SURFACE ENERGY AND WETTABILITY IN FLOTATION

by

Wan-Tai Yen

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Department of Metallurgical Engineering
McGill University
Montreal

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ABSTRACT

Heats of adsorption of hexane, benzene and 1,4-dioxane on quartz and Cab-O-Sil silica were measured by means of gas chromatography. Heats of adsorption values on quartz were larger than those obtained on Cab-O-Sil for all the adsorbates. Silica surfaces were modified by reaction with alcohols and chlorosilanes. Modifed surfaces resulted in lower values of heats of adsorption for benzene and 1,4-dioxane. However, the heat of adsorption of hexane remained essentially unchanged following the surface modification.

Wettability of silica surfaces was investigated by contact angle measurements of water and glycerol. Clean silica surfaces gave zero contact angle for water. Silica surfaces modified with alcohols and silanes on the other hand gave finite contact angle values. The actual value of the contact angle depended on the surface tension of the liquid, the molecular structure and the surface coverage of the adsorbed species. The following equation was used to describe the contact angle (θ), on treated silica surfaces:

$$\text{Cos}\,\theta = \text{Cos}\,\theta_1 - (\text{Cos}\,\theta_1 - \text{Cos}\,\theta_2)\,\frac{qa}{100}$$

where θ_1 and θ_2 are the contact angles on unmodified and modified surface with maximum coverage respectively, q is the number of adsorbed molecules per 100 $\mathring{A}^2$ and a is the effective cross sectional area of the adsorbed molecule. The cross sectional areas of the alkoxy groups determined from the contact angle values were in close agreement with the calculated values.

Floatability of the treated silicas was correlated in terms of the contact angles, surface coverages, work of adhesion and the heats of adsorption of the model compounds. Floatability increased with increasing surface coverages or decreasing heats of adsorption. Recovery was 100% when the contact angle was equal to or larger than 40 degrees; or the net heat of adsorption of a model compound on a treated surface was less than 60% of the value obtained on the unmodified silica.

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FOREWORD

The objective of the investigation described in this thesis was to correlate the floatability of quartz and silica in terms of their surface energies. The surface properties of the silicas were altered by reaction with alcohols and chlorosilanes. The changes in the surface properties thus effected were measured in terms of the heats of adsorption of the model compounds. The floatability of the modified silicas was correlated in terms of changes in their surface energies.

This thesis is discussed in six parts.

Chapter 1: Introduction. Review of the physical and chemical properties of silica surfaces.

Chapter 2: Heats of adsorption measurements of the model compounds on the silica surfaces by means of gas chromatography.

Chapter 3: Contact angle measurements of water and glycerol on the silica surfaces.

Chapter 4: Calculations of the dispersion forces and the work of adhesion from contact angle values.

Chapter 5: Flotation data is examined in terms of the contact angle values, work of adhesion and heats of adsorption.

Chapter 6: Claims to original research and suggestions for further work.

TABLE OF CONTENTS

CHAPTER 3: CONTACT ANGLE MEASUREMENTS

CHAPTER 4: SURFACE ENERGY AND CONTACT ANGLE

CHAPTER 5: FLOTATION

LIST OF FIGURES

Page

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

LIST OF TABLES

Page

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Flotation is a method of concentrating finely divided solid mineral particles from an aqueous suspension. It involves agitation of an aqueous suspension of the mineral with air under conditions such that the air bubbles adhere to the particles of the desired mineral. The rising bubbles transport the mineral to the surface of the flotation vessel, where the froth of particle-laden bubbles can be skimmed off. The success of the flotation process obviously depends on the physical and chemical interactions between the liquid, solid and the gaseous phases. To understand the basic principles of flotation, it is necessary to study the physical and chemical properties of the mineral surfaces in relation to the nature and composition of the bulk phase. Measurements of the interfacial energies (1-3), adsorption (4,5), and contact angles (6-8) etc. have been used to elucidate the mechanism of flotation.

1.2 SURFACE TENSION

Surface tension implies that an actual state of tension exists between the surface molecules forming an imaginary "skin" or film in the surface region of a pure liquid substance. Numerous methods have been developed for the measurement of surface tension (9,10). Of the various methods, the most attractive seems to be the one in which a film of liquid is pulled out of the body of the lqiuid by a knife-edge or wire upon the application of a suitable tension.

Water has a rather large value of the surface tension, 72.8 dynes per cm. at 20°C. Organic liquids on the other hand have low surface tension values, i.e., of the order of 20 to 40 dynes per cm. at room temperature.

The surface tension of aqueous solutions of organic substance is intermediate between that of water and the solute, invariably much closer to that of the solute than might be expected. This effect is related to the excess of solute molecules at the interface as compared to its concentration in the bulk phase. The surface tension of aqueous solutions of inorganic salts on other hand does not differ greatly from that of pure water. Since most fused salts have surface tensions greater than that of water, it might have been expected that salts dissolved in water would raise its surface tension. At moderate concentrations of the solutes the surface tension increases to a slight extent although the increase is much less than would be expected on the basis of additivity.

1.3 THE CHARACTERISTICS OF SOLID SURFACES

The surface of a solid can be characterized by its surface energy. Theoretical calculations of the surface energies have been made for simple crystals (11,12). The calculations are based on a classical model of the crystals, and the results are only rough approximations. Van der Hoff and Benson (11) evaluated the surface energy of lithium fluoride by using a quantum mechanical model.

The first experimental determination of the surface energy of a solid was made by Lipsett, Johnson and Maass (12). From the heats of solution of coarse and finely divided sodium chloride and the surface areas, they calculated the surface energy of sodium chloride. To date, accurate experimental techniques for the direct measurement of the surface energy of crystals are not available. Indirect methods of surface energy determination have been used. Table 1 lists the values of surface energies of some common minerals (13).

a) Silica Surface

Silica surfaces are invariably covered with chemisorbed water. By determining the specific surface area and the heat of solution of silica devoid of chemisorbed water,

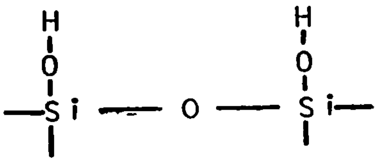
TABLE 1: Surface Energies of Some Minerals

Minerals	Face	Surface Energy, ergs/cm^2
Gypsum	010	39
Calcite	100	78
Fluorite	---	146
Apatite	prism	186
Feldspar	---	358
Quartz	---	780
Topaz	prism	1080
Corundum	---	1550

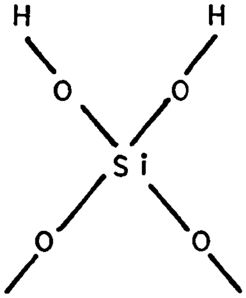
Brunauer, Kantro and Weise (14) reported the surface energy to be 259 ± 3 ergs/cm^2. From the surface energy of the completely dehydrated silica and its heat of hydration, a value of 129 ergs/cm^2 has been reported for the surface energy of fully hydroxylated silica (15). The large difference in the surface energies of the dehydrated and hydrated silica surfaces indicates the effect of adsorbed species and suggests a possible means of altering the surface properties of silicas.

The rupture of the silicon-oxygen-silicon bonds at the surface may be represented as follows (16):

Sites of the type $\equiv Si^+$ are considered to interact with water to yield surface hydroxyl groups. These hydroxyl groups may be of two types. The term "vicinal" hydroxyl groups is applied to the OH groups that are adjacent to one another, i.e.:



and the term "geminal" has been used to describe the



hydroxyl groups attached to the same silicon atom.

The silanol surface of silica can be investigated by infrared spectroscopy. A sharp and slightly asymmetric band at 3747 cm^{-1} is joined by a broad band that has maximum absorption at about 3500 cm^{-1}. The sharp band of 3747 cm^{-1} is assigned to the "isolated" (i.e., not hydrogen bonded) or free OH groups. Absorption in the 3600-3700 cm^{-1} region appears to be caused by weakly hydrogen bonded OH groups. Absorption centered in the 3400-3500 cm^{-1} region is attributed to the strongly hydrogen bonded OH groups and/or the adsorbed H_2O. The band at 3500 cm^{-1} has also been attributed to the "geminal" OH groups (17,18). Bands at 1635, 1870 and 2000 cm^{-1} appear to arise from combinations and/or overtones of the lattice vibrations (19,20).

The number of hydroxyl groups remaining on the surface after various heat treatments in vacuum has been investigated by determining the amount of water liberated during the dehydration process (21). It has been reported (21) that the hydrated silica surface when evacuated at 200°C contains about 8.0μ moles of OH/m^2, of which about 4.3μ moles represent the free hydroxyl groups and the rest are hydrogen bonded. This corresponds to 4.8 OH groups per 100 $\mathring{A}^2$. Considering the possibility that 2 OH groups may be attached per Si atom, there may be as many as 6 or more OH groups per 100 A^2 of the silica surface.

The hydration and dehydration of the silica surfaces have been studied by many investigators (22,23). The conclusion of these workers can be summarized as follows:

1. Physically adsorbed water is completely removed by pumping at room temperature.
2. Hydrogen bonded silanol groups start to condense and eliminate water at about 170°C.
3. Hydration is completely reversible for samples dehydrated at 400°C.
4. Above 400°C hydration is not reversible. The amount of hydration that can occur is inversely proportional to the temperature of the heat treatment.

5. Above 850°C no chemisorption of water occurs and the surface is rendered hydrophobic.
6. Sintering starts to occur at 900°C.

b) The Surface of Quartz

Weyl (24,25) has pointed out that, when a quartz crystal is cleaved, there must be two kinds of surfaces produced, one terminating in an oxygen atom with an excess of electrons and a negative charge, the other teminating in Si atoms with a deficiency of electrons and a positive charge. Several workers have reached the conclusion that, when quartz is pulverized, the surface of the particles is greatly perturbed. Armstrong (26) visualizes the disordered zone to be 0.5 micron or more in thickness. According to Dempster and Ritchie (27), the surface of finely ground quartz consists of a disturbed layer containing non-quartz silica. When the quartz particles are ground below 5 to 10 microns, the non-quartz content increases markedly. From the electron diffraction studies, Gibb et al. (28) reported the thickness of the amorphous surface layer to be 30 to 60 millimicrons.

c) Adsorption

Although the surface energies of pure solids are difficult to measure the changes in their energies brought about as a result of coming in contact with a reactive material are relatively easy to measure. The process by which atoms or molecules of a material, called "adsorbate", become attached to the solid surface, called "adsorbent", is known as "adsorption". The solid surfaces invariably consist of adsorption sites with a broad distribution of energies and irregular surface pattern. The density of these sites may be extremely low or high as to form a continiuum. They may be independent of each other or they may interact with their nearest neighbors. The forces binding the foreign molecules to a surface may be physical, including van der Waal's attraction forces and the forces developed by dipoles and ions as they approach the surface; or they may be equivalent to the forces in chemical bonds involving molecular orbital overlap. Adsorption can be classified as physisorption and chemisorption.

In chemisorption, the adsorbate enters the crystal lattice through chemical reaction at the inner double layer. The extent of this depends on the dimensions of the species being adsorbed and how closely they approximate the dimensions of the crystal lattice ions, the structure and composition of the mineral surface layer, and the solubility of the compounds formed. These factors, in general, lead to the high selectivity of chemisorption.

Physical adsorption takes place in the outer double layer. Any ions may be adsorbed, irrespective of their nature, dimensions or size of charge, since only the overall electrical balance is important. Consequently, physical adsorption can not be selective in relation to the solid.

1.4 THE SOLID-LIQUID INTERFACE

When a liquid is brought in contact with a solid surface there is molecular interaction between the two. A high energy surface attracts the molecules of the liquid more strongly than a low energy surface. The interaction between a liquid and a solid surface or the work of adhesion of a liquid on the solid surface can be investigated by measuring the contact angle. The contact angle for a given liquid on a low energy solid surface is larger than that on the high energy surface. On the other hand, the work of adhesion for a given liquid on the low energy surface is smaller than that on the high energy surface. The mathematical expressions of contact angle and the work of adhesion are given in Chapters 3 and 4.

1.5 OBJECTIVES OF THIS INVESTIGATION

The purpose of this investigation was to study the energetics of silica and quartz surfaces. This was done by measuring the heats of adsorption of hexane, benzene and 1,4-dioxane and contact angles of water and glycerol. Silica surfaces were then modified by reaction with normal alcohols and chlorosilanes. Changes in the surface properties as a result of these surface treatments were measured by changes in the heat of adsorption or the contact angle values. Floatability of the treated silicas was correlated in terms of the contact angles (wettability) of water or the heats of adsorption of the model compounds on these surfaces.

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CHAPTER 2

HEATS OF ADSORPTION MEASUREMENTS

2.1 INTRODUCTION

The floatability and selectivity of minerals in froth flotation depend upon the interaction of collectors with the mineral surfaces. The application of surface chemistry and thermodynamic principles to flotation systems has contributed much to the understanding of the flotation process (1).

Understanding of adsorption at the gas-liquid, gas-solid and liquid-solid interfaces is important in the selective flotation of a solid. Adsorption at the liquid-solid and gas-liquid interfaces has been investigated by many investigators (2,3). With very few exceptions inorganic solids are completely wetted by the aqueous phase. Therefore, the first step in flotation is to replace the solid-liquid interface by a solid-gas interface. Several experimental techniques, such as, infrared spectroscopy (4,5), radioactive tracers (6), electron diffraction (7), contact angle (8), surface area measurement (9) and electrochemical methods (10), have been used to study surfaces, and the adsorption processes. However, little work has been done to relate flotation to the interaction energy between the solid surface and the adsorbed species. Intensive studies of adsorption at the gas-solid interfaces is therefore required for a proper understanding of the flotation mechanism.

In this part of the investigation, gas chromatography was used to study the vapour-solid adsorption phenomena. Heats of adsorption were obtained for three compounds on Cab-O-Sil silica and natural quartz surfaces. Furthermore, the surface properties of these adsorbents were modified by reaction with alcohols and silanes and the changes thus effected were expressed in terms of changes in the heats of adsorption of the three adsorbates. Relationships between the heats of adsorption of these minerals and their floatability will be presented in Chapter 5.

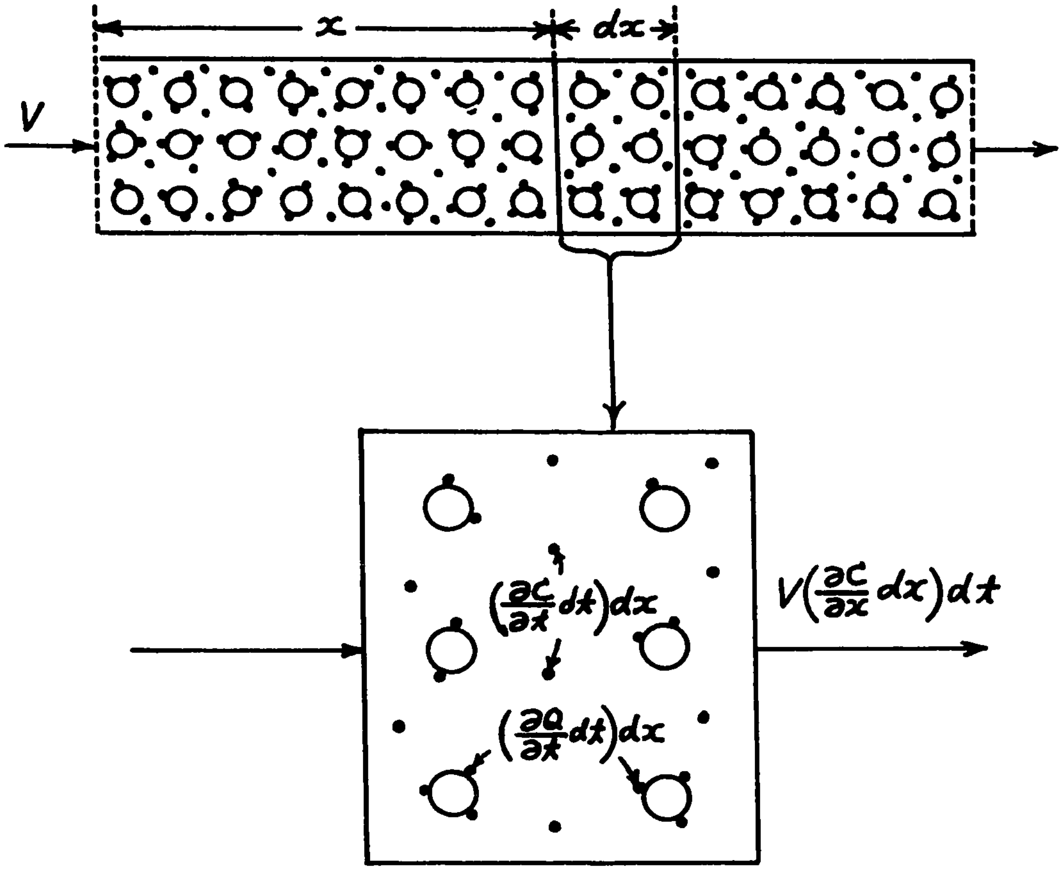
2.2 THEORY

The theoretical treatment was originally presented by Wilson (11), De Vault (12), Weiss (13) and Glueckauf (14) for the case of solid-liquid chromatography. Recently, Habgood (15) and others (16) gave relationships for the case of ideal gas-solid chromatography.

Consider a cross sectional layer of the column of thickness dX, with the carrier gas at a linear velocity V moving to distance X from the injecting time t, Figure 1. Assume that the concentration of adsorbate in the moving phase is C (moles per centimeter of the column) and the

Figure 1: The Distribution of Adsorbate and Adsorbent in a Gas Chromatographic Column

● Adsorbate, ○ Adsorbent


x
dx
V
$\left(\frac{\partial c}{\partial t}dt\right)dx$
$\left(\frac{\partial q}{\partial t}dt\right)dx$
$V\left(\frac{\partial c}{\partial x}dx\right)dt$

concentration in the stationary phase is Q (moles per centimeter of column). Since dX is small, $\partial C/\partial X$, $\partial C/\partial t$ and $\partial Q/\partial t$ may be considered substantially constant through the section. The difference between the concentration at the front of the section and that at the rear is $(\partial C/\partial X)\,dX$. The amount of adsorbate carried out of the section by the flowing gas stream exceeds the amount carried in by $V(\partial C/\partial X)(dX)\,dt$. The amount of the adsorbate in the gas phase in the section increased by the amount $(\partial C/\partial t)(dt)dX$. The amount of adsorbate adsorbed on the adsorbent in the section increases by the amount $(\partial Q/\partial t)(dt)dX$. Therefore, a material balance for a single component over an increment section of an ideal chromatographic column is given by:

$$V(\partial C/\partial X)(dX)dt + (\partial C/\partial t)(dt)dX + (\partial Q/\partial t)(dt)dX = 0$$

or

$$V(\partial C/\partial X) + (\partial C/\partial t) + (\partial Q/\partial t) = 0 \quad ....(1)$$

Since the concentration in the stationary phase is a function of the concentration in the moving phase, $Q = f(C)$, and the concentration in the moving phase is a function of the distance and time, the following relationship can be substituted into equation (1):

$$\partial Q/\partial t = \frac{\partial}{\partial t} f(C) = f'(C)\ \partial C/\partial t$$

$$\partial X/\partial t = - \frac{\partial C/\partial t}{\partial C/\partial X}$$

to obtain:

$$\partial X/\partial t = \frac{V}{1 + f'(C)} \qquad \text{..............(2)}$$

This differential equation describes the distribution of adsorbate over the stationary and the moving phases in the column at equilibrium with the carrier gas moving at constant velocity V. Integration over the length of the column (from 0 to X) and the retention time (from 0 to t_r) gives:

$$\int_0^x dX = \int_0^{t_r} \frac{V\ dt}{1 + f'(C)}$$

$$X = \frac{V\ t_r}{1 + f'(C)} \qquad \text{..............(3)}$$

Since

$$V = F \cdot X/V_d \qquad \text{..............(4)}$$

$$C = P\ V_d/XRT_c \qquad \text{..............(5)}$$

$$Q = (qm/X)\ (1/273R) \qquad \text{..............(6)}$$

where

F = the flow rate of the carrier gas

V_d = free gas volume in the column

P = partial pressure of the adsorbate

R = gas constant

T_c = the column temperature

q = adsorbate in c.c. per gram of adsorbent (STP)

m = the mass of the adsorbent in the column

The derivative f'(C) can be written as:

$$f'(C) = \frac{\partial Q}{\partial C} = \frac{m}{V_d} \frac{T_c}{273} \frac{dq}{dP} \qquad \text{.............(7)}$$

From (4) and (7), equation (3) becomes:

$$F\ t_r - V_d = \frac{T_c}{273}\ m\ \frac{dq}{dP} \qquad \text{.............(8)}$$

$$V_r - V_d = \frac{T_c}{273}\ m\ \frac{dq}{dP} \qquad \text{.............(9)}$$

where V_r is the volume of gas necessary to pass through the full length of the column with partial pressure P. The quantity $V_r - V_d$ is therefore the net retention volume. dq/dP is the slope of the adsorption isotherm. As the net retention volume at 0^oC per gram of adsorbent is defined as the specific retention volume V_g, equation (9) can be rewritten as:

$$V_g = \frac{dq}{dP} = \frac{(V_r - V_d) \times 273}{T_c \times m} \quad ....(10)$$

Since V_r and V_d refer to the column temperature T_c, it is necessary to correct the measurements by a factor of T_c/T_f, where T_f is the flowmeter temperature. Hence

$$V_r = t_r\ F\ T_c/T_f$$

$$V_d = t_d\ F\ T_c/T_f$$

where t_r is the retention time of the adsorbate, t_d is the retention time of a non-adsorbed gas. Equation (10) then becomes:

$$V_g = \frac{(t_r - t_d)\ F \times 273}{T_f \times m} \quad ....(11)$$

For a linear adsorption isotherm, dq/dP is constant and independent of the adsorbate partial pressure. The specific retention volume in milliliters is numerically equal to the slope of the adsorption isotherm in milliliters (STP) per gram of adsorbent per atmospheric pressure.

$$V_g = \frac{q}{P} \quad \ldots\ldots\ldots\ldots\ldots(11a)$$

The Clausius-Clapeyron equation may be expressed as:

$$\left(\frac{\partial \ln \frac{q}{V_g}}{\partial T}\right)_q = \frac{\Delta H}{R\ T_c^2} \quad \ldots\ldots\ldots\ldots\ldots(12)$$

where ΔH is the isosteric heat of adsorption.
Integration of this equation gives:

$$\ln \frac{q}{V_g} = -\frac{\Delta H}{R\ T_c} + A \quad \ldots\ldots\ldots\ldots\ldots(13)$$

which at constant amount of the adsorbate reduces to:

$$\ln V_g = \frac{\Delta H}{R\ T_c} + B \quad \ldots\ldots\ldots\ldots\ldots(14)$$

where A and B are constants of integration. Thus, by plotting V_g against $1/T_c$, the isosteric heat of adsorption ΔH may be obtained. Throughout the investigation F was held constant at 30 cc/min. Since the variation in T_f due to changes in room temperature was assumed to be negligible it was only necessary to plot log $(t_r - t_d)$ against $1/T_c$ to obtain isosteric heat of adsorption.

