calculated curve.

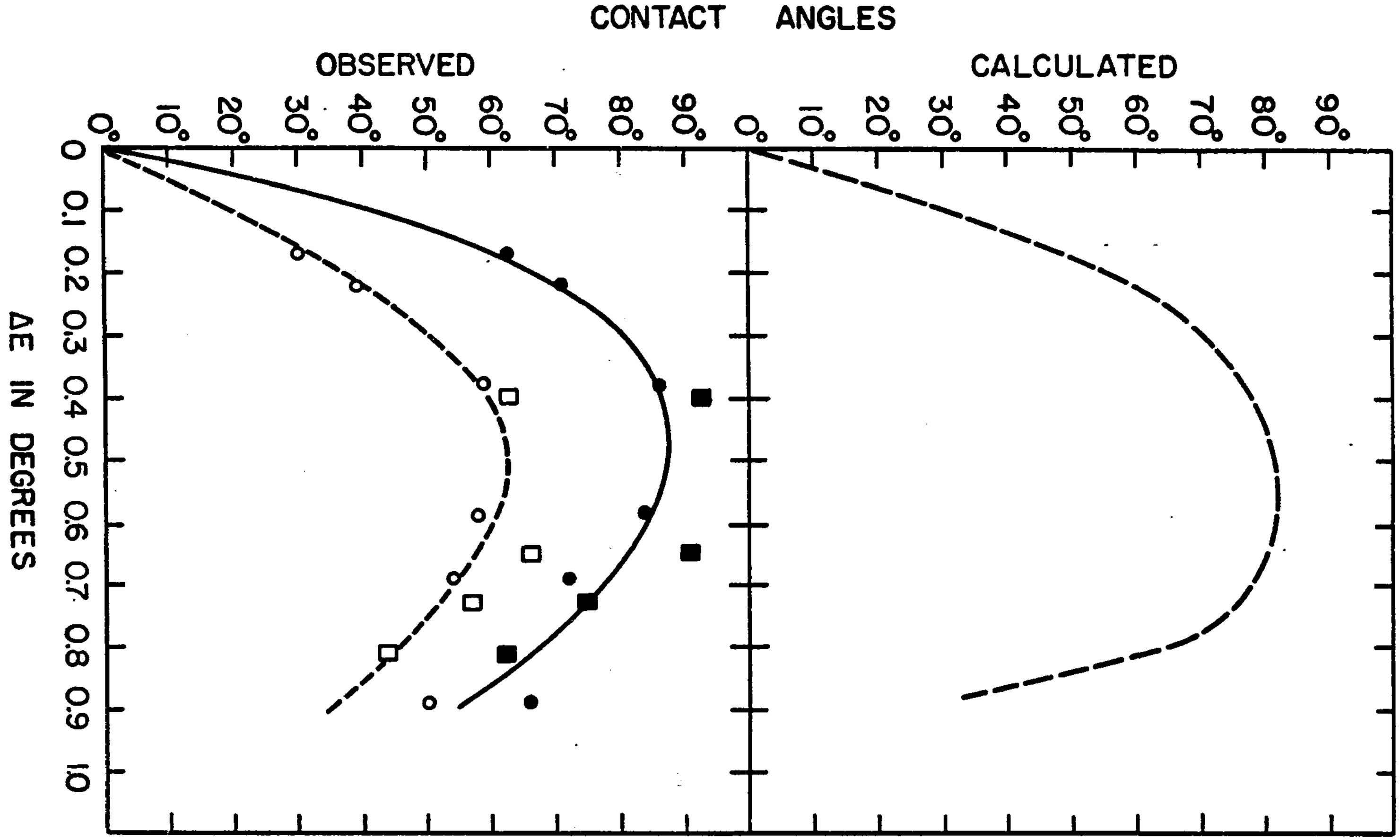

CONTACT ANGLES
OBSERVED
CALCULATED
0° 10° 20° 30° 40° 50° 60° 70° 80° 90°
0° 10° 20° 30° 40° 50° 60° 70° 80° 90°
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
ΔE IN DEGREES

Figure 17. Contact angles of aqueous solutions of decylamine on platinum at pH of 10.63. Observed advancing angles are represented by solid symbols and observed receding angles by open symbols. Squares represent contact angles measured at points denoted by triangles on the adsorption isotherms and are not expected in general to follow the smooth curves drawn for the circles corresponding to points on the initial isotherms. The dot-dashed curve for calculated contact angles was plotted using ΔE_m of 0.55° and the dashed curve using ΔE_m of 0.65°. $72.0\ P - 22.3\ R + 72.0\ S = \gamma_{LA} \cos \Theta$ was used for both calculated curves.