2.3 EXPERIMENTAL

a) Adsorbents:

i) Mineral Silica: Mineral silica (quartz) was ground and boiled with concentrated hydrochloric acid for several hours. The sample was then washed with distilled water until the filtrate showed no trace of chloride ion. The fraction between 48 and 65 mesh was used to pack the chromatographic columns.

ii) Cab-O-Sil Silica: In order to compare the results obtained with the mineral silica to pure silica, an amorphous thermal silica, Cab-O-Sil M-5 (particle size and surface area of 12 $m\mu$ and 199 ± 10 m^2/g respectively) was used. To assure steady flow in the chromatographic column, the original silica powder was converted into relatively granular form by wetting it with water followed by drying at 125°C under vacuum. The powder was then ground and sieved, and the fraction between 40 and 80 mesh sizes retained to pack the column.

b) Adsorbates: Reagent grade, n-hexane, benzene and 1,4-dioxane, were used as model compounds for saturated, unsaturated compounds and a compound with lone electron pairs respectively. It was hoped that the comparison of the heats of adsorption of these compounds on the two silicas would reveal the nature of the specific and non-specific interactions.

c) *Silica Surface Modification*: Both Cab-O-Sil and the mineral silicas were heated in the presence of trimethylchlorosilane and normal alcohols. Since the hydroxyl groups on these surfaces are reactive with these reagents (17,18) the surfaces were rendered partially hydrophobic. These reactions are summarized below.

$$\sim SiOH + (CH_3)_3SiCl \rightarrow \sim SiOSi(CH_3)_3 + HCl$$

$$\sim SiOH + ROH \rightarrow \sim SiOR + H_2O$$

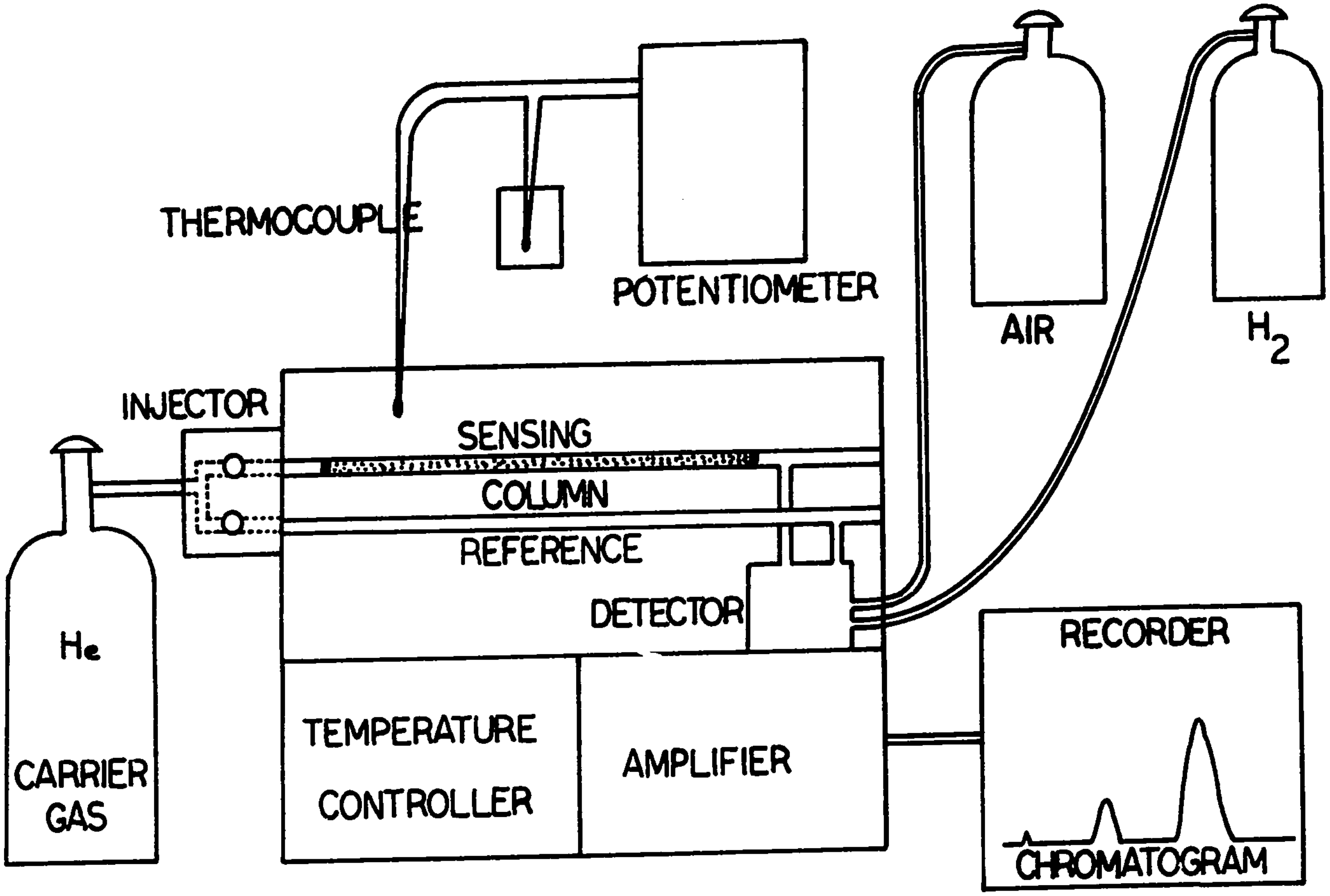
The treatments with alcohols were carried out in the liquid phase in a bomb. The temperature of the treatment was 300°C and was maintained for 2 hours. The treatments of silica with trimethylchlorosilane were done by refluxing with trimethylchlorosilane for one hour. After the treatments, the silica samples were washed with hexane and dried.

d) Apparatus: Perkin-Elmer Model 881 gas chromatograph equipped with hydrogen flame ionization detector with helium as carrier gas was used in this investigation, Figure 2.

The sensing columns were made from 1/4 inch O.D. stainless steel tubing and varied from 25 to 101 inches in length. Cab-O-Sil was packed in shorter columns while longer columns were used for the mineral silica. Freshly packed columns were conditioned at about 230°C for 3-4 hours at a flow rate slightly in excess of that used during the experiment, which was maintained at 30 cc/min. Samples of the adsorbate ranging from 0.1μl down to virtually zero were injected into the carrier gas stream with a microliter syringe. Methane was used as the reference gas.

The net retention times (time between the adsorbate and the reference peaks) and the peak heights were measured. The retention time varied with sample size when large samples were injected. Shorter retention times were found for larger samples. For small samples (peak height approaching zero), retention times were found to be independent of the peak height (i.e. sample size). From the plot of the net retention time against the peak height, the retention time at zero surface coverage was obtained. Net retention times at zero peak height were plotted against $1/T_c$ to obtain the heats of adsorption values.

Figure 2: Apparatus for Gas Chromatography



APPARATUS FOR GAS CHROMATAGRAPHY

2.4 RESULTS AND DISCUSSION

Isosteres for n-hexane, benzene and 1,4-dioxane (at surface coverage approaching zero) on unmodified and modified mineral and Cab-O-Sil silica surfaces are given in Figures 3, 4 and 5 respectively. Heat of adsorption obtained from the slopes of the isosteres for unmodified surfaces are listed in Table 1. All the adsorbates gave higher heats of adsorption on the mineral silica as compared to Cab-O-Sil. Furthermore, the heats of adsorption values for hexane and benzene are similar on the mineral, while on Cab-O-Sil benzene gave higher heat of adsorption than hexane.

Kiselev (19) reported calorimetric heats of adsorption values of 9.0 and 11.0 Kcal/mole for n-hexane and benzene respectively on Cab-O-Sil silica at half a monolayer coverage. Thus the values obtained in this investigation which were measured at surface coverage approaching zero are about 2 Kcal/mole higher than those reported by Kiselev. The dependence of the heats of adsorption on the surface coverage is related to the heterogeneous nature of the silica surfaces.

Figure 3: Plots of log $(t_r - t_d)$ Versus $10^3/T_c^o$ for Hexane on Silica Surfaces

○ untreated Cab-O-Sil

△ Cab-O-Sil treated with Trimethylchlorosilane

□ Cab-O-Sil treated with butanol

⬡ Cab-O-Sil treated with decanol

● untreated mineral silica

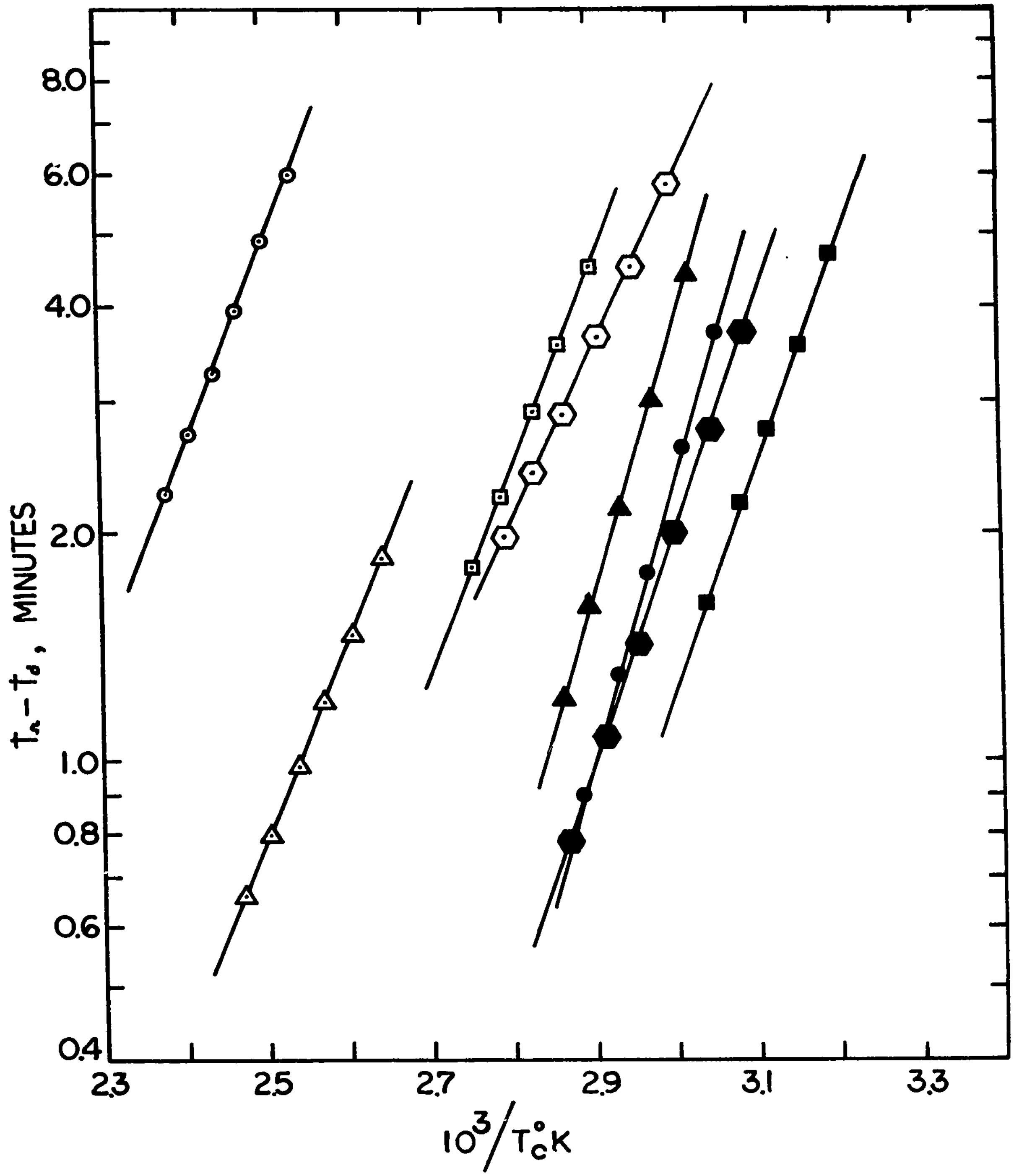
▲ mineral silica treated with Trimethylchlorosilane

■ mineral silica treated with butanol

⬢ mineral silica treated with decanol

Figure 4: Plots of log $(t_r - t_d)$ Versus $10^3/T^o_c$ for Benzene on Silica Surfaces

- ○ untreated Cab-O-Sil
- △ Cab-O-Sil treated with Trimethylchlorosilane
- □ Cab-O-Sil treated with butanol
- ⬡ Cab-O-Sil treated with decanol
- ● untreated mineral silica
- ▲ mineral silica treated with Trimethylchlorosilane
- ■ mineral silica treated with butanol
- ⬢ mineral silica treated with decanol



8.0
6.0
4.0
2.0
1.0
0.8
0.6
0.4
$t_r - t_d$, MINUTES
2.3
2.5
2.7
2.9
3.1
3.3
$10^3/T_c^\circ K$

Figure 5: Plots of log $(t_r - t_d)$ Versus $10^3/T^\circ_C$ for 1,4-Dioxane on the Silica Surfaces

○ untreated Cab-O-Sil

△ Cab-O-Sil treated with Trimethylchlorosilane

□ Cab-O-Sil treated with butanol

⬡ Cab-O-Sil treated with decanol

● untreated mineral silica

▲ mineral silica treated with Trimethylchlorosilane

■ mineral silica treated with butanol

⬢ mineral silica treated with decanol

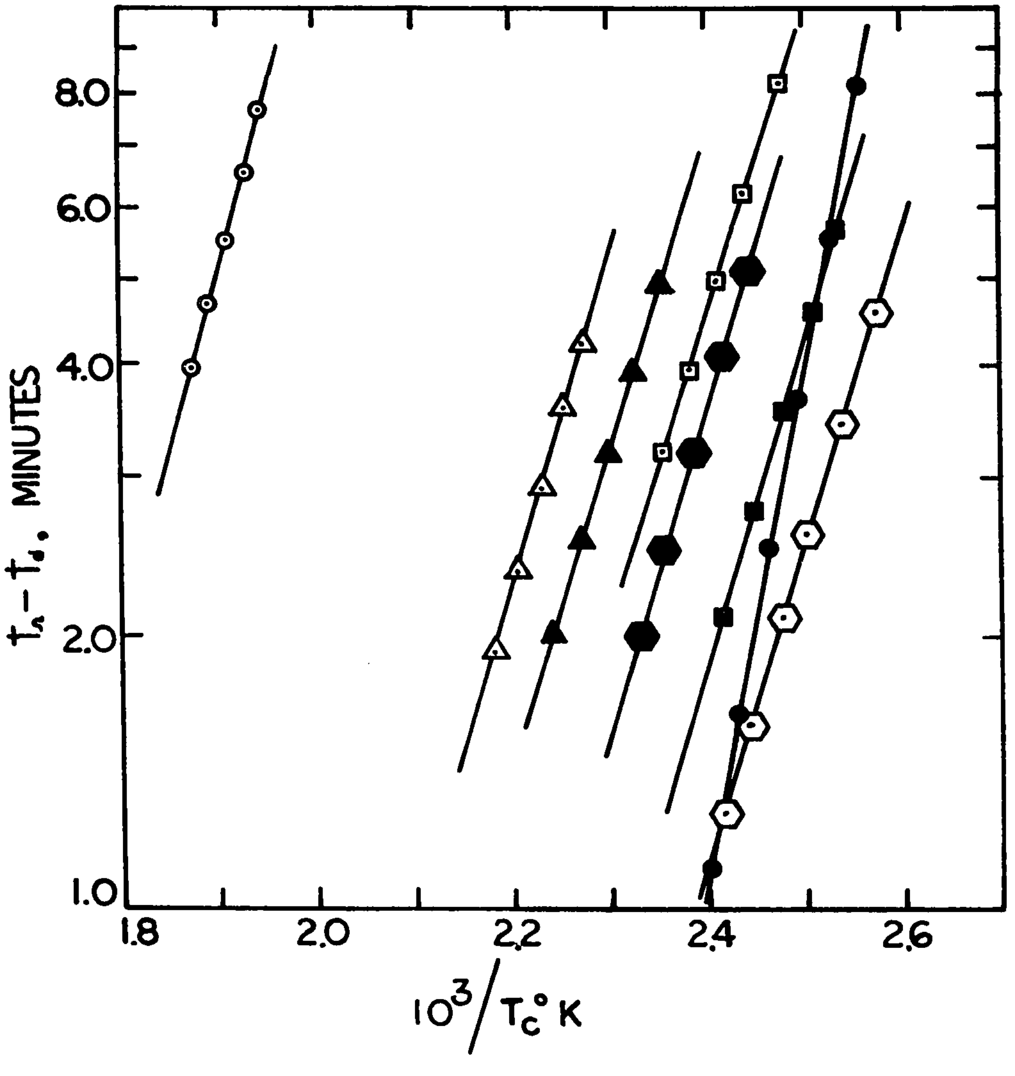

t_s - t_d, MINUTES
8.0
6.0
4.0
2.0
1.0
1.8
2.0
2.2
2.4
2.6
10^3/T_c °K

TABLE 1: Isosteric Heats of Adsorption on Untreated Silica Surfaces

Adsorbates	Adsorbents Cab-O-Sil	 Mineral
n-hexane	11.7 (Kcal/mole)	16.4 (Kcal/mole)
benzene	13.0 " "	16.6 " "
1,4-dioxane	18.5 " "	24.0 " "

The results obtained with Cab-O-Sil can be explained in terms of its surface chemistry and the molecular structure of the adsorbates. Fully hydroxylated silica surface may carry 6-8 OH groups/100 A^2 (18,20). These OH groups are found to be either hydrogen bonded to one another or free of such bonding. This difference in the physical state of the surface hydroxyl groups is manifested in heterogeneous adsorption properties of the silica surfaces. Because of the π-bonding interaction between the unshared electrons on the oxygen atom and an empty d-orbital on the silicon atom, the silanol groups on the silica surface are strongly protonized (21). Adsorbates with electron donating or proton accepting power (benzene, dioxane etc.) can therefore interact strongly via charge transfer, while saturated compounds (hexane etc.) are limited to interaction of dispersion forces only.

The results obtained with the mineral silica can be explained in terms of its physical and chemical heterogeneity, which will be discussed in the following sections.

Cab-O-Sil was prepared by hydrolysis of silicon tetrachloride at a high temperature and is completely amorphous. Mineral silica on the other hand was crystallized by the geological processes. It has higher density than Cab-O-Sil and undoubtedly possesses surface imperfections, which could serve as sites for strong dispersion forces. According to Weyl (22), when a quartz crystal is cleaved, two kinds of surfaces are produced; one terminating in oxygen atoms with an excess of negative charge, the other teminating in silicon atoms with a deficiency of electrons or positive charge. Such surfaces would enhance the adsorption energy of adsorbates especially those capable of specific interactions.

Another significant difference in the nature of the two silicas was revealed by atomic absorption spectroscopy. It was found that the mineral silica contained 12-50 ppm of each of Fe, Cu and Zn etc., where as Cab-O-Sil was free of these impurities. The metal ions are present in the mineral silica either as an inclusion or form co-ordinate linkages or both (23). In view of the fact that the heats of adsorption measurements were carried out at low surface coverages,it is possible that the presence of metal ions could cause high values on the mineral silica as compared to Cab-O-Sil.

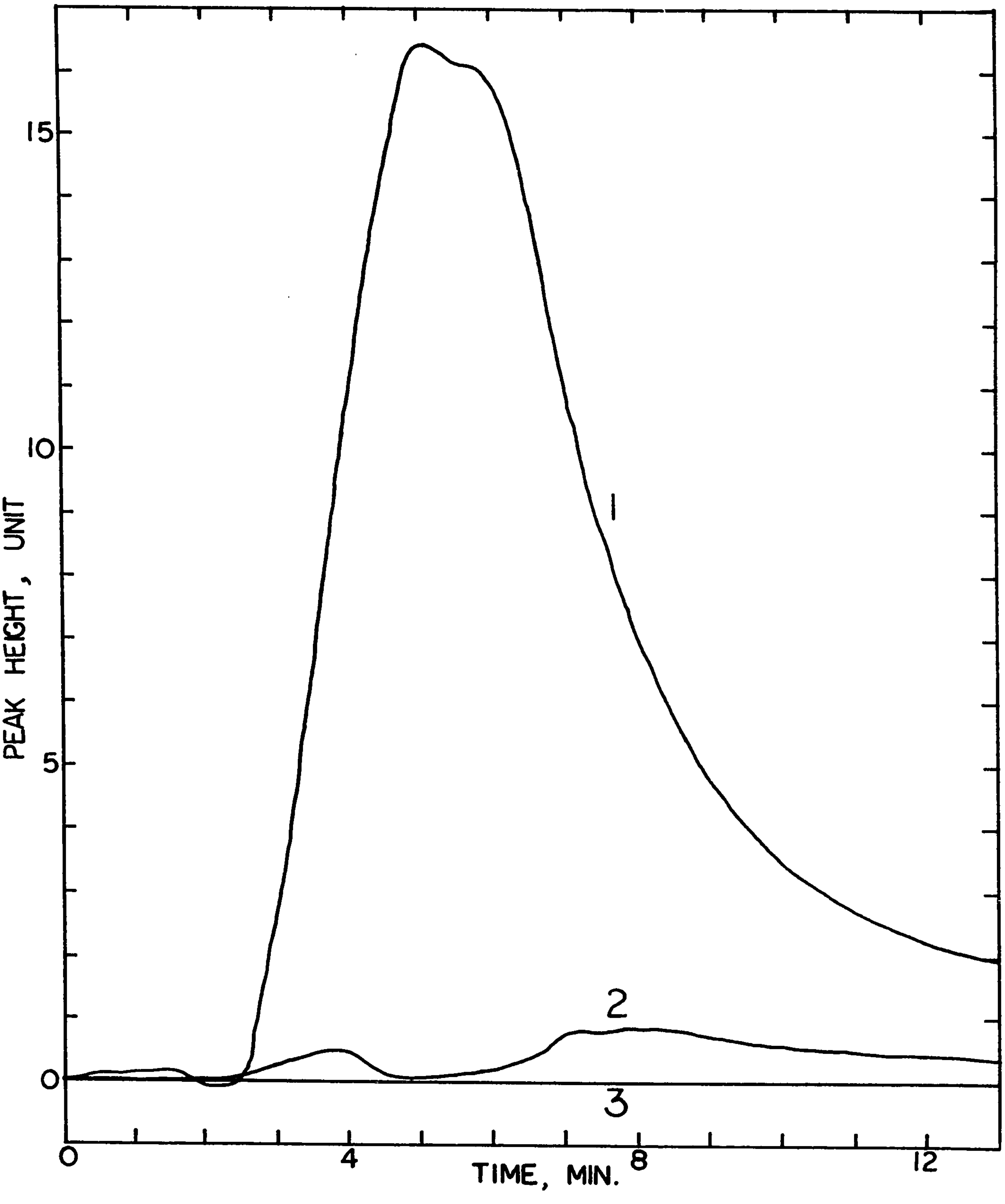
The presence of strongly adsorbing sites on the mineral silica surface was also revealed by a study of the effect of "aging" on the heats of adsorption of benzene and dioxane. For a freshly packed column, it was found that the elution peak increased in height with successive injection of constant size samples of the adsorbates. Furthermore, the elution peak shape which was asymmetrical for the new column became symmetrical for the aged column. This meant that a part of the adsorbate was retained on the adsorbent, and that the amount retained decreased with successive adsorbate samples. When the temperature of the aged column was raised from the operating temperature of 40-170°C to 250°C, a large peak was obtained (Figure 6) as a result of the elution of the adsorbed species. No such peak was observed if the temperature of a thoroughly conditioned column was raised from the operating temperature to 250°C.

Figure 6: Chromatograms for Adsorption of Dioxane or Benzene on Mineral Silica

1. Chromatogram obtained as a result of raising the temperature to 250°C of a column on which benzene or dioxane had been used at 150°C.

2. Base line of a conditioned but unused column as a result of the above temperature change.

3. Base line of a conditioned column at a fixed temperature.



PEAK HEIGHT, UNIT
15
10
5
0
1
2
3
0
4
8
12
TIME, MIN.

The effect of "aging" on the heat of adsorption was also determined. The heat of adsorption was maximum when the column was conditioned at elevated temperature after each measurement of the retention time. A value of 16.6 Kcal/mole for the heat of adsorption of benzene was determined following this procedure. However, after a series of adsorption tests, this value decreased to 8.4 Kcal/mole, which corresponds roughly to its heat of condensation. Similar effect was observed for dioxane, but not for hexane.

The results reported here are in accord with the heats of immersion values obtained with quartz and synthetic silica (24,25,26), the former giving higher values than the latter. Young and Bursh (24) attributed the high heats of immersion for quartz to the more intense electrostatic force field associated with the surface silanol groups. It was postulated that the polarity of the surface OH groups increased with crystallinity of the silica.

Table 2 and 3 list the heats of adsorption of the three adsorbates on silica surfaces modified by reaction with trimethylchlorosilane, n-butanol and n-decanol. n-hexane showed essentially no diminution in the heat of adsorption on the treated surfaces as compared to the untreated surfaces. Benzene and dioxane (which are capable of specific

TABLE 2: Isosteric Heats of Adsorption on Modified Cab-O-Sil Silica

Adsorbates	Surface Treatment Trimethylchlorosilane	 Butanol	 Decanol
Hexane	11.7 (Kcal/mole)	11.7 (Kcal/mole)	11.7 (Kcal/mole)
Benzene	11.9 " "	11.9 " "	10.7 " "
Dioxane	16.1 " "	16.0 " "	15.7 " "

TABLE 3: Isosteric Heats of Adsorption on Modified Mineral Silica

Adsorbates	Surface Treatment Trimethylchlorosilane	 Butanol	 Decanol
Hexane	16.4 (Kcal/mole)	16.4 (Kcal/mole)	16.4 (Kcal/mole)
Benzene	15.8 " "	13.9 " "	13.6 " "
Dioxane	16.3 " "	16.3 " "	15.8 " "

interaction with the surface hydroxyl groups) gave lower values on the treated surfaces - the order of decreasing heat of adsorption being trimethylchlorosilane<Butanol<Decanol. These results are in agreement with those obtained with low molecular weight methylsiloxanes on modified silica surfaces (27). It was shown that the decrease in the heat of adsorption of a compound was dependent on the size of the substituent groups and their concentration on the silica surface.

As mentioned in the experimental part, the treatments were designed for maximum modification of the surface although the extent of the reaction was not determined quantitatively. The diminution in the heat of adsorption values for benzene and dioxane on Cab-O-Sil surfaces could, however, be qualitatively related to the intensity of the infrared absorption peaks (C-H stretching at 2960 cm^{-1}) due to the chemisorbed alkyl groups. Similar measurements could not be made on the mineral silica because it was not possible to obtain its infrared spectra. However, diminution in the heats of adsorption obtained on modified mineral surfaces similar to that obtained on modified Cab-O-Sil surfaces suggests the presence of chemisorbed alkyl groups on the mineral surface.

2.5 CONCLUSION

Gas chromatography was used to investigate the nature of the interaction between three model compounds and the silica surfaces. Isosteric heats of adsorption at surface coverage approaching zero were measured for n-hexane, benzene and 1,4-dioxane on synthetic thermal silica and natural silica mineral. The results obtained with Cab-O-Sil (synthetic) silica agreed reasonably well with the reported values and could be explained in terms of the molecular structure of the adsorbates. Higher heats of adsorption values were obtained for all the adsorbates on the mineral quartz. Elution of constant size samples of benzene and dioxane on the mineral quartz revealed irreversible adsorption at ordinary temperatures. As a result, the heats of adsorption of these compounds on the mineral silica decreased with prolonged use. Silica surfaces were modified by reaction with trimethylchlorosilane and normal alcohols. Modified surfaces gave lower heats of adsorption for benzene and 1,4-dioxane. The heat of adsorption of n-hexane was essentially unchanged as a result of these treatments.

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CHAPTER 3

CONTACT ANGLE MEASUREMENTS

3.1 INTRODUCTION

The primary requisite for flotation is the attachment of air bubbles to the mineral particles. Thus sufficient attraction must exist between the mineral and air for the latter to be able to displace water at the mineral surface. If replacement of water by air is not possible, flotation from an aqueous phase would be impossible.

Contact angle measurement can be used to study the attraction between air and the mineral surface. The results of Taggart, Taylor and Ince (1) had shown considerable promise and the earlier work of Langmuir (2) and Sulman (3) was also encouraging. Traube and Mishizewa (4) have pointed out the connection between the contact angle, wetting, adhesion, adsorption and flotation. The contact angle data published by Wark and Cox (5) greatly enhanced our understanding of these systems. Recently, many investigators (6-10) have shown that contact angle can be correlated directly with flotation. Schulman and Leja (11-13) have reported that a mixed monolayer of collector and frother molecules at the solid-air interface produces high contact angle, a condition which is favorable for flotation. Bailey and Gray (14,15) have discussed some of the implications of contact angle hysteresis in flotation.

We have shown (Chapter 2), that the heat of adsorption of a substance on a solid surface depends upon the surface characteristics. Since the equilibrium contact angle of a liquid on a solid substrate is related to the liquid-air, solid-air and the solid-liquid interfacial energies, it is therefore obvious that there must be a relationship between the contact angle and the nature and the magnitude of the density of a surface-active substance on the mineral surface. Indeed, it has been shown that the nature of the collector is an important factor in flotation (16). Morrow (17) has investigated the relationship between contact angle and adsorption of dodecylammonium acetate on hematite. Although the contact angle increased with the concentration of the adsorbate the relationship between them was somewhat complex. Wark and Cox (5) showed that at small concentrations of potassium ethyl xanthate on galena the contact angle of water increased from 0 to an equilibrium value of 60. Similar effect has been reported for heptylic acid on sphalerite (18). Wadsworth, Canrady and Cook (19) have reported a linear relationship between contact angle and the adsorption of a collector. Philipoff, Cooke and Caldwell (20), Shafrin and Zisman (21) on the other hand have suggested a linear relationship between the consine of the contact angle and the density of adsorption. Gaudin (22), while disagreeing with the details of the above views, nevertheless admits the existence of a relationship between contact angle and the adsorption of a collector.

Contact angle values depend upon the method of measurement and the condition of the surface. The spread between the maximum and minimum contact angles measured on the same system is called hystersis (23). The penetration of the solid by the liquid is perhaps the most general cause of hysteresis of the contact angle (24). Adam (25) and Kawasaki (26) have reported that penetration by the liquid lowers the advancing angle only slightly, while the receding angle is affected to a larger extent.

In this chapter we will discuss the wettability of solid surfaces measured in terms of the contact angles of water and glycerol on these surfaces. Silica surfaces were modified by reaction with alcohols and silanes to various coverages. This enabled us to establish the relationship between contact angle and the surface coverage of the various functional groups.

3.2 THEORY

The behaviour of a liquid on a solid surface is characterized by a contact angle given by the Young's equation.

$$\mathrm{Cos}\ \theta = \frac{\gamma_{sa} - \gamma_{sL}}{\gamma_{La}} \qquad (1)$$

Where θ is the contact angle between the liquid and solid surface measured across the liquid phase.

γ_{sa} is the solid-air interfacial energy

γ_{sL} is the solid-liquid interfacial energy

γ_{La} is the liquid-air interfacial energy

The contact angle will be less than 90° if $\gamma_{sa} > \gamma_{sL}$ and greater than 90° if $\gamma_{sa} < \gamma_{sL}$. For a stable contact angle the inequality $(\gamma_{sa} - \gamma_{sL}) < \gamma_{La}$ must be satisfied. If $(\gamma_{sa} - \gamma_{sL}) \geq \gamma_{La}$, the liquid completely wets the solid surface.

Consider a mineral surface adsorbed with an incomplete monolayer of a collector. Let x_1 represent the fraction of the surface devoid of the collector and θ_1 the contact angle on this surface. Likewise, let x_2 be the fraction of the surface covered with the collector and θ_2 the contact angle on this surface. Then the contact angle on the composite (heterogeneous) surface would be given by (27-29,20):

$$\text{Cos } \theta = x_1 \text{ Cos } \theta_1 + x_2 \text{ Cos } \theta_2 \quad \ldots\ldots\ldots(2)$$

Since $x_1 + x_2 = 1$ ....(3)

equation (2) can be written as

$$\text{Cos } \theta = \text{Cos } \theta_1 - x_2 (\text{Cos } \theta_1 - \text{Cos } \theta_2) \quad \ldots\ldots\ldots(4)$$

For the clean mineral surfaces (with the exception of mica, molybdenite etc.) Cos θ_1 may be taken as one, i.e. complete wetting. Surfaces adsorbed with a monolayer of the collector however give a finite contact angle. Equation (4) therefore becomes:

$$\text{Cos } \theta = 1 - x_2 (1 - \text{Cos } \theta_2) \quad \ldots\ldots\ldots(5)$$

or

$$\text{Cos } \theta = 1 - Kx_2 \quad \ldots\ldots\ldots(6)$$

where K = 1 - Cos θ_2 is a constant. Larger coverage of the surface (x_2), gives larger but negative values of the Cos θ.

Assuming (q) to be the number of the adsorbate molecules per 100 $\mathring{A}^2$, and a the area covered by one adsorbate molecule in $\mathring{A}^2$, then $\frac{qa}{100}$ gives the fraction of the surface area covered by the adsorbate. Equation (5) can be written as:

$$\text{Cos}\,\theta = 1 - (1 - \text{Cos}\,\theta_2)\,\frac{qa}{100} \qquad \ldots\ldots(7)$$

From the measured values of the contact angle on the solid surfaces covered with a given density of the adsorbate molecules, it should be possible with the use of equation (7) to calculate the area covered by each molecule, i.e., the cross section area of the adsorbed molecule.

3.3 EXPERIMENTAL

a) Materials

Contact angle measurements were restricted to the amorphous thermal silica, Cab-O-Sil M-5. Its surface modification was described in Chapter 2. The surface coverages were established by total carbon analysis using the following formula:

$$N = \frac{6.02 \times 10^{23} \times C}{n \times 12 \times 199 \times 10^{18}}$$

Where N is the number of alkoxy group/100 $\mathring{A}^2$

C is the grams of carbon per gram of silica

n is the number of carbon atomsper alkoxy group

b) Contact Angle Measurement

A Perkin-Elmer KBr Die, was used to press roughly 30 mg silica samples into thin discs, or pellets under a pressure of 20,000 psi. The sessile drop technique was used throughout. Drops of water and glycerol, roughly 1 microliter in volume were placed on the silica discs with the help of a microliter syringe. Measurements were made at room temperature (i.e., $25^{o}C \pm 2^{o}C$). A horizontal style microscope with cross hair and scale objective was used to measure the angle between the solid-air and solid-liquid interfaces. Contact angle readings were made every 30 seconds on both sides of the drop. Measurements were made on 8 separate drops and the average was taken. Individual measurements differed by no more than $\pm 1^{o}$. Evaporation losses while not a problem in the case of glycerol were quite serious in the case of water. Attempts were made to minimize this effect by keeping open water in the assembly housing the microscope.

3.4 RESULTS AND DISCUSSION

The contact angle values for water and glycerol on the silica surfaces treated with alcohols and silanes are listed in Tables 1 and 2. It was observed that the volume of the water drop decreased gradually due to evaporation. However, the contact area between water and solid surface invariably remained constant until the disappearance of the liquid, Figure 1(a). Thus as the height of the drop decreased the contact angle decreased. Figure 2 shows the plot of contact angle versus time for water on silica surfaces treated with butanol to different surface coverages. Initially the decrease in the contact angle is small, but decreased more rapidly after a few seconds. The decrease in the volume of water may in part be due to the penetration of water into the porous matrix. Similar results were obtained with surfaces treated with other alcohols.

The results obtained with water on silica surfaces treated with silanes are shown in Figure 3. On surfaces with higher coverages of silyl groups (i.e. 3.57 or 5.33 silyl groups/100 $\mathring{A}^2$), it was found that as the height of the water drop decreased, the solid-liquid contact area also decreased there-by maintaining almost the same ratio between the drop height and the contact area, Figure 1(b).