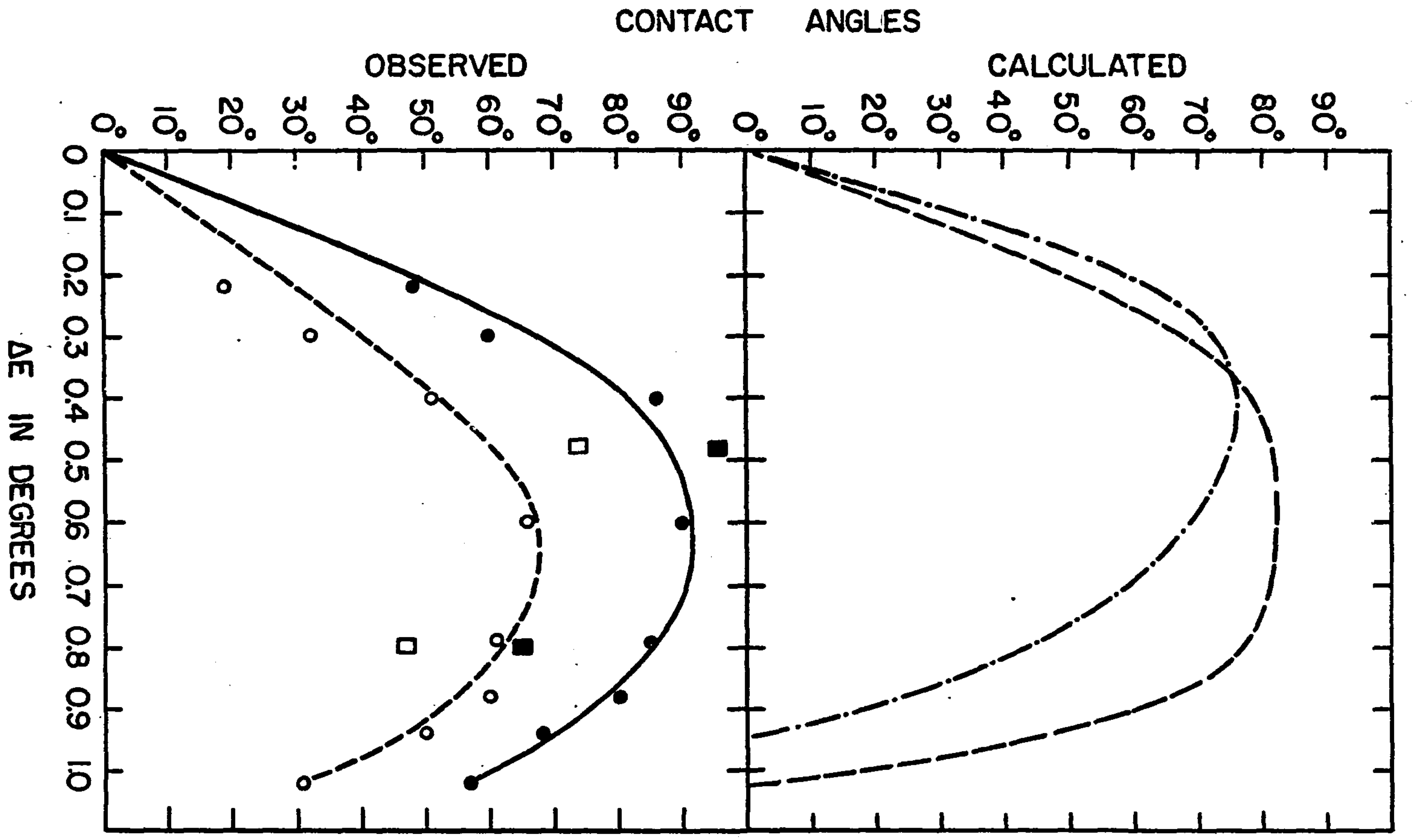

CONTACT ANGLES
OBSERVED
CALCULATED
0° 10° 20° 30° 40° 50° 60° 70° 80° 90°
0° 10° 20° 30° 40° 50° 60° 70° 80° 90°
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
ΔE IN DEGREES

Figure 18. Contact angles of aqueous solutions of decylamine hydrochloride on platinum at pH of 5.9 to 6.2. Observed advancing angles are represented by solid symbols and observed receding angles by open symbols. Squares represent contact angles measured at points denoted by triangles on the adsorption isotherms and are not expected in general to follow the smooth curves drawn for the circles corresponding to points on the initial isotherms. The dashed curve for calculated contact angles was plotted using $72.0\ P - 22.3\ R + 72.0\ S = \gamma_{LA} \cos \theta$. ΔE_m was 0.33° for the calculated curve.

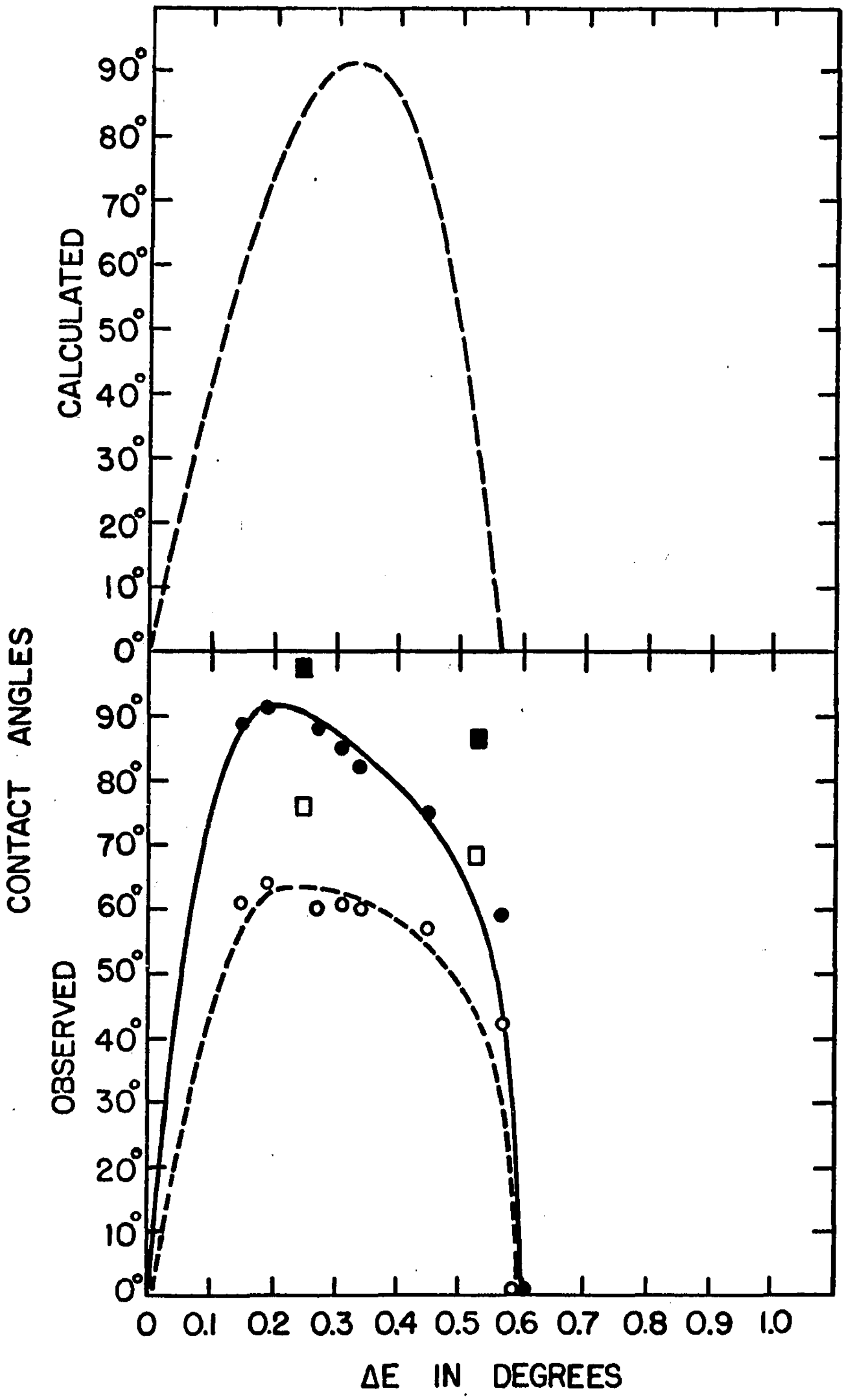

CONTACT ANGLES
CALCULATED
OBSERVED
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
ΔE IN DEGREES

Table 11. Contact angle data for decylamine on platinum at pH of 9.28-9.32 and 27.5-28.0° C. $\Delta E_m = 0.55^\circ$.

ΔE^a	Surface tension	P	R	S	Calculated angles in degrees		Observed angles in degrees Adv.	Rec.
.23	69.3	.58	.42	.00	62[b]	59[c]	92	65
.42	64.2	.27	.69	.04	84	79	90	72
.62(.61)	55.8	.09	.71	.20	85	85	86	68
.68(.69)	48.4	.00	.74	.26	87	90	79	64
.79(.80)	38.2	.00	.55	.45	58	74	60	44
.79	39.2	.00	.56	.44	61	75	66	47
.73	43.9	.00	.67	.33	78	85	72	57
.69	47.4	.00	.74	.26	87	85	79	63
.36	71.1	.35	.65	.00	81	77	96	76

[a] Second value used to calculate P, R, and S.

[b] Coefficient of P is 72.0, of R is -22.3, and of S is 72.0.

[c] Coefficient of P is 72.0, of R is -13.7, and of S is 40.0.

Table 12. Contact angle data for decylamine on platinum at pH = 10.08-10.1 and 26.0-27.0° C. $\Delta E_m = 0.55^\circ$.

ΔE^a	Surface tension	P	R	S	Calculated angles in degrees	Observed angles in degrees Adv.	Rec.
.12	70.7	.78	.22	.00	43[b]	64	38
.21(.20)	68.0	.64	.36	.00	56	69	48
.30	62.6	.46	.54	.00	71	73	50
.35	57.3	.37	.63	.00	78	75	53
.44	51.0	.25	.69	.06	82	80	57
.62(.60)	45.5	.11	.69	.20	81	77	54
.69(.73)	38.5	.00	.67	.33	75	62	42
.83(.82)	30.7	.00	.51	.49	39	51	26
.86(.87)	25.5	.00	.42	.58	0	0	0
.37	71.7	.33	.67	.00	83	90	70
.67	67.1	.04	.70	.26	86	88	67
.78	54.9	.00	.58	.42	72	83	63
.78	43.3	.00	.58	.42	66	68	50
.93	26.0	.00	.31	.69	0	0	0

[a] Second value used to calculate P, R, and S.

[b] Coefficient of P is 72.0, of R is -22.3 and of S is 72.0.

Table 13. Contact angle data for decylamine on platinum at pH of 10.58-10.71 and 27.0-28.5° C. $\Delta E_m = 0.55°$.

ΔE^a	Surface tension	P	R	S	Calculated angles in degrees	Observed angles in degrees	
						Adv.	Rec.
.17(.16)	71.3	.71	.29	.00	51[b]	63	30
.22(.25)	69.3	.55	.45	.00	65	71	39
.38	63.2	.35	.62	.03	78	86	59
.59	55.4	.13	.67	.20	81	84	58
.69(.75)	47.2	.00	.64	.36	76	72	54
.89(.88)	41.0	.00	.40	.60	33	66	50
.40	72.1	.31	.65	.04	81	93	63
.65	52.8	.07	.68	.25	81	91	66
.73	46.1	.00	.67	.33	79	75	57
.81	40.7	.00	.53	.47	57	62	44

[a] Second value used to calculate P, R, and S.

[b] Coefficient of P is 72.0, or R is -22.3, and of S is 72.0.

Table 14. Contact angle data for decylamine hydrochloride on platinum at pH of 5.9-6.2 and 27.0-29.0° C. $\Delta E_m = 0.33°$.

ΔE^a	Surface tension	P	R	S	Calculated angles in degrees	Observed angles in degrees	
						Adv.	Rec.
.15	67.2	.55	.45	.00	64[b]	89	61
.19(.20)	66.2	.39	.61	.00	77	91	64
.27	65.2	.27	.64	.09	80	88	60
.31(.30)	62.8	.15	.75	.06	89	85	61
.34(.35)	56.1	.09	.76	.15	89	82	60
.45	45.8	.00	.64	.36	75	75	57
.57(.56)	35.8	.00	.30	.70	0	59	42
.60	30.0	.00	.18	.82	0	0	0
.25	70.2	.36	.52	.12	71	98	76
.53	45.5	.00	.39	.61	39	87	68

[a] Second value used to calculate P, R, and S.