TABLE 1: Water and Glycerol Contact Angles on Silica Surfaces Treated with Alcohols

Treatment	Surface Coverage (Alkoxy groups/100Å^2)	Contact Angle, Degrees Water	Contact Angle, Degrees Glycerol
Methanol	1.05	spreads	20
	3.48	spreads	23
	3.86	spreads	33
	4.21	79	41
	4.50	111	52
Ethanol	0.76	spreads	24
	1.78	spreads	26
	2.73	45	39
	3.22	115	72
	3.59	128	115
Butanol	0.69	spreads	27
	1.43	spreads	29
	2.28	spreads	35
	2.59	110	51
	2.69	116	87
	3.04	127	105
Hexanol	0.57	spreads	23
	0.91	spreads	24
	1.47	51	33
	2.10	123	91
	2.46	133	122
	2.69	136	126
Decanol	0.46	spreads	26
	0.99	18	34
	1.62	116	92
	1.94	125	116
	2.03	127	120

TABLE 2: Water and Glycerol Contact Angle on Silica Surfaces Treated with Silanes

Treatment	Surface Coverage (Silyl Groups/100Å^2)	Contact Angle, Degrees Water	Contact Angle, Degrees Glycerol
	1.8	40	27
	2.5	90	40
CH_3SiHCl	3.6	113	71
	5.3	130	120
	5.6	131	122
	1.63	30	30
	2.24	104	43
$(CH_3)_2SiCl_2$	3.57	128	100
	5.33	134	125
	6.90	137	129
	1.28	30	30
$(CH_3)_3SiCl$	1.47	81	35
	1.70	131	100
	2.07	135	130

Figure 1: Water and Glycerol Drops in Silica Surfaces Treated with Alcohols and Silanes

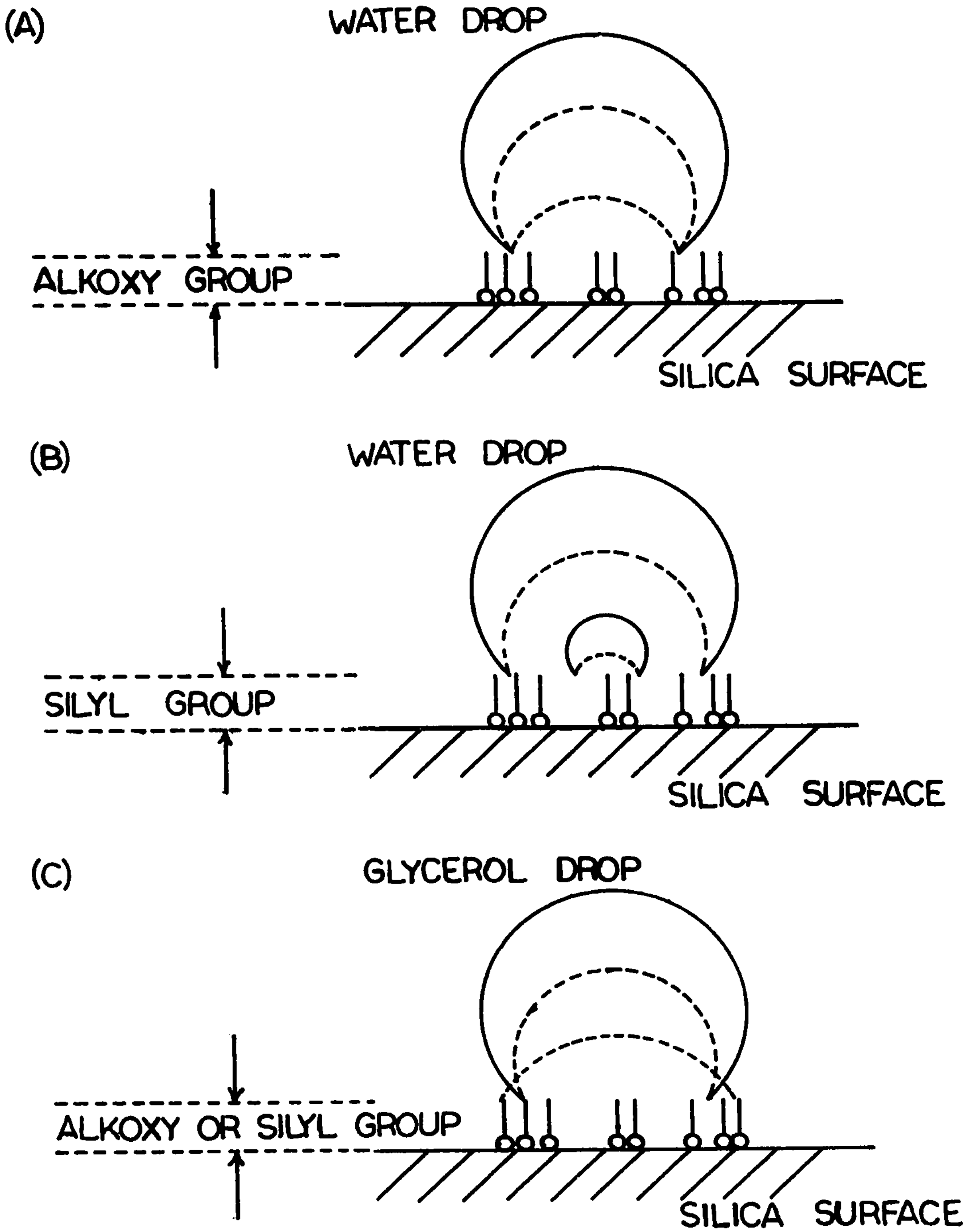
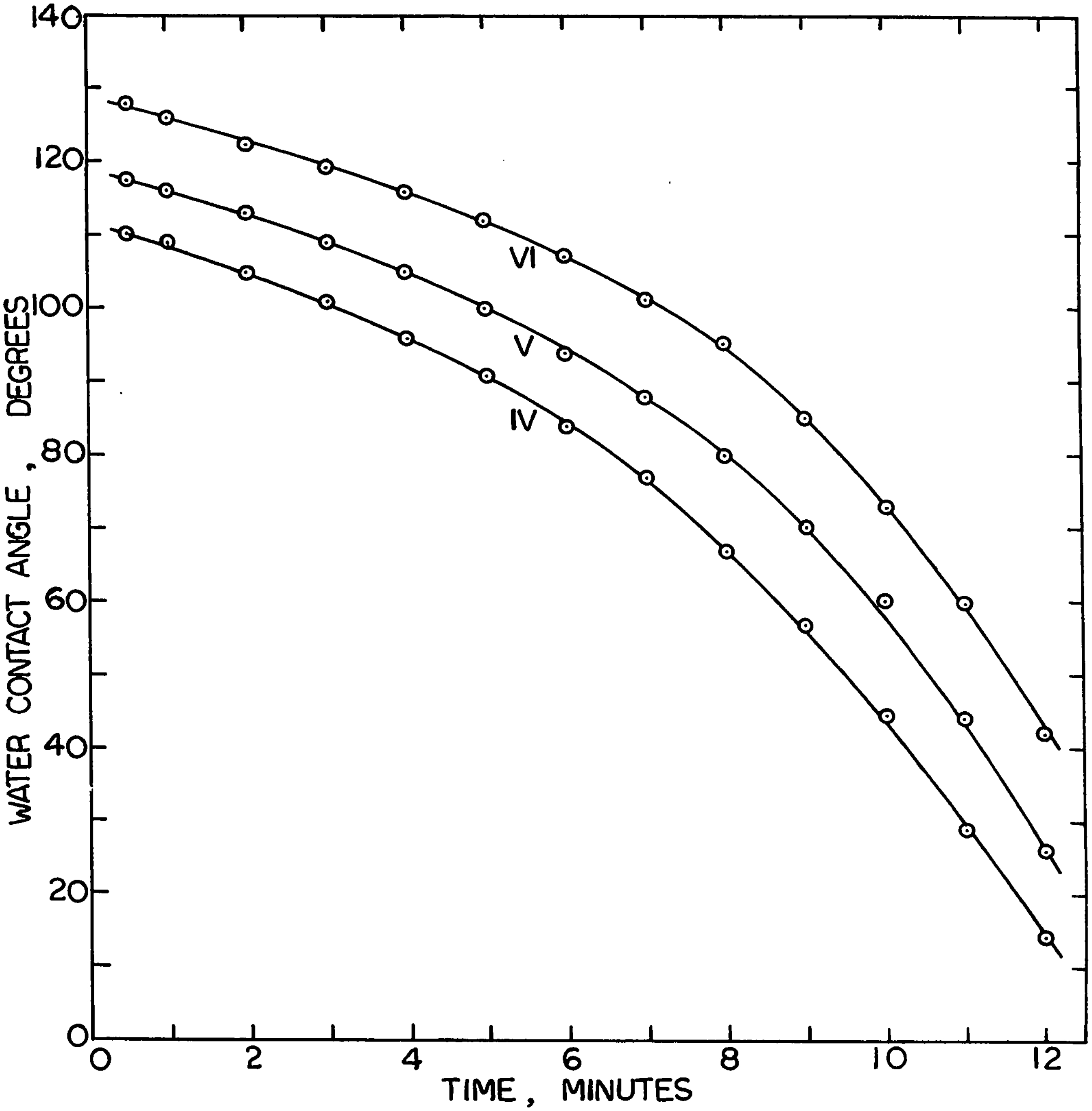

(A)
WATER DROP
ALKOXY GROUP
SILICA SURFACE
(B)
WATER DROP
SILYL GROUP
SILICA SURFACE
(C)
GLYCEROL DROP
ALKOXY OR SILYL GROUP
SILICA SURFACE

Figure 2: Water Contact Angle on Butanol Treated Silica Surfaces as a Function of Time

(IV) 2.59 butoxy groups/100 $\mathring{A}^2$

(V) 2.69 butoxy groups/100 $\mathring{A}^2$

(VI) 3.04 butoxy groups/100 $\mathring{A}^2$



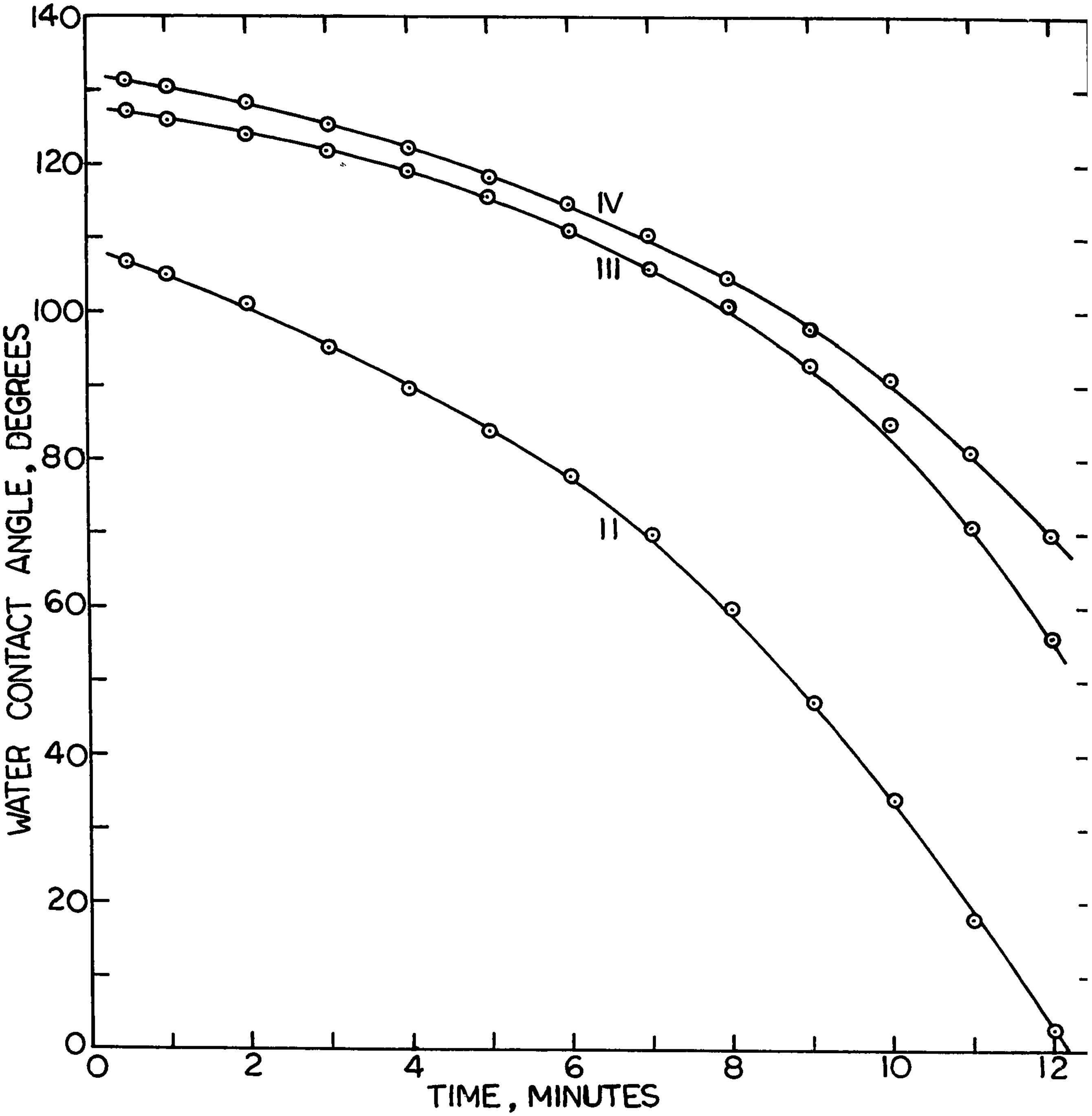
140
120
100
80
60
40
20
0
WATER CONTACT ANGLE , DEGREES
0
2
4
6
8
10
12
TIME , MINUTES
VI
V
IV

Figure 3: Water Contact Angle on $(CH_3)_2SiCl_2$ Treated Silica Surfaces as a Function of Time

(II) 2.24 silyl groups/100 Å^2

(III) 3.57 silyl groups/100 Å^2

(IV) 5.33 silyl groups/100 Å^2



140
120
100
80
60
40
20
0
WATER CONTACT ANGLE, DEGREES
0
2
4
6
8
10
12
TIME, MINUTES
IV
III
II

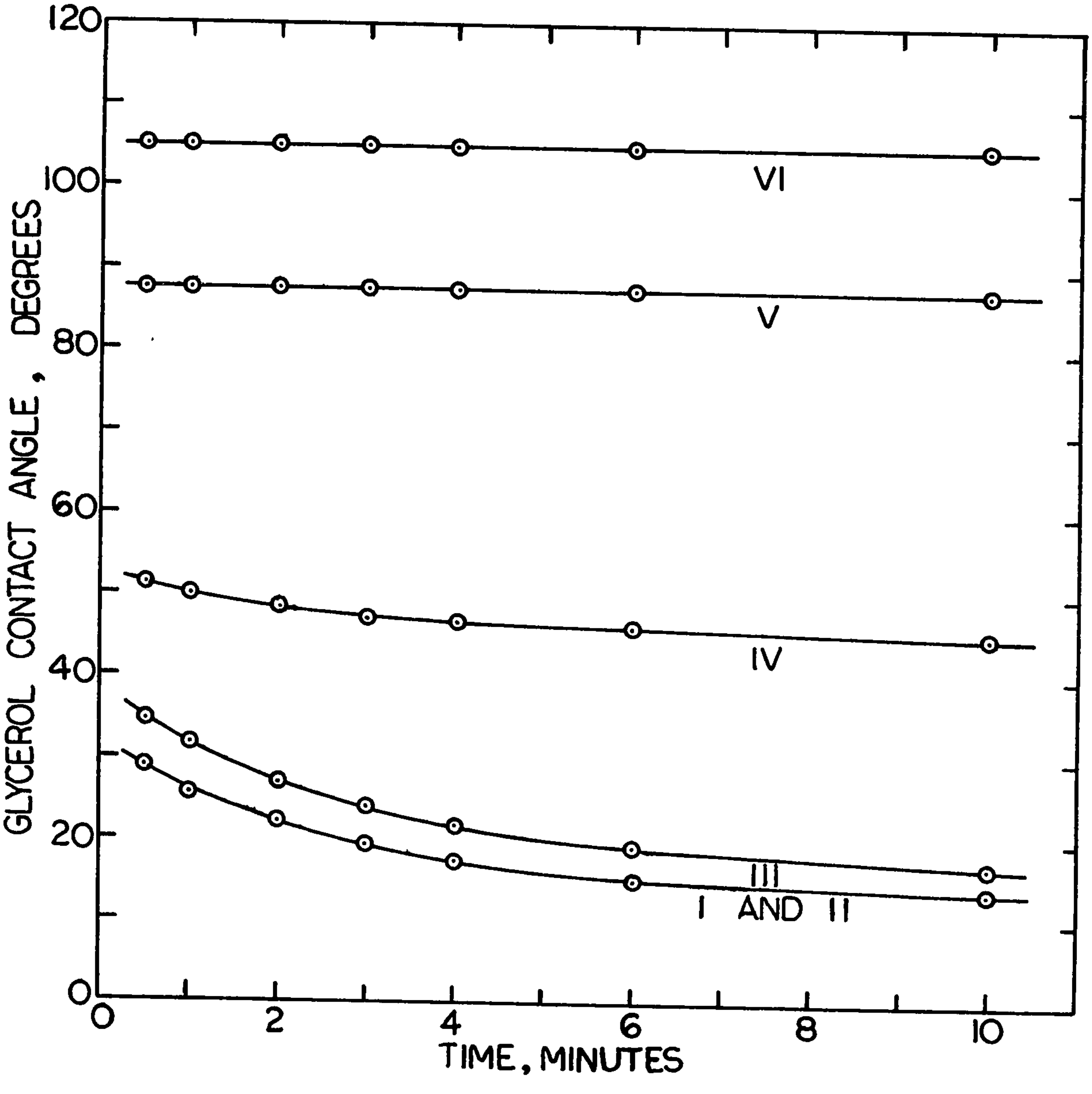
The retraction of the solid-liquid interface may reflect the homogeneous nature of the surfaces treated with silanes. On heterogeneous surfaces on the other hand as the drop evaporates the solid-liquid interfacial area remains constant causing the contact angle to decrease. Other investigators have made similar observations (30,31).

It was found that at low surface coverages of the alkoxy or silyl groups the spreading of the drops was practically instantaneous. This aspect of the results will be further discussed in later sections.

In order to overcome the effects of evaporation on the contact angles of water, glycerol, a relatively non-volatile liquid, was employed as a model compound for water. The dependence of the contact angle of glycerol on time on surfaces treated with alcohols and silanes is shown in Figures 4 and 5 respectively. It was found that the contact area of glycerol on all surfaces whether treated with alcohols or silanes increased slowly, Figure 1(c). On surfaces with maximum coverage of the alkoxy or silyl groups the glycerol drop was particularly stable giving constant value of the contact angle over long periods of time. At low surface coverage of the alkoxy groups, i.e., 0.69, 1.43 and 2.28 butoxy groups/100 $\mathring{A}^2$ or 1.63 silyl groups/100 $\mathring{A}^2$,

Figure 4: Glycerol Contact Angle on Butanol Treated Silica Surfaces as a Function of Time

I 0.69 butoxy groups/100 Å^2
II 1.43 butoxy groups/100 Å^2
III 2.28 butoxy groups/100 Å^2
IV 2.59 butoxy groups/100 Å^2
V 2.69 butoxy groups/100 Å^2
VI 3.04 butoxy groups/100 Å^2



120
100
80
60
40
20
0
GLYCEROL CONTACT ANGLE, DEGREES
0
2
4
6
8
10
TIME, MINUTES
VI
V
IV
III
I AND II

Figure 5: Glycerol Contact Angle on $(CH_3)_2SiCl_2$ Treated Silica Surfaces as a Function of Time

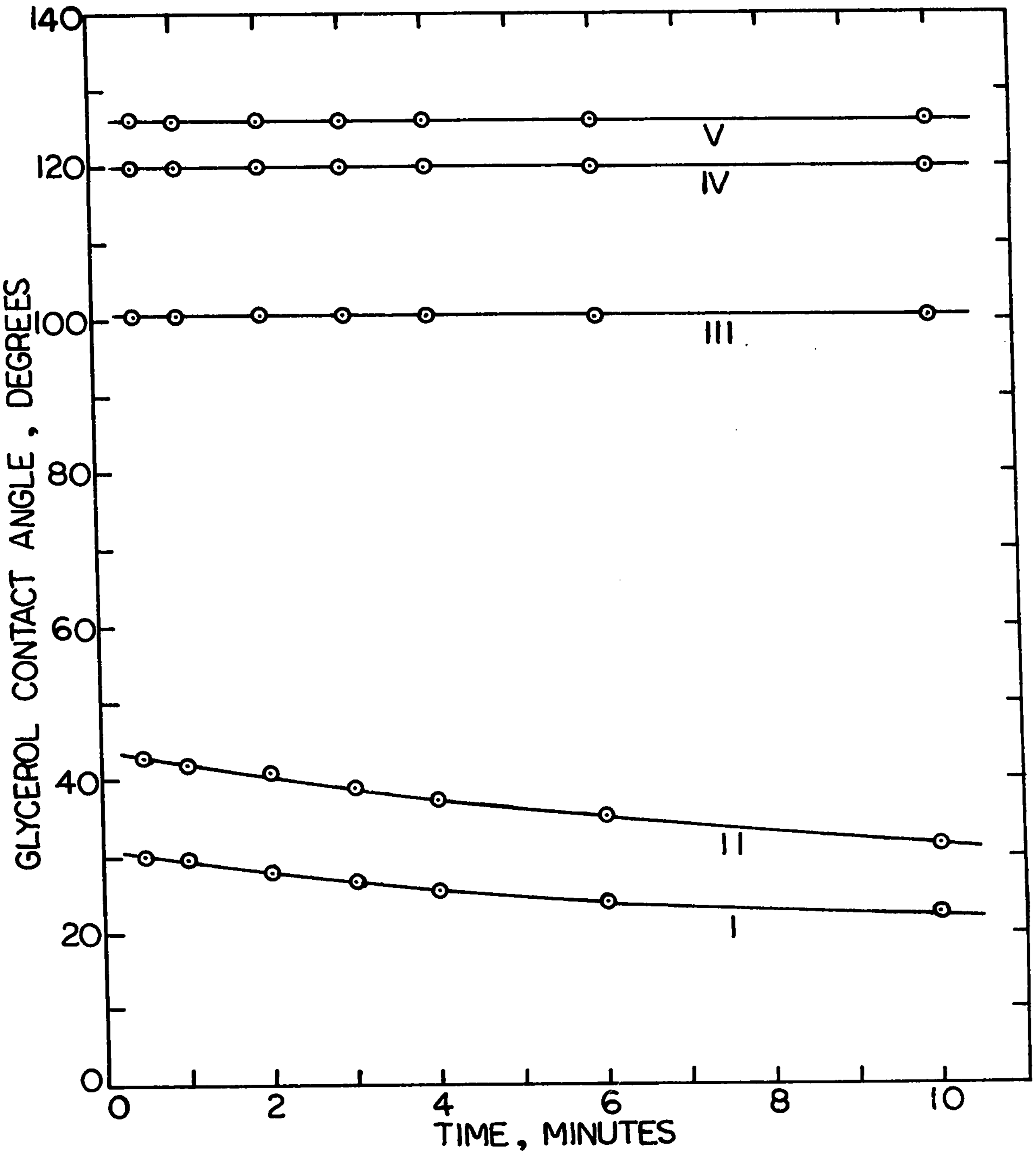
I 1.63 silyl groups/100 Å^2

II 2.24 silyl groups/100 Å^2

III 3.57 silyl groups/100 Å^2

IV 5.33 silyl groups/100 Å^2

V 6.90 silyl groups/100 Å^2


140
120
100
80
60
40
20
0
GLYCEROL CONTACT ANGLE , DEGREES
0
2
4
6
8
10
TIME, MINUTES
V
IV
III
II
I

where as the water drop spread instantaneously, the glycerol contact angle decreased only slowly,approaching zero only after a long time. The magnitude of the contact angle and its stability are thus governed by: 1) the molecular structure of the liquid or its surface tension, and 2) the nature of the interaction between the liquid and the surface of the adsorbent or the adsorbed species.

a) The Effect of Liquid Surface Tension

Upon comparing the contact angles for water and glycerol on a given surface (Figure 2 versus Figure 4, and Figure 3 versus Figure 5), it can be clearly seen that the former always gave the larger values. For example, on a surface covered with 3.04 butoxy groups/100 $\mathring{A}^2$, the contact angles for water and glycerol were 128° and 105° respectively. Similarly on a surface with 5.33 silyl groups/100 $\mathring{A}^2$, where-as water gave a contact angle of 131°, the contact angle for glycerol was 120°. This can be easily explained by comparing the work of adhesion and cohesion of the liquids on the solid surfaces.

The spreading coefficient ($S_{\ell s}$) for a liquid (ℓ) on a solid (s) is defined as (32,33):

$$S_{\ell s} = W_{\ell s} - W_{\ell} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

Where $W_{\ell s}$ is the work of adhesion of a liquid on the solid and W_{ℓ} is the work of cohesion of the liquid.

Since,

$$W_{\ell} = 2\ \gamma_{a\ell} \qquad \ldots\ldots\ldots\ldots\ldots(9)$$

$$W_{\ell s} = \gamma_{a\ell}\ (\mathrm{Cos}\ \theta + 1) \qquad \ldots\ldots\ldots\ldots\ldots(10)$$

Thus,

$$S_{\ell s} = W_{\ell s} - 2\ \gamma_{a\ell} \qquad \ldots\ldots\ldots\ldots\ldots(11)$$

or

$$S_{\ell s} = \gamma_{a\ell}\ (\mathrm{Cos}\ \theta - 1) \qquad \ldots\ldots\ldots\ldots\ldots(12)$$

$$\mathrm{Cos}\ \theta = \frac{S_{\ell s}}{\gamma_{a\ell}} + 1 \qquad \ldots\ldots\ldots\ldots\ldots(13)$$

From equation (13), it is clear that for the liquid to spread on the solid $S_{\ell s}$ must be equal to or larger than zero. A finite contact angle will be obtained only when $S_{\ell s}$ becomes negative and the spreading coefficient decreased with increasing liquid surface tension. The more negative the values of $S_{\ell s}$, the larger the contact angle for the liquid on the solid. Fox and Zisman (34) have shown that as the surface tension of the liquid $\gamma_{a\ell}$ decreases, the contact angle θ on a given surface decreases and the spreading coefficient $S_{\ell s}$ becomes less negative. Therefore, a liquid with larger surface tension would give the larger contact angle.

b) The Effect of Molecular Structure of the Adsorbed Species

Water was found to spread instantaneously on a surface with 2.28 butoxy groups/100 $\mathring{A}^2$ while glycerol gave a contact angle of 35° on the same surface (Figures 2 and 4). On the other hand, the contact angles for water and glycerol on a surface with 2.24 $(CH_3)_2Si$-groups/100 $\mathring{A}^2$ were 107° and 43° respectively (Figures 3 and 5). These results indicate that the chemical structure of the adsorbed species is an important factor in determining the value of the contact angle.

An alkoxy group is a straight chain hydrocarbon with $-CH_2-$ groups ending in a $-CH_3$ group. A silyl group is a side chain hydrocarbon with $-CH_3$ groups only. Adam (35) and others (34,36) reported that methylene groups have 30% higher attraction for water than methyl groups. For example, hexamethylethane, which has nothing but methyl groups, gave contact angle of 115°, while cycloparaffins with CH_2 groups, gave a contact angle of 104°. The difference between these values reflects the difference in the packing of the terminal groups of aliphatic chains. The difference in the contact angles on silica surfaces treated with alcohols and silanes could be explained in the same fashion.

Figure 6, illustrates a simplified model of the alkoxy and silyl groups on the silica surface. If the hydroxyl groups on the silica surfaces were only partially reacted with alcohols or silanes, then the hydrophobicity of the reacted surface will depend primarily on the ability of the alkoxy or silyl group to cover up the hydroxyl groups. Figure 6(c) shows that a silyl group is larger than the hydroxyl groups with the $-CH_3$ groups stretching over the hydrophilic -OH groups. Therefore, the degree of hydrophobicity of a silane treated surface should increase as the number of $-CH_3$ groups in a silane molecule increases. Figure 6(b) indicates that the alkoxy groups of aliphatic alcohols should stand perpendicular or inclined to the silica surface. The ability of the alkoxy groups to cover the unreacted -OH groups depends mainly on the number of $-CH_2$ groups. Methanol, comprising of only one $-CH_3$ group could not effectively shield the -OH groups. Therefore, the only way to obtain hydrophobic silica surface by reacting with methanol would be to replace most of the -OH groups with methoxy groups. Hexanol and decanol having longer chains could on the other hand produce hydrophobic silica surfaces at coverages lower than that for methanol because of their shielding effects. Thus a few long alkoxy groups have the same effect as a large number of short chain alkoxy groups.

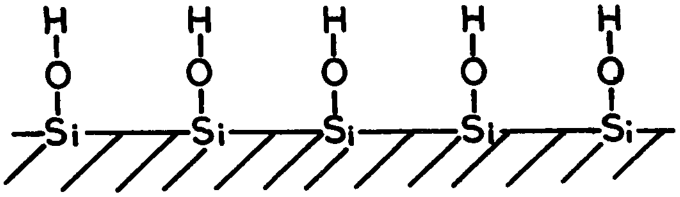
Figure 6: The Configuration of the Alkyl and Silyl Groups on Silica Surfaces

A. Silica surface prior to modifications

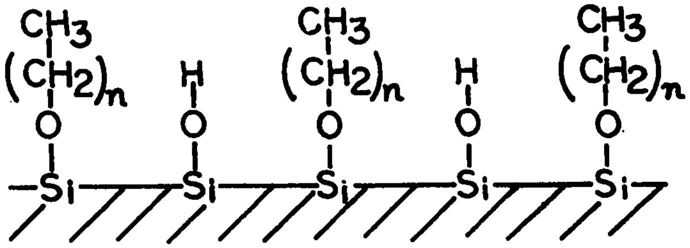
B. Silica surface treated with alcohols

C. Silica surface treated with silanes

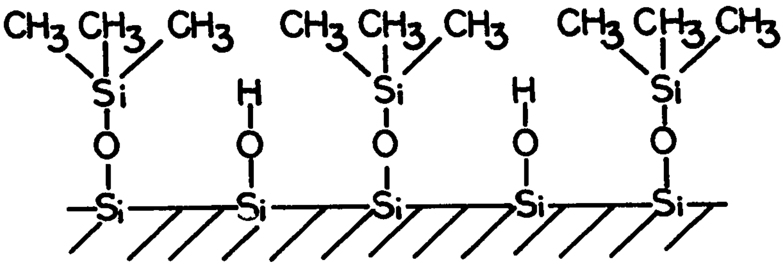
(A)


H H H H H
O O O O O
Si Si Si Si Si

(B)


CH3 CH3 CH3
(CH2)n H (CH2)n H (CH2)n
O O O O O
Si Si Si Si Si

(C)


CH3 CH3 CH3 CH3 CH3 CH3 CH3 CH3 CH3
Si H Si H Si
O O O O O
Si Si Si Si Si

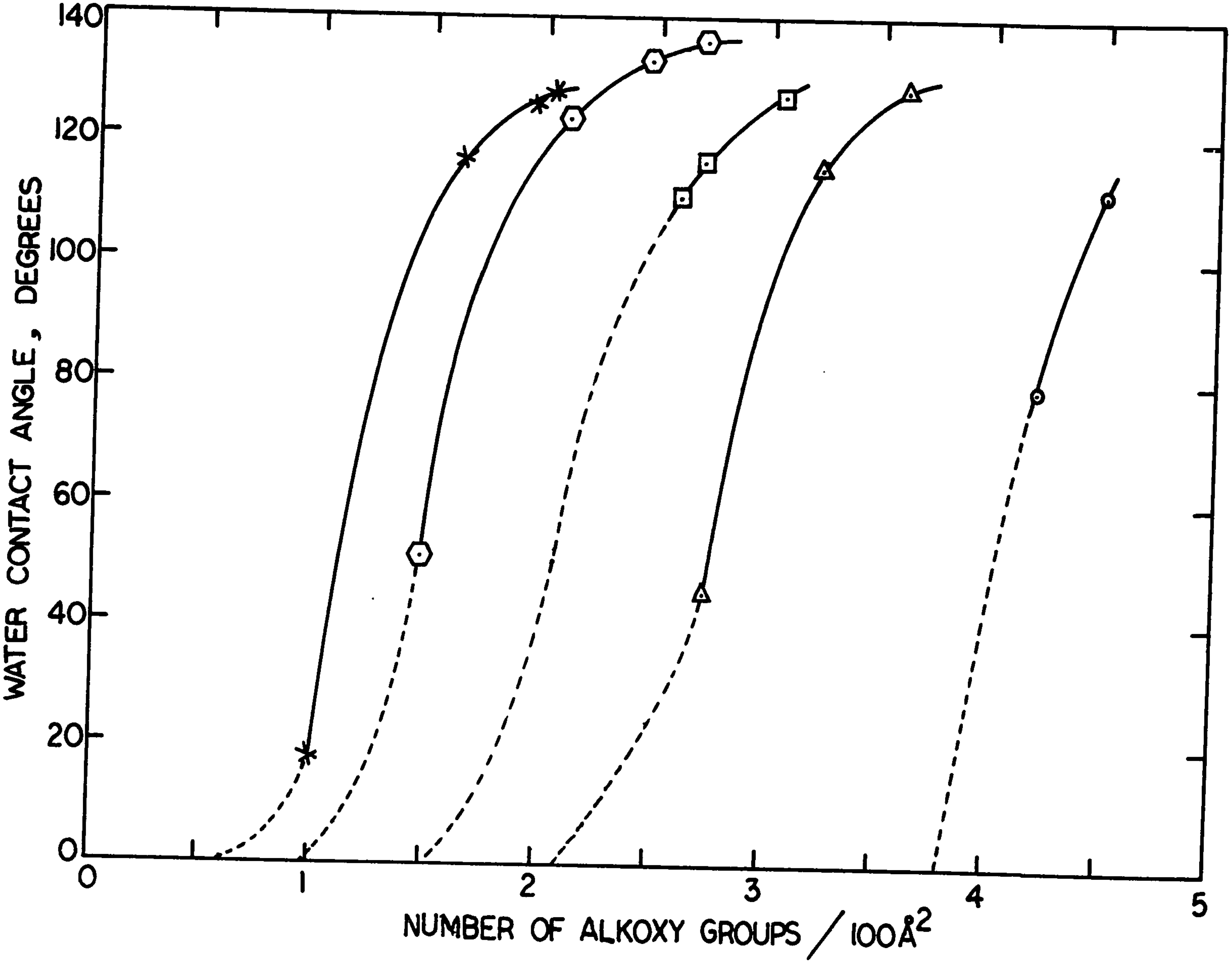
c) Contact Angle and Surface Coverage

The contact angle values for the various systems have been plotted as a function of the surface coverage in Figures 7-10 and listed in Tables 1 and 2. In Figure 7, contact angles for water on silica surfaces treated with alcohols have been plotted as a function of the number of alkoxy groups/100 $\mathring{A}^2$. At low surface coverages water spreads immediately before a contact angle measurement can be made. Dashed lines are used to extrapolate the curves to zero contact angle in order to indicate the surface coverage at which spreading begins. At surface coverages below this limiting value (different for different alcohols) the water molecules are able to penetrate the alkoxy groups and therefore wet the silica surfaces giving zero contact angle. The plots of θ versus q for the various alcohols are almost parallel to each other. The curves are practically linear between the values of 20° and 120°, showing large increase in θ with small increase in surface coverage. Above 120°, the curves approach a maximum value asymtotically depending upon the characteristics of the adsorbed species.

Similar results were obtained with glycerol on silica surfaces treated with alcohols, Figure 8. Surfaces which gave zero contact angle for water gave values ranging

Figure 7: Water Contact Angle on Alcohol Treated Silica Surfaces Versus Surface Coverages

o	Silica surface treated with methanol
Δ	Silica surface treated with ethanol
□	Silica surface treated with butanol
⬡	Silica surface treated with hexanol
*	Silica surface treated with decanol



WATER CONTACT ANGLE, DEGREES
0
20
40
60
80
100
120
140
NUMBER OF ALKOXY GROUPS / 100Å^2
0
1
2
3
4
5

Figure 8: Glycerol Contact Angle on Alcohol Treated Silica Surfaces Versus Surface Coverage

o	Silica surface treated with methanol
△	Silica surface treated with ethanol
□	Silica surface treated with butanol
⬡	Silica surface treated with hexanol
*	Silica surface treated with decanol

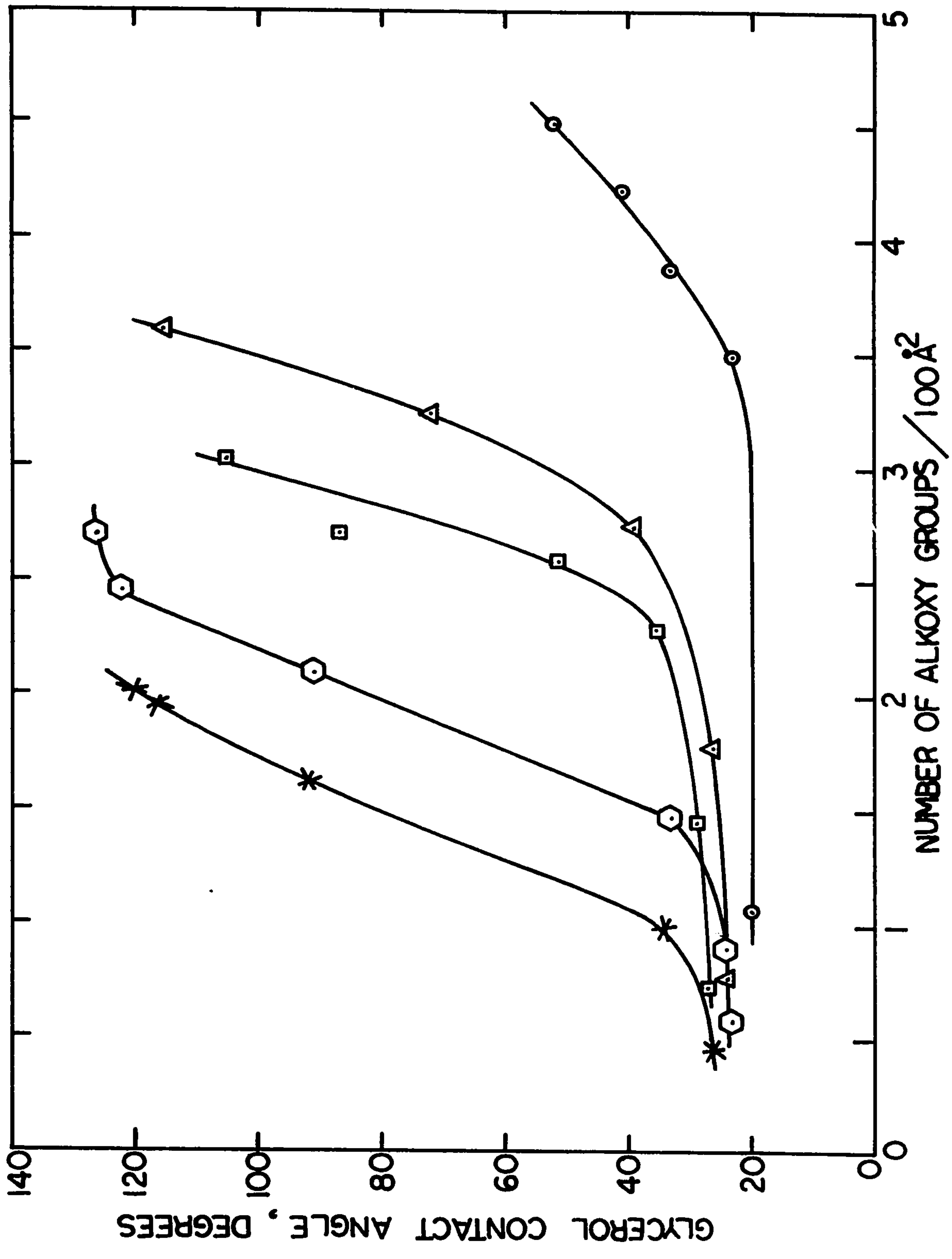
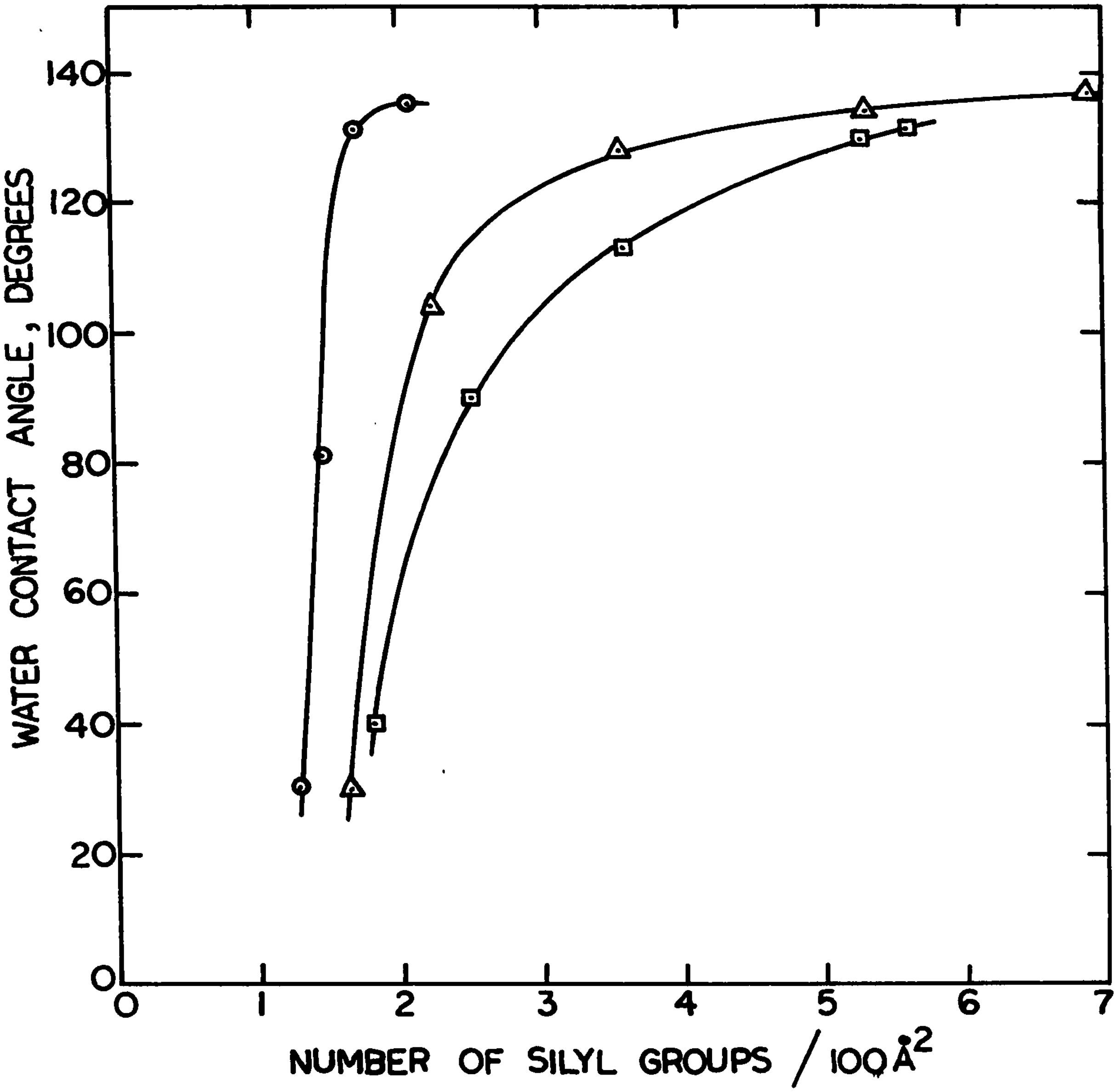