[b] Coefficient of P is 72.0, of R is -22.3, and of S is 72.0.

Table 15. Contact angle data for decylamine on platinum at pH of 10.63 and 28.0-28.5° C. $\Delta E_m = 0.55°$ and $\Delta E_m = 0.65°$.

ΔE	Surface tension	P	R	S	Calculated angles in degrees	Observed angles in degrees	
						Adv.	Rec.
.22	70.8	.60	.40	.00	61[a]	48	19
.30	70.4	.46	.54	.00	73	60	32
.40	68.3	.35	.58	.07	75	86	51
.60	64.0	.25	.40	.35	58	90	66
.79	56.8	.11	.34	.55	45	85	61
.88	48.1	.02	.36	.62	38	80	60
.94	39.3	.00	.29	.71	0	68	50
.48	71.5	.29	.55	.16	74	96	74
.80	36.2	.09	.36	.55	0	65	47
.22	70.8	.66	.34	.00	56[b]	48	19
.30	70.4	.54	.46	.00	66	60	32
.40	68.3	.38	.62	.00	79	86	51
.60	64.0	.22	.64	.14	80	90	66
.79	56.8	.09	.60	.31	74	85	61
.88	48.1	.00	.65	.35	77	80	60
.94	39.3	.00	.55	.45	59	68	50
1.02	28.3	.00	.43	.57	0	57	31
.48	71.5	.26	.74	.00	88	96	74
.80	36.2	.08	.61	.31	66	65	47

[a] Coefficient of P is 72.0, of R is -22.3, and of S is 72.0. $\Delta E_m = 0.55°$.

[b] Coefficient of P is 72.0, of R is -22.3, and of S is 72.0. $\Delta E_m = 0.65°$.

V. THEORY

A. Adsorption

A comparison of ΔE values obtained for films at the solid-solution interface in this study with ΔE values obtained for films at the solid-air interface in an earlier study (19) suggested that adsorption in the present study was multimolecular at higher concentrations. A study of several adsorbed films of decylamine formed in cetane and in aqueous solutions and withdrawn for optical readings indicated that the ellipsometer reading corresponding to a monolayer of decylamine was about 0.55° at the solid-air interface. Films obtained in aqueous solution gave readings as high as 1.1° at high concentrations of amine. Since the sensitivity of the ellipsometer in air and in solution was virtually the same, it was concluded that double layer adsorption occurred in solution.

The BET (4) multilayer theory of gas adsorption was applied to the present adsorption data to see whether it could be used as an empirical representation of the data. The BET equation as transformed by Joyner *et al*. (20) becomes for this study:

$$\Delta E = \frac{\Delta E_m \, C \sum_{i=1}^{n} i x^i}{1 + C \sum_{i=1}^{n} x^i} \qquad 1.$$

ΔE_m refers to the ellipsometer value for a monolayer; C is a constant related to the heat of adsorption of the monolayer and the heat of liquefaction of the adsorbate; n is the number of layers that can adsorb; and x is the reduced concentration, c/c_o, of the adsorbate.

The constant c_o was arbitrarily chosen as the concentration at which a precipitate appeared in the adsorption trials of Figures 8 through 11, although the precipitation may have been associated with the formation of a complex with the buffer. The critical micelle concentration was chosen as c_o for the adsorption trial of Figure 12. The values of c_o and n used are shown in Table 16. A lower value than 0.55° for ΔE_m was indicated by the adsorption isotherm of Figure 12, corresponding to adsorption from acidic solution, and n = 3 was used in the BET calculations. This treatment was not applied to adsorption results on chromium.

Table 16. BET data and results for the adsorption of decylamine on platinum.

Figure	c_o	ΔE_m	C	n
8	9.0×10^{-4} M	0.58°	35.52	2
9	8.0×10^{-4} M	0.59°	12.07	2
10	4.0×10^{-4} M	0.60°	9.43	2
11	6.0×10^{-4} M	0.76°	64.64	2
12	4.8×10^{-2} M	0.33°	46.31	3

Rearrangement of equation 1 gives:

$$\sum_{i=1}^{n} iX^{i}/\Delta E = \sum_{i=1}^{n} X^{i}/\Delta E_m + 1/\Delta E_m C \qquad 2.$$

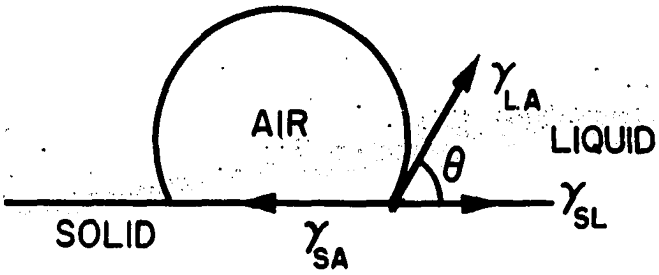
ΔE_m was determined for each system from the slope of a plot of $\sum_{i=1}^{n} iX^{i}/\Delta E$ versus $\sum_{i=1}^{n} X^{i}$. C was determined from the value of ΔE_m and the intercept. The least squares method was used to obtain the best fit of the data. The pertinent data for these plots as well as the calculated ΔE values from equation 1 are given in Tables 6 through 10. The values of ΔE_m and C obtained are given in Table 16. BET plots using calculated values are represented by dashed lines in Figures 8 through 12. In all but one case, data for c/c_0 less than 0.5 was used to calculate ΔE_m and C.