GLYCEROL CONTACT ANGLE, DEGREES
0
20
40
60
80
100
120
140
NUMBER OF ALKOXY GROUPS/100Å²
0
1
2
3
4
5

Figure 9: Water Contact Angle on Silane Treated Silica Surfaces Versus Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$



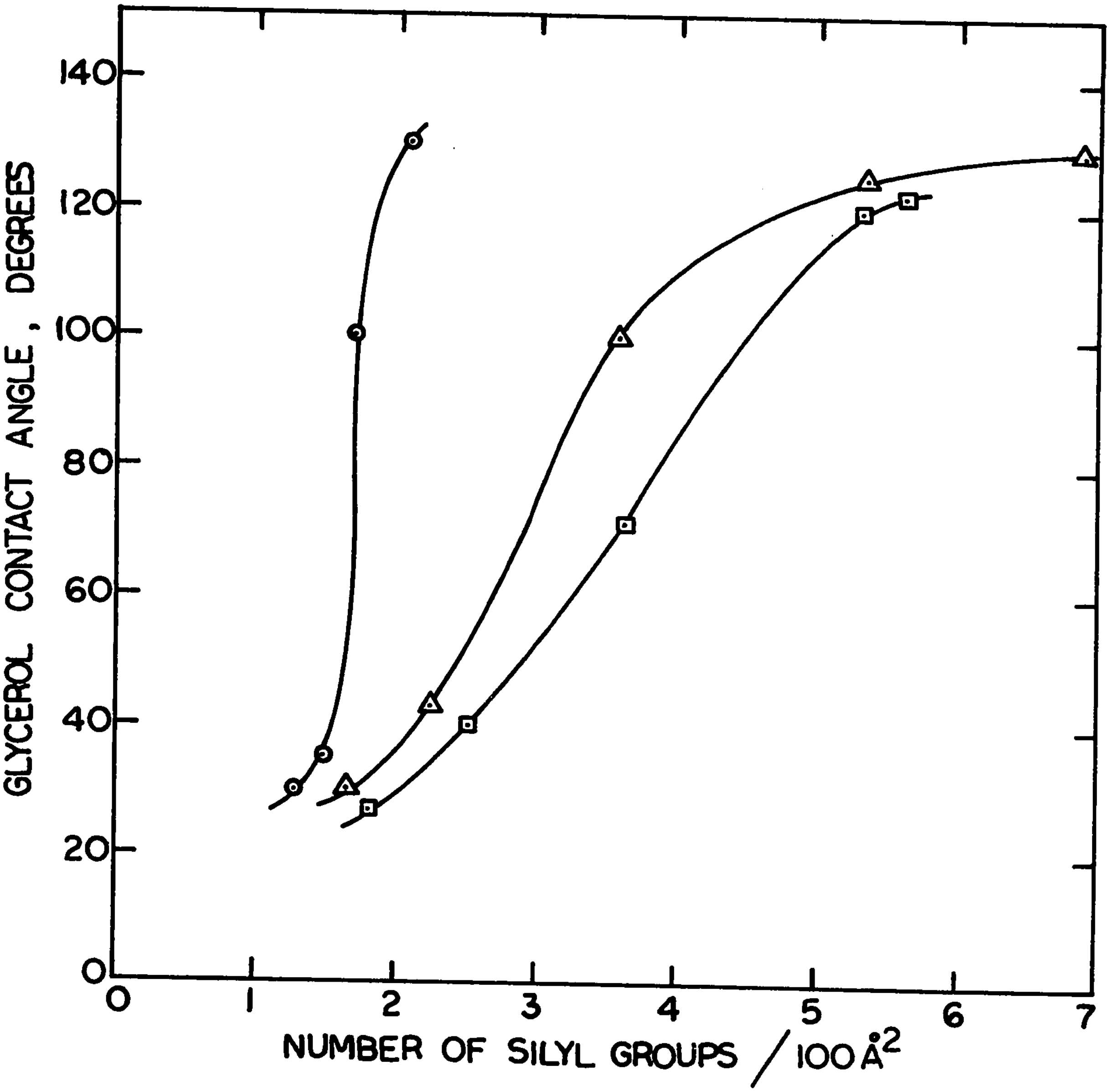
WATER CONTACT ANGLE, DEGREES
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS / 100 Å^2

Figure 10: Glycerol Contact Angle on Silane Treated Silica Surfaces Versus Surface Coverages

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$



140
120
100
80
60
40
20
0
GLYCEROL CONTACT ANGLE , DEGREES
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS / 100 Å^2

from 35°-40° for glycerol. The curves in this section tend to be horizontal. Above 40°, the various curves are essentially linear and parallel to each other. The surfaces treated with methanol appear to be an exception giving small dependence of contact angle on surface coverage. Above 120°, the curves appear to become horizontal although this tendency is not as pronounced as in the case of water, Figure 7.

On surfaces treated with silanes the contact angles for water and glycerol also increased with increasing surface coverage, Figures 9 and 10. This effect is most pronounced for surfaces treated with trimethylchlorosilane. Again, above 120°, the curves tended towards a maximum value of the contact angle.

It is obvious that the curves in Figures 7-10 array themselves from left to right in the order of decreasing number of carbon atoms in the adsorbed species. This demonstrates that the long chain alcohols or large side chain silanes require smaller number of alkoxy or silyl groups per unit area to obtain a given value of the contact angle as compared to the short chain groups. Figures 11-14 show the number of alkoxy and silyl groups required to produce contact angles of 60°, 90°, and 110° etc. for water and glycerol. Silica surfaces treated with decanol required 1.5 alkoxy groups/100 $\mathring{A}^2$ to obtain contact angle of 110° for water.

Figure 11: Surface Coverage Required for Different Carbon Chain Length Alcohols to Obtain the Same Value of Water Contact Angle

A. Water contact angle at 60°

B. Water contact angle at 90°

C. Water contact angle at 110°

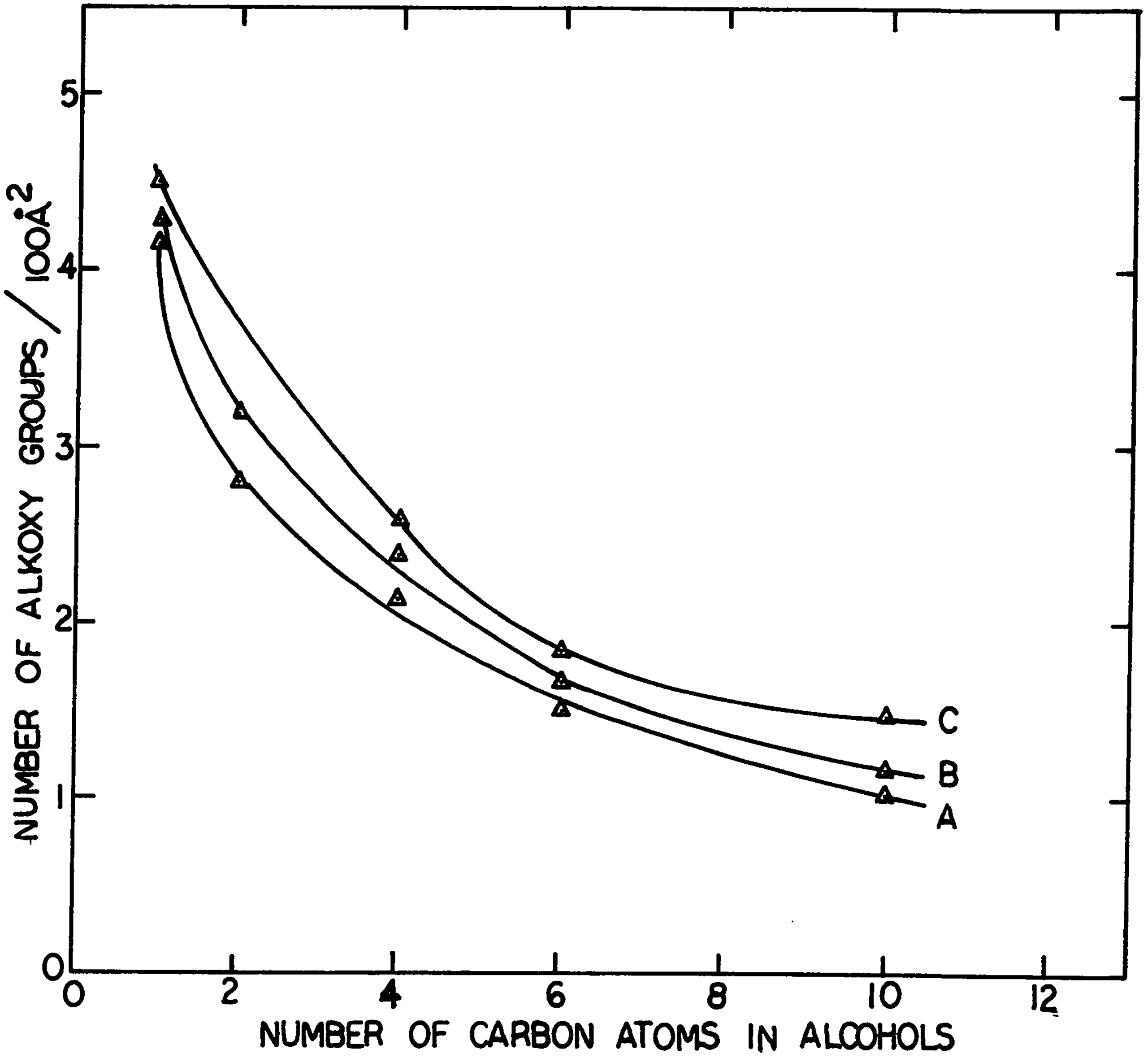

NUMBER OF ALKOXY GROUPS / 100Å^2
0
1
2
3
4
5
0
2
4
6
8
10
12
NUMBER OF CARBON ATOMS IN ALCOHOLS
C
B
A

Figure 12: Surface Coverage Required for Different Carbon Chain Length Alcohols to Obtain the Same Value of Glycerol Contact Angle

A. Glycerol contact angle at 60^o

B. Glycerol contact angle at 90^o

C. Glycerol contact angle at 110^o

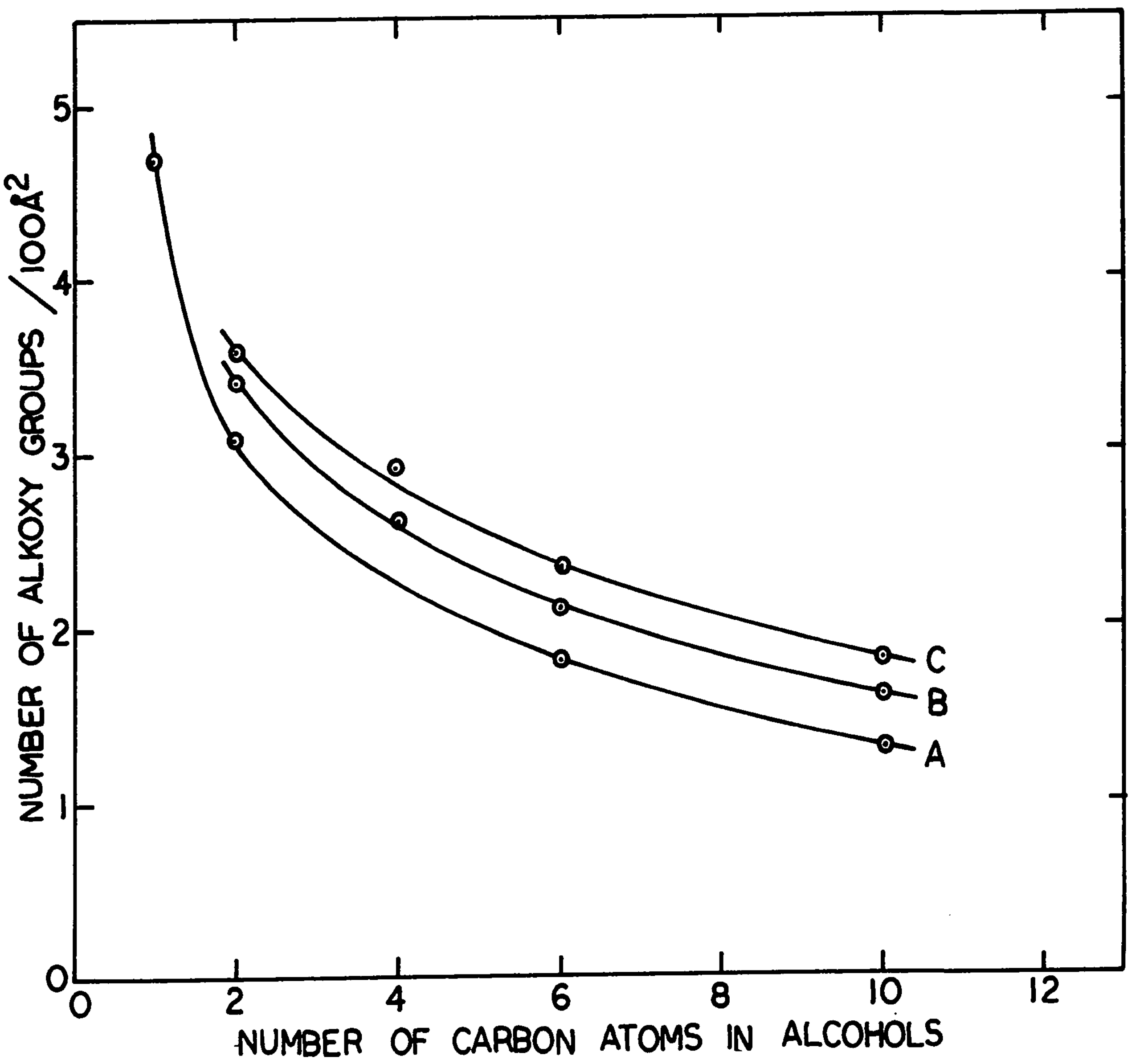

NUMBER OF ALKOXY GROUPS / 100Å²
0
1
2
3
4
5
0
2
4
6
8
10
12
NUMBER OF CARBON ATOMS IN ALCOHOLS
C
B
A

Figure 13: Surface Coverage Required for Different Silanes to Obtain the Same Value of Water Contact Angle

A. Water contact angle at 60°

B. Water contact angle at 90°

C. Water contact angle at 110°

D. Water contact angle at 130°

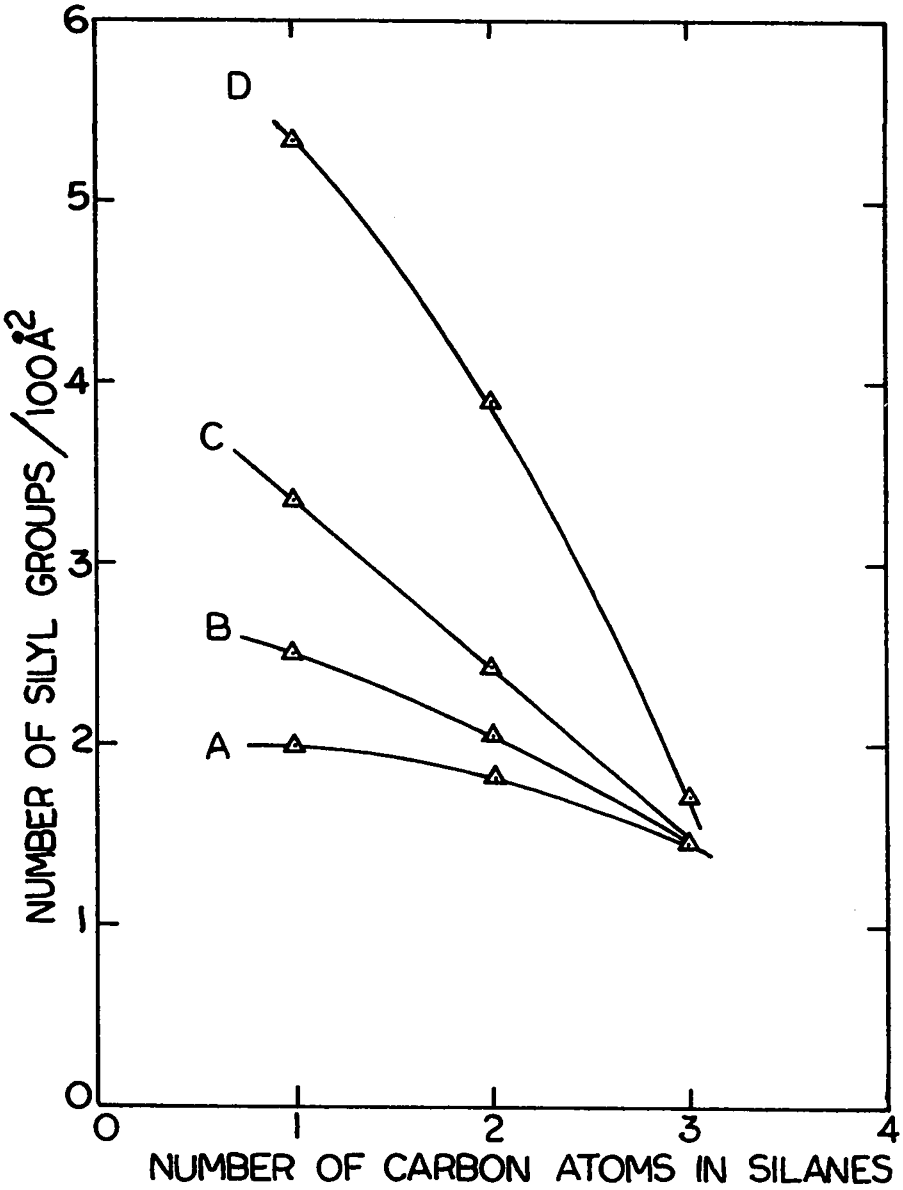
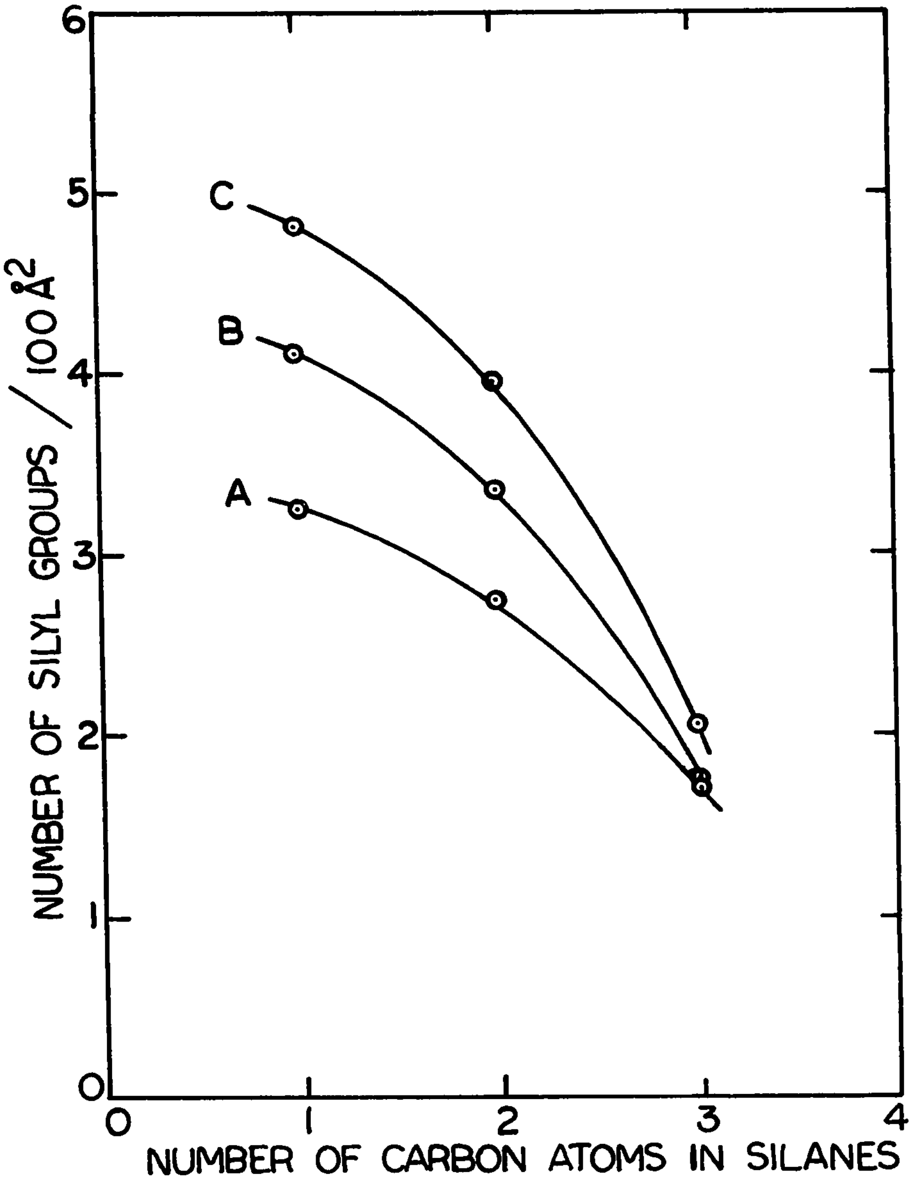