The BET theory provided an approximate fit in the mean to the data but failed to be flexible enough to follow the change in curvature of Figures 8 through 11. This change in curvature was also found in several other adsorption trials of decylamine on platinum not included with the present data.

B. Wetting

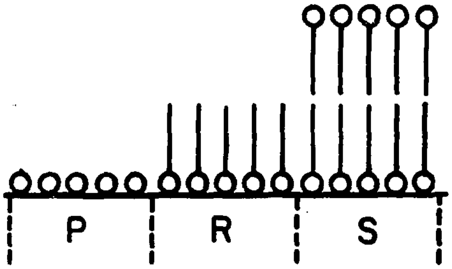
The model proposed to explain the wetting results in this study is illustrated in Figure 19. The contact angle θ is most often described in terms of Young's equation:

Figure 19. The model proposed for calculating contact angles.



$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos\theta$$

YOUNGS EQUATION



$P+R+S=1$

○ = WATER

○—— = POLAR-NON-POLAR MOLECULE

W = WATER

U = MONOLAYER

M = MULTILAYER

$$P(\gamma_{WA} - \gamma_{WL}) + R(\gamma_{UA} - \gamma_{UL}) + S(\gamma_{MA} - \gamma_{ML}) = \gamma_{LA} \cos\theta$$

MODIFIED YOUNGS EQUATION

$$\gamma_{SA} - \gamma_{S1} = \gamma_{LA} \cos \theta$$

which relates the components of the surface and interfacial tensions in the plane of the solid.

The present model considers that the surface of the solid is divided into regions variously covered with adsorbed water, adsorbed decylamine monolayer, and adsorbed decylamine double layer. It is proposed that the fraction of each present can be inferred, at any concentration, from the adsorption isotherm. The molecules in the first layer adsorbed are presumed to be attached to the solid principally by their polar groups such that their hydrocarbon chains are exposed to the adsorption medium. The molecules in the second layer are postulated to adsorb on those of the first in the opposite orientation, with polar groups directed toward the adsorption medium. The effective surface energy is considered to be the average of the individual energies of the fraction P of adsorbed water, the fraction R of adsorbed decylamine monolayer, and the fraction S of adsorbed decylamine double layer. Representative regions of each type of area are assumed to be of sufficient size that edge effects can be ignored.

The surface tension between the solid and air in Young's equation, γ_{SA}, is replaced by $P\,\gamma_{WA} + R\,\gamma_{UA} + S\,\gamma_{MA}$, where W refers to water, U to monolayer, and M to double layer. Similarly the interfacial tension between the solid and the liquid in Young's equation, γ_{SL}, is replaced by $P\gamma_{WL} + R\gamma_{UL} + S\gamma_{ML}$. The resulting modified Young's equation:

$$P(\gamma_{WA}-\gamma_{WL}) + R(\gamma_{UA}-\gamma_{UL})+S(\gamma_{MA}-\gamma_{ML})=\gamma_{LA}\cos\theta$$

is used to calculate contact angles, where γ_{LA} is the experimentally determined surface tension of the adsorption medium.

The same value for $\gamma_{WA}-\gamma_{WL}$ was used in all of the contact angle calculations. The interfacial tension between the adsorbed water and the solution, γ_{WL}, was assumed to be zero. The surface tension of water, γ_{WA}, was used as 72.0 dynes/cm.

The value of $\gamma_{UA}-\gamma_{UL}$ depends on the closeness of packing of the hydrocarbon tails of the decylamine monolayer. The value on various hydrocarbon surfaces may be estimated by using the contact angle of water on the surfaces and Young's equation. The contact angle of water on crystalline $C_{36}H_{74}$, paraffin and polyethylene is reported by Fox and Zisman (21) as 111°, 108°, and 94° respectively. The value of $\gamma_{UA}-\gamma_{UL}=\gamma_{LA}\cos\theta$ becomes for these surfaces: -25.8, -22.3, and -5.1 dynes/cm. The ΔE value for a close-packed monolayer of decylamine would be expected to be about 0.87° if the area per molecule were the same as the area per molecule for octadecylamine which has a ΔE value of 1.49°. If it is assumed that the area per molecule of octadecylamine is 20.5 Å^2, the value for a close-packed film on water, the area per molecule for a decylamine film, corresponding to the observed ΔE of 0.55°, would be about 32 Å^2. This large area per molecule indicates that the monolayers of decylamine are not very close-packed, but agrees reasonably with estimates of molecular areas at the air-solution interface discussed earlier. The values of $\gamma_{UA} - \gamma_{UL}$ assumed for contact angle calculations were -22.3 dynes/cm. and -13.7 dynes/cm., the average of -22.3 and -5.1 dynes/cm.

The double layer was considered on the one hand as having the polar groups hydrated and covered with a water multilayer. In this case the value of $\gamma_{MA} - \gamma_{ML}$ can reasonably be taken as 72.0 dynes/cm. as in the case of $\gamma_{WA} - \gamma_{WL}$. If the hydrated surface were more like concentrated ammonium hydroxide, the value would be about 58.0 dynes/cm. On the other hand, ellipsometer measurements indicated that at least portions of double layers were removed by the receding solution when the films were withdrawn from solution. If the double layer were entirely removed by the air bubble in contact angle measurements, the value of γ_{MA} would be that of an adsorbed monolayer. This value has been estimated as about 22 dynes/cm. by Fox and Zisman (21). The value of γ_{ML} would be approximately zero in this case since it would be essentially the interfacial tension between two similar hydrocarbon layers. The values of $\gamma_{MA} - \gamma_{ML}$ used in contact angle calculations were 72.0 dynes/cm. and 40.0 dynes/cm., the average value of 58.0 and 22.0 dynes/cm.