D
C
B
A
6
5
4
3
2
1
0
0
1
2
3
4
NUMBER OF SILYL GROUPS /100Å^2
NUMBER OF CARBON ATOMS IN SILANES

Figure 14: Surface Coverage Required for Different Silanes to Obtain the Same Value of Glycerol Contact Angle

A. Glycerol contact angle at 60^{o}

B. Glycerol contact angle at 90^{o}

C. Glycerol contact angle at 110^{o}



NUMBER OF SILYL GROUPS / 100 Å^2
0
1
2
3
4
5
6
C
B
A
0
1
2
3
4
NUMBER OF CARBON ATOMS IN SILANES

However, an additional 0.35, 1.10 and 3.00 alkoxy groups/$100\overset{o}{A}^2$ were required for silicas treated with hexyl, butyl and methyl alcohols respectively to give the same contact angle values. Similar conclusion can be drawn from Figure 12 depicting the data for glycerol. The curves corresponding to various contact angles are parallel (Figures 11 and 12), due to the similar structure of the alkoxy groups. However, on surfaces treated with silanes (as shown in Figures 13-14) the curves with different slopes were obtained. To obtain the same value of contact angle, the additional number of silyl group required in the case of less bulky silane is greater than in the case of silanes with bulky sides. For example, silica treated with CH_3SiHCl_2 required 2.0 silyl groups/100 $\overset{o}{A}^2$ to obtain a contact angle of 60° for water. An additional 1.35 silyl groups/100 $\overset{o}{A}^2$ would be needed to obtain a contact angle of 110°. Silica treated with $(CH_3)_3SiCl$ on the other hand required 1.45 silyl groups/$100\overset{o}{A}^2$ to obtain a contact angle of 60° for water, and an additional 0.25 silyl groups/100 $\overset{o}{A}^2$ only to produce a contact angle of 110°. The unequal distance between the curves is thus due to the different structures of the silyl groups.

d) The Cross-Sectional Area of the Adsorbed Species

The surface area covered by an alkoxy group can be determined by superimposing the curves in Figures 7-10. The distances,by which the different curves will have to be moved in order to superimpose them,should be related to the cross-sectional areas of the alkoxy groups giving those curves. Superimposition in terms of contact angles implies superimposition in terms of the surface properties from the point of view of coating or shielding of the surface with the various alkyl groups. The curves giving the contact angles for water and glycerol versus the number of alkoxy groups were superimposed. The same was done for surfaces covered with silyl group - but only up to coverages of about 4 groups/100 $\mathring{A}^2$. Surface coverages greater than 4 groups/100 $\mathring{A}^2$ were due to the polymerization of the silanes and therefore represented a situation much more complex in respect of the size of the groups.

The ratios of areas of the long chain to short chain hydrocarbons for alcohols and silanes obtained in this fashion are summarized in Tables 3 and 4. A cross-sectional area of 18.4 $\mathring{A}^2$ for a methanol molecule calculated by the density method (37-39) was used as a standard. The surface areas covered by other alkyl groups could be cal-

TABLE 3: Ratios of the Areas Covered by Various Alkoxy Groups to that of the Methoxy Group Obtained by Superimposing the Plots of Water and Glycerol Contact Angle Versus Surface Coverage

Treatment of Silica	Water	Glycerol
Methanol	1.00	1.00
Ethanol	1.30	1.30
Butanol	1.85	1.85
Hexanol	2.60	2.60
Decanol	2.90	2.90

TABLE 4: Ratios of the Areas Covered by Silyl Groups to that of the Methyl Silyl Group Obtained by Superimposing the Plots of Water and Glycerol Contact Angle Versus Surface Coverage

Treatment of Silica	Water	Glycerol
CH_3SiHCl_2	1.00	1.00
$(CH_3)_2SiCl_2$	1.25	1.35
$(CH_3)_3SiCl$	1.64	1.80

culated by multiplying the cross-sectional area of a methanol molecule by the appropriate shift factors listed in Table 3. The cross-sectional areas calculated from the contact angle data for water and glycerol are listed in columns 2 and 3 of Table 5. These values compare favorably with the values calculated from density and adsorption measurements. The values reported by McClellan and Harnsberger (39) were obtained by the adsorption method. Rao and Das (40) calculated the molecular cross-sectional area by regarding the alcohol molecules as spheres. Allen and Patel (41) obtained the cross-sectional area by adsorption of alcohols on finely divided powders.

The cross-sectional area of silanes calculated from the contact angle data are given in Table 6. Methyldichlorosilane has only one CH_3 group. The area covered by one methyldichlorosilane molecule was assumed to be 21 $\mathring{A}^2$. The areas covered by other two silanes were then calculated according to the ratios given in Table 4. The area occuppied by one trimethylchlorosilane molecule turned out to be 34.7 $\mathring{A}^2$ (based on the contact angle of water) and 37.8 $\mathring{A}^2$ (based on the contact angle of glycerol). These values compare favorably with the values obtained by the density (37,38) and the Stober methods (42). The Stober

TABLE 5: The Cross-Sectional Areas of the Alkoxy Groups

	Measured Values, A^2			Cross-Sectional Area, A^2 (From the Literature)		
Treatment of Silica	From Water Contact Angle	From Glycerol Contact Angle	Calculated Values by the Density Method(37-39)*	McClellan & Harnsberger(39)	Rao & Das(40)	Allen & Patel(41)
Methanol	18.4	18.4	18.4	21.9	21.2	----
Ethanol	23.9	23.9	23.1	28.3	27.0	21.1
Butanol	34.0	34.0	31.2	35.4	36.0	22.4
Hexanol	47.8	47.8	38.5	----	----	27.6
Decanol	53.4	53.4	50.9	----	----	53.1

$$* \quad \sigma = 1.091 \left(\frac{M}{N\rho}\right)^{2/3} \text{cm}^2$$

where σ is the cross-sectional area

M is molecular weight

N is Avogadro's number

ρ is the density in grams/cc.

TABLE 6: The Cross-Sectional Areas of the Silyl Groups

	Measured Values, A^2			Cross-Sectional Area, $\AA^2$ (From the Literatures)	
Treatment of Silica	From Water Contact Angle	From Glycerol Contact Angle	Calculated Values by the Density Method(37-39)*	Stober (42)*	Herzberg, Marian & Vermeulen (31)
CH_3SiHCl_2	21.0	21.0	33.9	----	----
$(CH_3)_2SiCl_2$	26.2	28.4	37.5	----	----
$(CH_3)_3SiCl$	34.7	37.8	38.7	34.8	27.7

$$* \quad \sigma = 1.091 \left(\frac{M}{N\rho}\right)^{2/3} \text{ cm}^2$$

where σ is the cross-sectional area

M is the molecular weight

N is the Avogadro's number

ρ is the density in grams/cc.

method assumes a square model for silane with Si-C as 1.89 $\mathring{A}$ and C-H as 1.08 $\mathring{A}$. Assuming silane to be circular in cross-section, Herzberg (31) obtained a value of 27.7 $\mathring{A}^2$. The calculated values of methyldichlorosilane and dimethyldichlorosilane may be larger due to the relatively large contribution of the chlorine atom to their molecular weights. Upon reaction with the silica surface however, only the $-Si(CH_3)_n$ groups are retained on the surface. Therefore, the values obtained by the contact angle should be comparatively small compared to the values obtained by the density method.

The cross-sectional areas of the various alkyl groups were also calculated by using equation 7. According to Zisman (43), the maximum possible contact angle for water is 156^o. Using this value in conjunction with the values obtained on the various surfaces (Tables 1 and 2), the cross-sectional areas of the alkoxy and the silyl groups were calculated, Tables 7 and 8. The cross-sectional area can also be obtained from the slope of the Cos θ versus q plot, which equals $(1 - \text{Cos } \theta_2)\frac{a}{100}$. These results are also listed in Table 7 and are found to be in agreement with those calculated by the density method. In order to obtain the cross-sectional areas graphically (by using equation 7), it appears that contact angle values in the range of 90^o-135^o

TABLE 7: The Cross-Sectional Areas of the Alkoxy Groups Obtained with the Use of Equation (7) (see Text)

	Analytical Values			Graphical Values		
Treatment	Water Contact Angle, θ	Number of Alkoxy Groups/100Å^2, q	Cross-Sectional Area, a, Å^2	Average a, Å^2	Slope	Cross-Sectional Area, Å^2
Methanol	111°	4.5	15.8	15.8	0.296	15.5
Ethanol	128°	3.59	23.5	23.3	0.45	23.5
	115°	3.22	23.0			
Butanol	110°	2.59	27.0	27.5	0.53	28.0
	116°	2.69	27.9			
	127°	3.04	27.5			
Hexanol	123°	2.10	37.7	35.5	0.678	35.4
	133°	2.46	35.5			
	136°	2.69	33.4			
Decanol	116°	1.62	46.4	43.7	0.825	43.0
	125°	1.94	42.4			
	127°	2.03	42.2			

TABLE 8: The Cross-Sectional Areas of the Silyl Groups Obtained with the Use of Equation (7) (see Text)

Treatment	Water Contact Angle, θ	Number of Alkoxy Group, q	Cross-Sectional Area, a	Average Cross-Sectional Area, A^2
CH_3SiHCl_2	90°	2.5	20.9	20.5
	113°	3.6	20.2	
$(CH_3)_2SiCl_2$	104°	3.24	29.0	26.3
	128°	3.57	23.6	
$(CH_3)_3SiCl$	81°	1.47	30.0	41.3
	131°	1.70	50.8	
	135°	2.07	43.0	

give the best results. At low surface coverages spreading or penetration of the liquid becomes a serious factor. The discontinuity in the plots of Cos θ versus q (Figures 15 and 16) may be due to these reasons.

On surfaces treated with silanes, the slope of the Cos θ versus q plots changes with surface coverages, Figures 17 and 18. At low coverages, the small value of <u>a</u> obtained from experimental data is attributed to the penetration of water.

e) The Orientation of the Adsorbed Molecules

If the alkoxy groups stood perpendicular to the silica surface, then the area covered by an alkoxy group should be roughly 20.7 $\mathring{A}^2$. If on the other hand, they were to lie horizontally on the surface, then the area covered by a group would be equal to the cross-sectional area of the side. These values for the various alcohols are listed in Table 9 and compared to their cross-sectional areas determined experimentally. It is obvious that the measured values lie between the two geometrical values of the cross-sectional areas. This implies that the alkoxy group are neither completely perpendicular nor parallel to the surface. They stand inclined at an angle sweeping a conical volume of revolution.

Figure 15: Cosine of Water Contact Angle on Alcohol Treated Silica Surfaces Versus Surface Coverage

o Silica surface treated with methanol

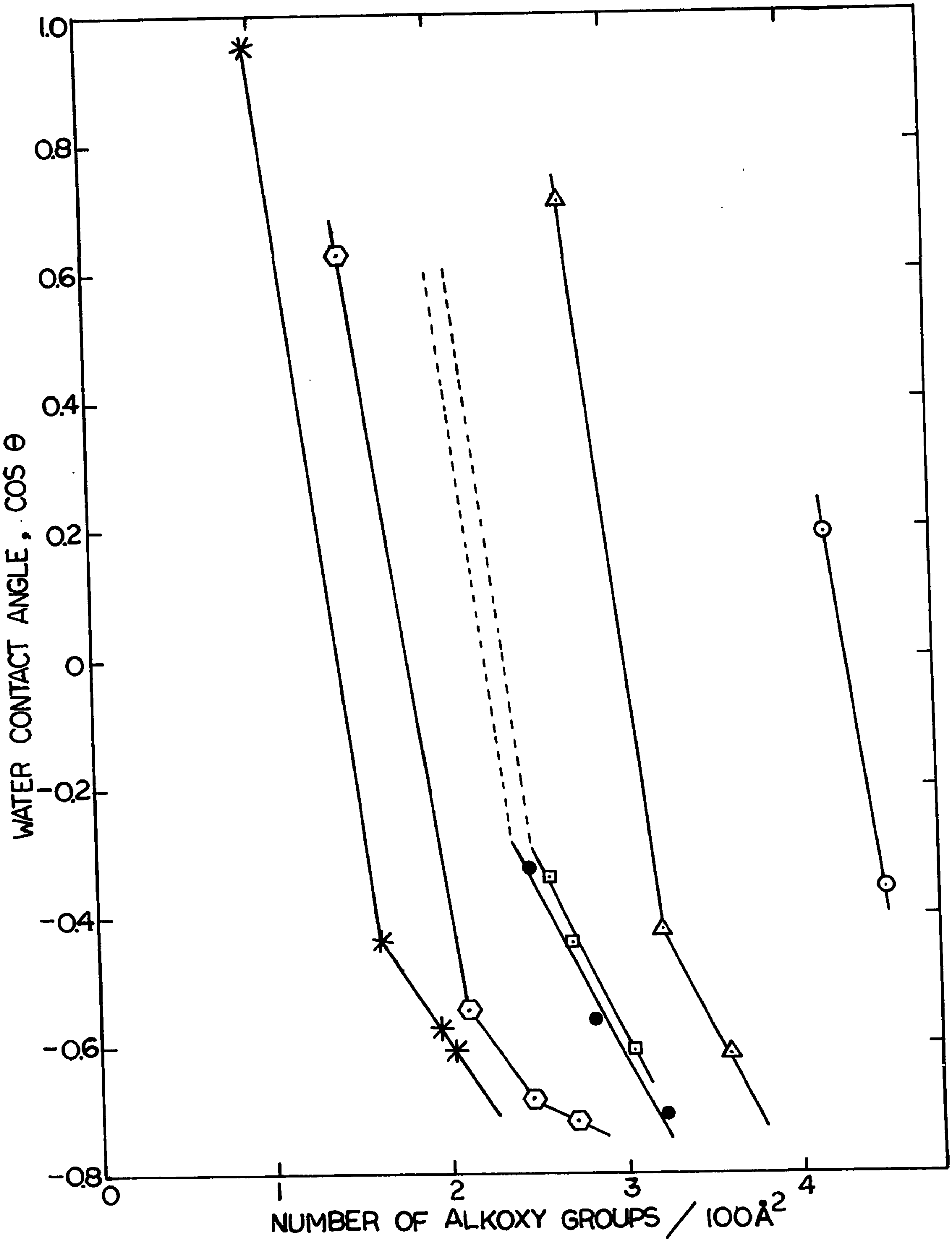
Δ Silica surface treated with ethanol

● Silica surface treated with propanol

□ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
WATER CONTACT ANGLE, COS Θ
0
1
2
3
4
NUMBER OF ALKOXY GROUPS / 100Å²

Figure 16: Cosine of Glycerol Contact Angle on Alcohol Treated Silica Surfaces Versus Surface Coverage

o Silica surface treated with methanol

△ Silica surface treated with ethanol

● Silica surface treated with propanol

◘ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol

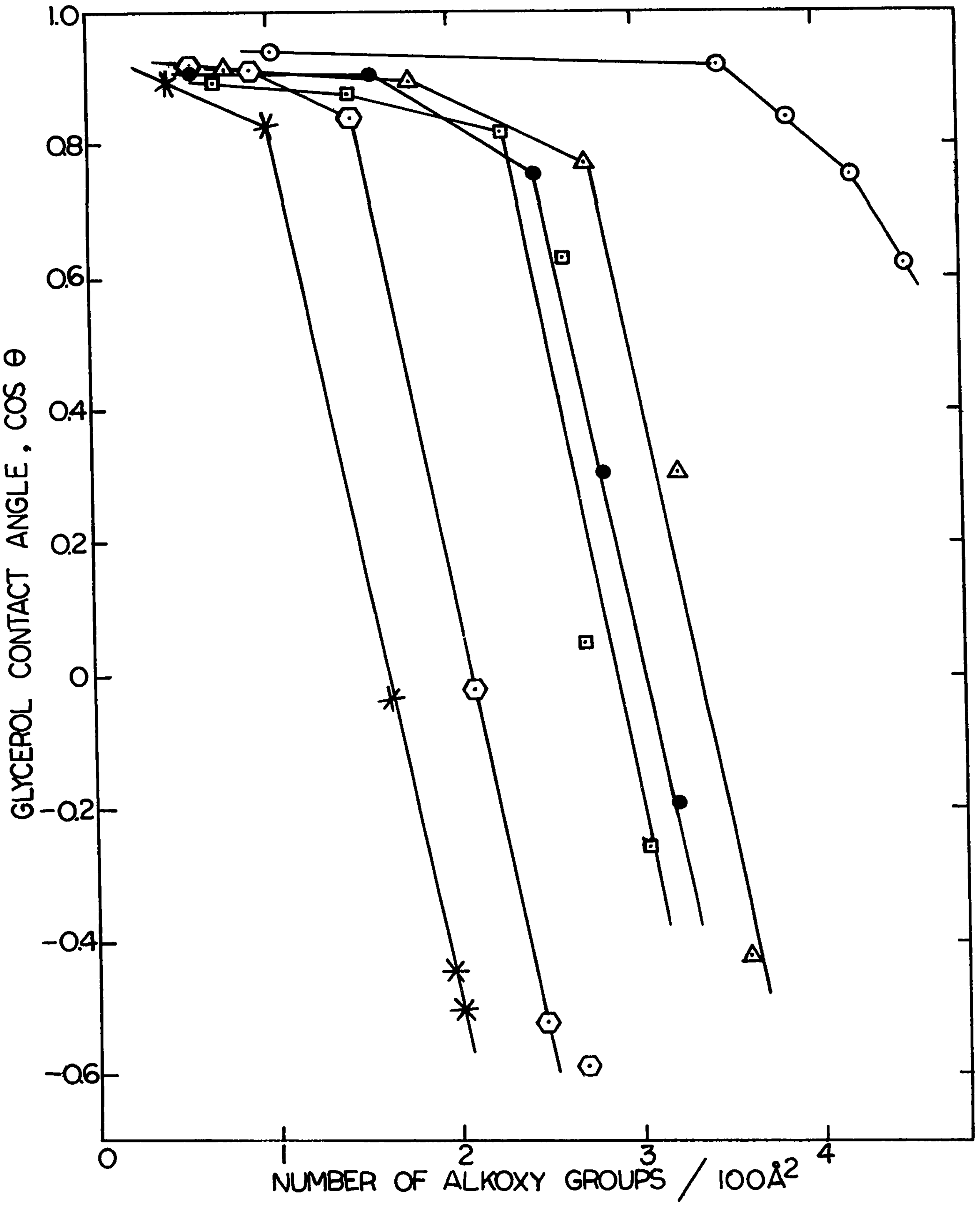
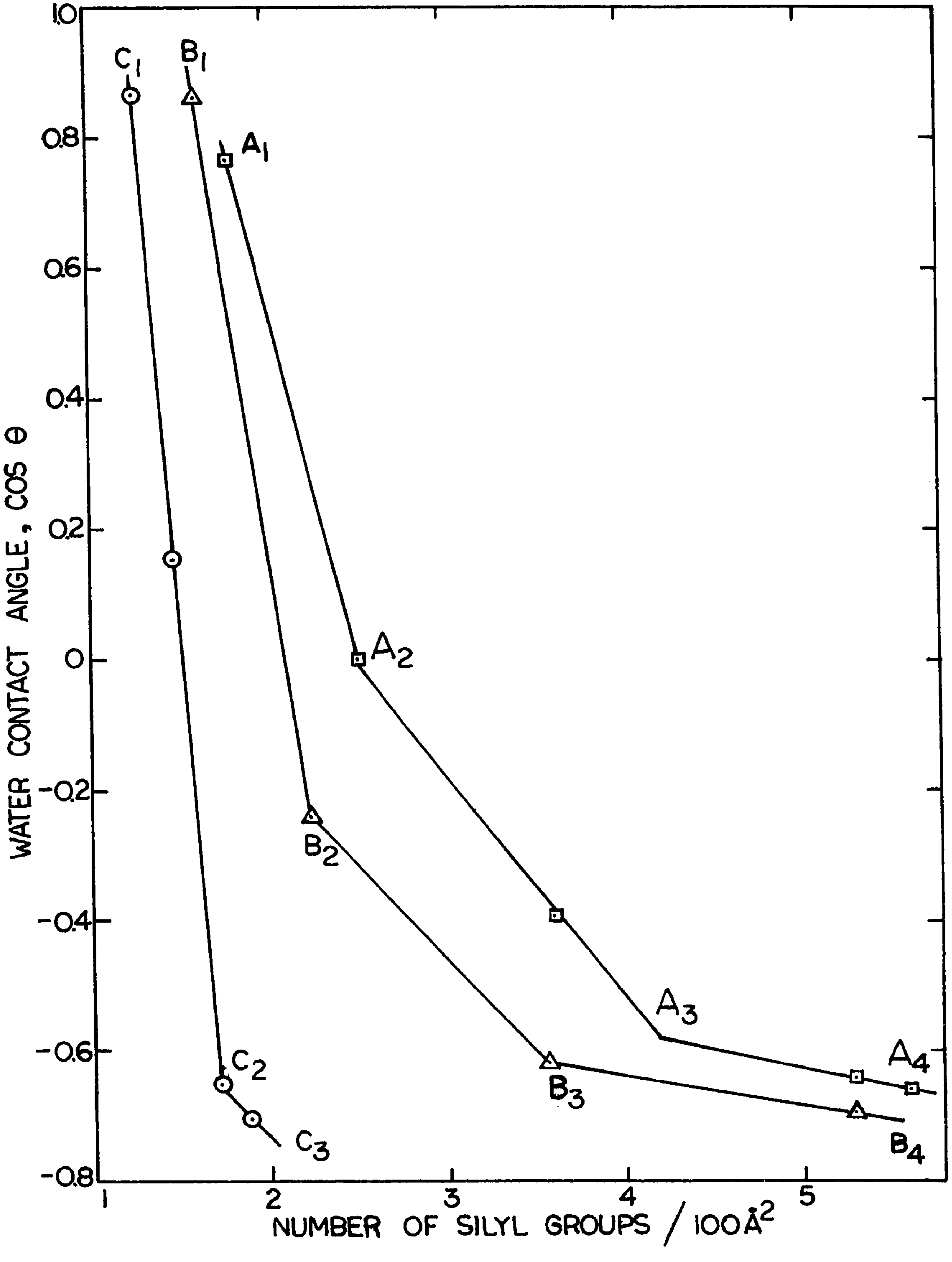