The shape of adsorption isotherms suggested that double layer adsorption began before monolayer adsorption was complete. The dotted lines of Figures 8 through 12 and the dot-dashed line of Figure 11 represent the postulated adsorption of molecules in the first layer, ΔE_u. The fraction P is then equal to $(\Delta E_m - \Delta E_u)/\Delta E_m$, the fraction S is equal to $(\Delta E - \Delta E_u)/\Delta E_m$, and the fraction R is equal to $1 - (P + S)$.

Figure 14 illustrates two contact angle calculations employing different equations but the same ΔE_m of 0.55°. The dot-dashed line was calculated by using 72.0 P - 13.7 R + 40.0 S. The dashed line was calculated by using 72.0 P - 22.3 R + 72.0 S. Both curves represent the behavior of the mean of the observed advancing and receding contact angles fairly well. The dot-dashed curve implies complete wetting at a higher value of ΔE than does the dashed curve.

The contact angle curves in Figures 15 and 16 were calculated by using a ΔE_m of 0.55° and 72.0 P - 22.3 R + 72.0 S. Both curves represent the observed advancing angles better than a mean of the observed advancing and receding angles. The curve of Figure 15 predicts complete wetting at virtually the same value of ΔE as the observed wetting occurred.

The dot-dashed curve in Figure 17 was calculated by using a ΔE_m of 0.55° and 72.0 P - 22.3 R + 72.0 S. The maximum of the curve lies at too low a ΔE value and the curve also predicts complete wetting at too low a ΔE value. A value of 0.65° was chosen as being intermediate of the 0.76° BET value for this system and the observed ΔE of 0.55° for a decylamine layer to see what effect this would have on the calculated curve using the same equation. The maximum of the curve was shifted to a more reasonable ΔE value and the curve was a better representation of the mean of the observed advancing and receding contact angles. Complete wetting also occurred at a more reasonable value.

The use of 0.55° for ΔE_m for the adsorption from acidic solution is obviously inappropriate as judged by the isotherm of Figure 12, and leads to unreasonable calculated values of contact angles. The isotherm indicates that ΔE_m of the monolayer is considerably lower than 0.55°. It is not surprising that the amine cation, together with a counter ion and possible water of hydration, may occupy a larger area than the neutral amine molecule. The value of 0.33° from the BET fit of the isotherm was chosen for ΔE_m since no other estimate was available. The calculated curve for the acidic solution using $\Delta E_m = 0.33°$ and 72.0 P - 22.3 R + 72.0 S did not represent the observed contact angles as accurately as did the previous curves, but did predict wetting at a reasonable value of ΔE. It is not expected that the model of Figure 19 should apply as accurately to the amine ion as to the neutral amine.

The P, R, and S values along with the calculated contact angles are listed in Tables 11 through 15. Values of ΔE that appear in parenthesis indicate an adjustment of the observed ΔE values to the smooth curve drawn to represent the adsorption data.

Points represented by triangles on the adsorption isotherms and by squares in the plots of contact angles correspond to an adsorption cycle later than the first. They cannot be expected to fall on the contact angle curves corresponding to the initial adsorption cycle since the surface tensions of solutions at these points were often appreciably higher than for points on the initial isotherms of comparable ΔE values. Contact angles were calculated for these points, however, and the results are listed in Tables 11 through 15. Fairly good agreement with observed angles was obtained if it was assumed that the P, R, and S distribution was the same as if the points were on the initial isotherm.

VI. DISCUSSION

A. Adsorption

The major problem in adsorption studies was in obtaining and preparing adsorbents which consistently gave well-behaved adsorption isotherms. It was possible to prepare platinum surfaces which gave adsorption isotherms of the same general character for a particular adsorption system from trial to trial. The adsorption results for chromium, however, varied from trial to trial and were complicated by erratic kinetic effects.

The adsorption results on chromium indicated that adsorption paralleled that at the solution-air interface, being quite low at early stages of adsorption; whereas, appreciable adsorption occurred on the platinum surfaces before much adsorption occurred at the solution-air interface. When appreciable adsorption did occur on the chromium, the surface tension of the adsorption medium was usually low, accounting at least in part for the lower contact angles observed on chromium than on platinum.

The decylamine molecule was probably the adsorbing species in the alkaline region when there were comparable concentrations of the molecule and the ion present. The low affinity of the amine ion for the surface was demonstrated in the adsorption trial at pH of 5.9 to 6.2 where a high concentration of decylamine hydrochloride was necessary before appreciable adsorption occurred. It is possible, however, that protonation of a surface oxide layer suppressed adsorption of the ion in the acid region. The decylamine molecule probably did not contribute much more than several percent of the total adsorption in the trial of pH of 5.9 to 6.2 since the fraction of the amine molecules present at this pH was very low.

The greater adsorption obtained in the non-buffered system of pH = 10.63 in comparison with the adsorption obtained in the buffered system of pH = 10.58 to 10.71 at similar amine concentrations may have been a result of the state of the platinum surface or may have been an effect of the buffer. The buffer may have competed with the decylamine in adsorption or formed a complex with the decylamine. The inhibition of adsorption at the solution-air interface in the presence of buffer paralleled approximately the inhibition of adsorption at the solid-solution interface, further indicating the possibility of a complex existing in the buffered system. The behavior of the systems was not sufficiently consistent from one trial to another to permit interpretation of the data in terms of the pH of the adsorption medium.

The amount of decylamine that remained after allowing films from adsorption trials to stand in contact with water or buffer for long periods of time was termed firm adsorption. If it were assumed that $\Delta E_m = 0.55^{\circ}$, the amount of firm adsorption of decylamine on platinum was about sixty percent of a monolayer and the amount of firm adsorption of decylamine on chromium was about forty percent of a monolayer. The amount of firm adsorption in a previous study (19) for films of octadecylamine adsorbed from cetane on chromium and studied at the solid-air interface was about forty percent of a monolayer when the amine was removed with benzene.

The triangular adsorption points in Figure 8, representing a desorption isotherm, followed the adsorption isotherm until the amount of decylamine corresponding to firm adsorption was reached. In Figures 9 through 12 the triangular adsorption points were measured after replacing the solution of maximum concentration in the initial adsorption isotherm by buffer or water and repeating the adsorption cycle. The adsorption obtained on repeating the adsorption cycle was sometimes greater than adsorption on the initial adsorption isotherm and may have resulted from the firmly adsorbed molecules providing a framework conducive to adsorption.

The change in curvature of the adsorption isotherms was a result of the adsorption of molecules in the second layer before the first layer was completed. The failure of the BET theory to follow this change in curvature is probably associated in part with the failure of the theory to consider the lateral interactions of molecules which are appreciable in the case of decylamine. Hansen <u>et</u> <u>al</u>. (22) found that the

BET theory represented their adsorption data for the adsorption of short-chain polar organic molecules from aqueous solution on various adsorbents as well as it represented data for adsorption of gases on solids. The influence of the lateral interactions in the latter case would be somewhat less than in the present study.

The values of ΔE_m of 0.58°, 0.59°, and 0.60° obtained with the BET theory in the buffered systems nevertheless are in fairly good agreement with the 0.55° obtained for films adsorbed from solution. The high value of 0.76° obtained for ΔE_m with the BET theory in the non-buffered system of pH = 10.63 results from the low weighting of the experimental points at small values of c/c_o. The area per molecule of 30.4 Å^2 for this system at the air-solution interface was not appreciably different from the corresponding area per molecule of 31.2 Å^2 for the buffered system of pH = 10.58 to 10.71. A lower value of ΔE_m for the non-buffered system at a pH of 5.9 to 6.2 is suggested by the shape of the adsorption isotherm and by the larger area per molecule of the adsorbing decylamine ions. No experimental results were obtained to assess independently the reliability of the value of 0.33° obtained with the BET theory. The area per molecule for the 0.33° film was estimated as 54 Å^2. Tamamushi and Tamaki (23) found the even larger area per molecule of 101 Å^2 for dodecylamine hydrochloride on alumina by using the BET value obtained for a monolayer and the surface area of the alumina.

The long plateau from about 0.04 M to 0.10 M in the adsorption isotherm at pH of 5.9 to 6.2 begins at the critical micelle concentration of the system which is about 0.04 M to 0.05 M. The formation of micelles reduces the proportion of ions available for adsorption and further adsorption does not occur again until the critical micelle concentration is greatly exceeded. Tamamushi and Tamaki (23) observed a similar plateau in their adsorption studies on alumina but did not report an increase in adsorption after exceeding the critical micelle concentration.

B. Wetting

Leja (24) reported a study of the adsorption of sodium dodecyl sulphate on barite in which the contact angle rose to a maximum and declined to zero as adsorption increased. The results were discussed in terms of monolayer and multilayer patches, but no quantitative theory was reported for the contact angle behavior.

A theory relating contact angles to surface coverage for the adsorption of polar-non-polar molecules from aqueous solution is reported by Sasaki _et_ _al_. (7). The theory was applied to the wetting of paraffin by aqueous ethanol solutions and to the anti-wetting of galena by aqueous ethyl xanthate solutions. Adsorption was inferred from the Gibbs adsorption isotherm in the paraffin-alcohol system and from equilibrium constants in the galena-xanthate system, but no independent check of adsorption was available. In the derivation of the theory it was assumed that there were certain fractions of the surface of the solid on which no water or polar non-polar molecules adsorbed while in the present theory it was assumed that the entire surface would be covered with various fractions of adsorbed water, decylamine monolayer, and decylamine double layer. In the paraffin-alcohol system it was assumed that the surface tension of the solid was constant and that the interfacial tension varied while in the present study both the surface tension and the interfacial tension were assumed to vary.

Hysteresis in the present study is thought to result, at least in part, from the surface heterogeneity arising from the patches of adsorbed water, adsorbed decylamine monolayer, and adsorbed decylamine double layer present at various stages of adsorption. The value of the advancing angle would be influenced by the tendency of the advancing solution to move spontaneously over the high energy patches of adsorbed water and adsorbed decylamine double layer, and to halt at low energy patches of decylamine monolayer. The value of the receding angle would tend to be lowered by patches of adsorbed water and decylamine double layer which would resist the inward movement of the periphery of the receding solution.

The theory proposed for wetting considers an area average of the patches of adsorbed water, decylamine monolayer and decylamine double layer on the surface. As a result, the theory might be expected to yield calculated contact angle curves which would fall between the observed advancing and receding contact angles. In some cases the calculated contact angle curves were approximately the mean of the observed advancing and receding contact angles while in other cases they more nearly represented the observed advancing angles.

The contact angle curves calculated by using the equation:

$$P(\gamma_{WA} - \gamma_{WL}) + R(\gamma_{UA} - \gamma_{UL}) + S(\gamma_{MA} - \gamma_{ML}) = \gamma_{LA} \cos \theta$$

depended, of course, on the selection of the variables associated with the equation. Once the value for a monolayer, ΔE_m, and the adsorption of molecules in the first layer, ΔE_u, were chosen, the fractions P, R, and S of adsorbed water, decylamine monolayer, and decylamine double layer were fixed. The value of ΔE_m undoubtedly varied somewhat from system to system in the present studies since the area per molecule depends upon the nature of the platinum surface in the particular adsorption trial. The choice of ΔE_u was purely subjective. While the exact shape of the calculated contact angle curves depends upon the choice of ΔE_u, the general aspect of the curves is quite insensitive to the choice.

The value of 72.0 dynes/cm. for $\gamma_{WA} - \gamma_{WL}$ is a reasonable value since any lower value would imply that the initial surface of the platinum would not be wet by the water. In view of the large area per molecule of 32 $\mathring{A}^2$ estimated for adsorbed monolayers of decylamine, the value of -13.7 dynes/cm. used for $\gamma_{UA} - \gamma_{UL}$ is perhaps more reasonable than the value of -22.3 dynes/cm. used for $\gamma_{UA} - \gamma_{UL}$ in contact angle calculations. Since it was observed experimentally that at least part of double layers were removed by the receding solution on withdrawing a slide from solution, the value of 40.0 dynes/cm. used for $\gamma_{MA} - \gamma_{ML}$ seems more reasonable than the value of 72.0 dynes/cm. used for $\gamma_{MA} - \gamma_{ML}$ in contact angle calculations.

VII. SUMMARY

A solution to the long-existing problem of studying adsorption *in situ* and wetting on the same surface was provided by a polarimetric optical method. Satisfactory adsorption isotherms and wetting measurements were obtained for aqueous solutions of decylamine on platinum. Studies were also made on chromium but results were erratic and quite time dependent.

The character of the adsorption isotherms of decylamine on platinum was such that much could be inferred about the adsorbed molecules. In the basic region the adsorption occurred stepwise suggesting the formation of a second layer of decylamine which was subsequently verified experimentally. The isotherms in the acidic region indicated that adsorption was multimolecular in character and that the area per molecule of the adsorbed ions were larger than the area per molecule of the adsorbed molecules in the basic region. The adsorption isotherm in the acidic region exhibited a plateau extending from the critical micelle concentration to about twice the critical micelle concentration, after which the amount of adsorption increased rapidly as the solution approached saturation. The plateau resulted from the formation of micelles causing a reduction in the proportion of ions available for adsorption.

Any trend of the adsorption isotherms as the pH was varied between narrow limits in the basic region was obscured by the lack of reproducibility from one trial to another. The presence of buffer also complicated the interpretation of data since it reduced adsorption apparently either by competing for adsorption or by forming a complex with the decylamine. The only desorption isotherm measured followed the initial adsorption isotherm until an amount of firmly adsorbed amine corresponding to about sixty-five percent of a monolayer was reached which was not removed by standing for several hours in the adsorption medium or in buffer. The BET function for multilayer adsorption was able to fit the observed adsorption isotherms in the mean, but was unable to follow closely the adsorption occurring stepwise in the basic region.

A model was proposed for correlating wetting results with the concurrently measured adsorption isotherms. The isotherms were used to determine the fraction of the surface variously covered with patches of adsorbed water, adsorbed decylamine monolayer, and adsorbed decylamine double layer. The surface and interfacial energies in Young's equation were replaced by the average energies of the above patches, a reasonable value for each patch being available from data reported in the literature.

The model was successful in predicting the general behavior of the observed contact angles and usually predicted complete wetting near the observed value. The calculated contact angle curves generally fell between the observed advancing and receding contact angles, the maximum of the curve occurring near the maximum of the advancing and receding contact angles. The use of one or another of several reasonable values for surface and interfacial energies affected the exact shape of the calculated curves, but not the general aspect of the curves.

VIII. LITERATURE CITED

1. A. F. Taggart, T. C. Taylor, and C. R. Ince, Trans. Am. Inst. Mining Met. Engrs., 87, 285 (1930).

2. E. G. Shafrin and W. A. Zisman, J. Colloid Sci., 4, 571 (1949).

3. Y. Fu, R. S. Hansen, and F. E. Bartell, J. Phys. Chem., 52, 374 (1948).

4. S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc., 60, 309 (1938).

5. A. M. Gaudin and F. W. Bloecher, Jr., Trans. Am. Inst. Mining Met. Engrs., 187, 499 (1950).

6. A. M. Gaudin and J. G. Morrow, Mining Engr., 6, 1196 (1954).

7. T. Sasaki, H. Kumanomido, and T. Tsunoda, Proc. 2nd Intern. Congr. Surface Activity, 3, 153 (1957).

8. H. J. Trurnit, Arch. Biochem. Biophys., 47, 251 (1953).

9. ________, ibid., 51, 176 (1954).

10. P. Drude, Ann. physik. Chem., 36, 532 (1889).

11. ________, ibid., 36, 865 (1889).

12. ________, ibid., 39, 481 (1890).

13. B. L. Murr and C. T. Lester, J. Am. Chem. Soc., 77, 1684 (1955).

14. W. D. Harkins and H. F. Jordan, ibid., 52, 1751 (1930).

15. H. B. Klevens, J. Am. Oil Chemists' Soc., 30, 74 (1953).

16. A. W. Ralston and C. W. Hoerr, J. Am. Chem. Soc., 64, 772 (1942).

17. C. W. Hoerr, M. R. McCorkle, and A. W. Ralston, ibid., 65, 328 (1943).

18. D. J. Brown, J. Colloid Sci., 13, 286 (1958).

19. L. S. Bartell and R. J. Ruch, *J. Phys. Chem.*, *60*, 1231 (1956).

20. L. G. Joyner, E. B. Weinberger, and C. W. Montgomery, *J. Am. Chem. Soc.*, *67*, 2183 (1945).

21. H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, *7*, 428 (1952).

22. R. S. Hansen, Y. Fu, and F. E. Bartell, *J. Phys. Chem.*, *53*, 769 (1949).

23. B. Tamamushi and K. Tamaki, *Proc. 2nd Intern. Congr. Surface Activity*, *3*, 449 (1957).

24. J. Leja, *ibid.*, *3*, 273 (1957).

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