1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
GLYCEROL CONTACT ANGLE , COS Θ
0
1
2
3
4
NUMBER OF ALKOXY GROUPS / 100Å^2

Figure 17: Cosine of Water Contact Angle on Silane Treated Silica Surfaces Versus Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

o Silica surface treated with $(CH_3)_2SiCl$



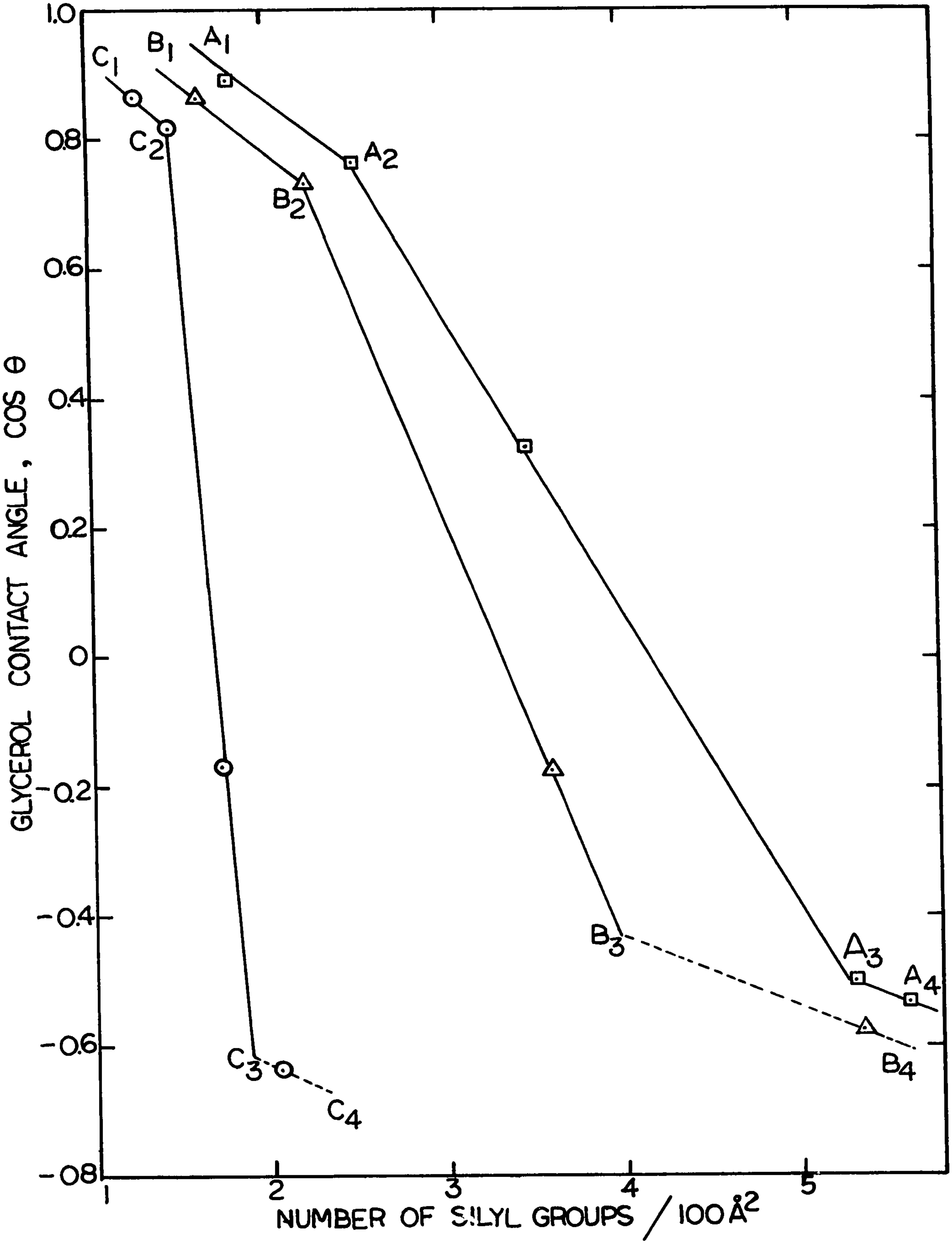
WATER CONTACT ANGLE, COS Θ
NUMBER OF SILYL GROUPS / 100Å^2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
1
2
3
4
5
C$_1$
C$_2$
C$_3$
B$_1$
B$_2$
B$_3$
B$_4$
A$_1$
A$_2$
A$_3$
A$_4$

Figure 18: Cosine of Glycerol Contact Angle on Silane Treated Silica Surfaces Versus Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$



GLYCEROL CONTACT ANGLE, COS θ
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
1
2
3
4
5
NUMBER OF SILYL GROUPS / 100 Å^2
A$_1$
A$_2$
A$_3$
A$_4$
B$_1$
B$_2$
B$_3$
B$_4$
C$_1$
C$_2$
C$_3$
C$_4$

TABLE 9: The Length, Cross-Sectional Area and the Orientation Angle of the Alkoxy Groups

Treatments	Length Å	Cross-Sectional area of the end, Å^2	Cross-Sectional area of the side, Å^2	Measured Values of Cross-Sectional Area (Table 5)	Orientation Angle
Methanol	4.7	20.7	21.4	18.4	90°
Ethanol	6.8	20.7	30.9	23.9	84.8°
Butanol	10.4	20.7	47.5	34.0	71.8°
Hexanol	13.8	20.7	----	47.8	64.5°
Decanol	20.6	20.7	----	53.4	69.6°

The angle of revolution obviously increased with the length of the alkoxy group. Methoxy groups are held essentially perpendicular to the surface while the butoxy groups are held at an average of 70° from the surface.

In the case of silyl group, the mean area covered by a silyl group agrees with the calculated cross-sectional area. Hence it can be concluded that the silyl groups are held almost perpendicular to the silica surface. This is obviously due to the short length of the silane molecules.

3.5 CONCLUSION

Contact angles of water and glycerol were measured on silica surfaces treated with various alcohols and silanes. The values of the contact angles depended on the surface tension of the liquid and the chemical structure of the functional groups adsorbed on the surface. At moderate to high surface coverages the contact angle was larger for water than for glycerol. Within certain limits, the following equation was used to describe the dependence of contact angle (θ) on the surface coverages:

$$\text{Cos}\ \theta = \text{Cos}\ \theta_1 - (\text{Cos}\ \theta_1 - \text{Cos}\ \theta_2)\ \frac{ga}{100}$$

For water, θ_1 and θ_2 are 0° and 156° respectively. From the contact angle for water on surfaces whose coverages in terms of the number of alkyl groups was known, it was possible to determine the cross-sectional areas of the adsorbed species. These values are in good agreement with the calculated values and the values given in the literature. At low surface coverages the results were affected by penetration of water through the adsorbed species. As a result, the measured contact angle values were lower than the estimated values.

The contact angle versus surface coverage plots were displaced towards higher coverages as the number of carbon atoms in the alkoxy groups decreased indicating that the larger groups are more effective in achieving a certain degree of hydrophobicity as compared to the smaller groups. Most plots could be superimposed by moving along the surface coverage axis. From the magnitude of the shifts involved and the corss-sectional area of methanol, it was possible to calculate the cross-sectional areas of the other alkyl groups.

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CHAPTER 4

SURFACE ENERGY AND CONTACT ANGLE

4.1 INTRODUCTION

The equilibrium contact angle of a liquid on a solid is related to the liquid-air, solid-air and solid-liquid interfacial energies. There have been many attempts to connect the contact angle with the surface energy of the solid. Elton (1) combined the Young's equation (2) with Antonoff's Law (3) and postulated that the contact angle is finite if the surface tension of the liquid is larger than that of the solid. Zisman and his co-workers (4-6) have shown that for a series of liquids on a given solid, the contact angle decreased with decreasing surface tension of the liquid. For a homolog-ous series of liquids, the increase in the cosine of the equilibrium contact angle with decreasing liquid surface tension is linear for a given solid, unless the molecules in the solid surface are bonded to the adsorbate molecules.

Gaudin and Morrow (7) have calculated the energy of adsorption of dodecylamine on quartz and hematite from measurements of contact angle as a function of the collector adsorption. Their results showed marked reduction in the energy of adsorption with increasing surface coverages. De Bruyn and his co-workers (8,9) showed from thermodynamic analysis of a three phase flotation system that for a solid to become floatable, the adsorption density of the collector at the solid-gas interface must exceed its adsorption density at the solid-liquid interface. They concluded that in a collector system the increase in the contact angle was due to a decrease in the surface tension of the mineral-air interface, a decrease which has to be larger than the decrease in the surface tension of the mineral-liquid interface.

In Chapter 3 of this thesis it was shown that the contact angle is a function of the surface treatment. In this chapter we will discuss the energetics of the alcohol and silane treated surfaces. Change in the surface energy following the surface modification are related to the magnitude of the contact angle.

4.2 THEORY

The Young's equation (2):

$$\mathrm{Cos}\ \theta = \frac{\gamma_{sa} - \gamma_{s\ell}}{\gamma_{\ell a}} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

is usually combined with the Dupre equation (11,12)

$$W_{s\ell} = \gamma_{sa} + \gamma_{\ell a} - \gamma_{s\ell} \quad \text{...............(2)}$$

to give

$$W_{s\ell} = \gamma_{\ell a} (1 + \text{Cos } \theta) \quad \text{...............(3)}$$

or

$$\text{Cos } \theta = \frac{W_{s\ell}}{\gamma_{\ell a}} - 1 \quad \text{...............(3a)}$$

where θ is the contact angle between the liquid and the solid surface measured across the liquid phase.

γ_{sa} is the solid-air interfacial energy.

$\gamma_{s\ell}$ is the solid-liquid interfacial energy.

$\gamma_{\ell a}$ is the liquid-air interfacial energy.

$W_{s\ell}$ is the work of adhesion between solid and liquid.

Equation (3a) shows that Cos θ is a function of $W_{s\ell}$ and $\gamma_{\ell a}$. Since $\gamma_{\ell a}$ is constant or changes only slightly in an actual flotation system, Cos θ depends mainly on $W_{s\ell}$. The plot of Cos θ versus $W_{s\ell}$ should be a straight line with the slope of $1/\gamma_{\ell a}$ and an intercept of -1.

If a finite contact angle is obtained, then Cos θ is limited between +1 and -1, and the work of adhesion has to be:

$$-1 < \frac{W_{s\ell}}{\gamma_{a\ell}} - 1 < +1 \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

or

$$0 < W_{s\ell} < +2\,\gamma_{\ell a} \qquad \ldots\ldots\ldots\ldots\ldots(4a)$$

If $W_{s\ell} \geq 2\,\gamma_{\ell a}$, the solid surface will be completely wetted by the liquid. In the case of $W_{s\ell} \leq 0$, a maximum contact angle of 180° will be obtained and the solid will be completely wetted with the gas phase.

A relationship between the contact angle and the surface coverage has been described previously (Chapter 3) in terms of the following equation:

$$\text{Cos}\,\theta = \text{Cos}\,\theta_1 - (\text{Cos}\,\theta_1 - \text{Cos}\,\theta_2)\,\frac{qa}{100} \quad \ldots.(5)$$

where θ is the contact angle on the modified surface.

θ_1 is the contact angle on the surface with no collector adsorption.

θ_2 is the contact angle on the surface with maximum collector adsorption (or maximum possible contact angle).

q is the number of adsorbed species per 100 $\mathring{A}^2$.

a is the area covered by a single species.

Since $\cos \theta_1$ equals one for water on clean mineral surfaces, equation (5) may written as:

$$\cos \theta = 1 - (1 - \cos \theta_2) \frac{qa}{100} \qquad \text{.........(5a)}$$

By combining equations (3a) and (5) or (5a), the following equation which relates the work of adhesion and the surface coverage is obtained:

$$W_{s\ell} = \gamma_{\ell a} [1 + \cos \theta_1 - (\cos \theta_1 - \cos \theta_2) \frac{qa}{100}] \qquad \text{.........(6)}$$

or

$$W_{s\ell} = \gamma_{\ell a} [2 - (1 - \cos \theta_2) \frac{qa}{100}] \qquad \text{.........(6a)}$$

As described previously, if $\gamma_{\ell a}$ and $\cos \theta_2$ are taken as constant, then $W_{s\ell}$ will be a function of the surface coverage $\frac{qa}{100}$. The higher the surface coverage, the lower the work of adhesion and larger the value of the contact angle. Since most minerals have very high surface energies, they are invariably treated with collectors in order to reduce the surface energies and thereby obtain a suitable contact angle for flotation to occur.

Fowkes (10-12) has reported expressions giving the contribution of the dispersion forces to the contact angle and the heat of adsorption of a gas on the solid surfaces. The contact angle of a liquid on a given solid may be described as follows, provided that $\gamma_{a\ell} > \gamma_{as}$, and the equilibrium film pressure of the adsorbate vapor on the solid surface is zero (13).

$$\cos\theta = -1 + 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_\ell^d}}{\gamma_{a\ell}}\right) \qquad \text{..........(7)}$$

where γ_s^d is the dispersion force contribution to the surface free energy of the solid, and

γ_ℓ^d is the dispersion force contribution to the surface free energy of the liquid.

The heat of adsorption is described by the following equation (14):

$$\Delta H_{ads} = 2\gamma_\ell - 2\sqrt{\gamma_\ell^d\gamma_s^d} - 2T\left(\frac{d\gamma_\ell}{dT} - \sqrt{\gamma_\ell^d}\,\frac{d\sqrt{\gamma_s^d}}{dT} - \sqrt{\gamma_s^d}\,\frac{d\sqrt{\gamma_\ell^d}}{dT}\right)$$

$$\text{..........(8)}$$

where γ stands for the dispersion force and the subscripts, s, ℓ stand for solid and liquid respectively.

It can be seen from equations (7) and (8) that there exists a relation between contact angle and heat of adsorption, even though it is not a simple relation.

Combining equations(3) and (7), we obtain:

$$W_{\ell s} = 2 \sqrt{\gamma_s^d} \cdot \sqrt{\gamma_\ell^d} \qquad \text{..........(9)}$$

which shows that $W_{\ell s}$ is a function of the dispersion forces of the solid and the liquid.

4.3 RESULTS AND DISCUSSION

a) Work of Adhesion and Contact Angle

From the contact angle results obtained in the previous chapter, the work of adhesion was calculated using equation (3) or (3a) and the results are listed in Tables 1 and 2. Plots of Cos θ and the work of adhesion are shown in Figures 1 and 2. Figures 1 and 2 also give the plots of γ_s^d according to equation 7. The slopes of the plots are equal to the surface tensions of the liquids, i.e., 72.8 dynes/cm for water and 63.4 dynes/cm for glycerol at room temperature. Zero contact angle will be obtained when the work of adhesion is equal to or larger than the twice the value of the liquid surface tension. The magnitude of the

TABLE 1: Data for Silica Surfaces Treated with Alcohols

			From Water Contact Angle		From Glycerol Contact Angle	
		Heat of Adsorption Kcal/mole, ΔH	$W_{s\ell}$ ergs/cm^2	γ_s^d dynes/cm	$W_{s\ell}$ ergs/cm^2	γ_s^d dynes/cm
Methanol	I	23.30	----	----	123	102
	II	19.40	----	----	122	100
	III	18.35	----	----	116.6	92.2
	IV	16.55	86.8	86.5	111	82.8
	V	15.50	46.7	25.0	102.3	70.6
Ethanol	I	21.80	----	----	121	100
	II	20.70	----	----	120	98
	III	19.00	124.4	116.8	112.6	86.5
	IV	17.50	42.0	20.2	83	46.2
	V	16.40	28.0	9.0	36.6	9.0
Butanol	I	21.00	----	----	120	98.0
	II	20.50	----	----	119	94.1
	III	18.80	----	----	115	84.7
	IV	18.00	47.9	26.0	103	72.2
	V	17.70	40.9	19.4	66.5	29.2
	VI	16.00	29.0	9.6	47	15.2
Hexanol	I	20.02	----	----	122	100
	II	19.60	----	----	121	100
	III	18.76	118.8	161.0	117	92.2
	IV	17.40	33.2	12.9	62.3	26.0
	V	16.40	23.2	6.25	29.8	5.8
	VI	14.20	20.4	4.84	26.1	4.8
Decanol	I	19.10	----	----	120	98
	II	18.20	142.0	231.0	116	90.2
	III	17.50	40.9	19.4	61.2	25.0
	IV	17.20	31.1	10.9	35.6	9.8
	V	14.90	29.0	9.6	31.7	6.8

TABLE 2: Data for Silica Surfaces Treated with Silanes

		Heat of Adsorption Kcal/mole, ΔH	From Water Contact Angle		From Glycerol Contact Angle	
			$W_{s\ell}$ ergs/cm^2	γ_s^d dynes/cm	$W_{s\ell}$ ergs/cm^2	γ_s^d dynes/cm
CH_3SiHCl_2	I	21.40	128	187	120	96
	II	19.55	73	60.8	112	84.6
	III	17.70	44.4	23.0	84	47.6
	IV	15.80	26	7.8	31.7	6.8
	V	14.00	25	7.3	29.8	5.8
$(CH_3)_2SiCl_2$	I	20.60	136	210	118	94
	II	18.3	55	34.8	110	81
	III	16.6	28	9.0	52.4	18.5
	IV	14.8	22.2	5.8	27	4.8
	V	13.6	20.4	4.8	23.7	4.0
$(CH_3)_3SiCl$	I	20.23	136	210	118	94
	II	18.35	84	81	115	90.2
	III	-----	25	7.3	52.4	18.5
	IV	16.80	21.3	5.8	22.6	3.2

Figure 1: Water Contact Angle Versus the Work of Adhesion and Solid Dispersion Forces

Open: Alcohols treated surfaces

Closed: Silanes treated surfaces

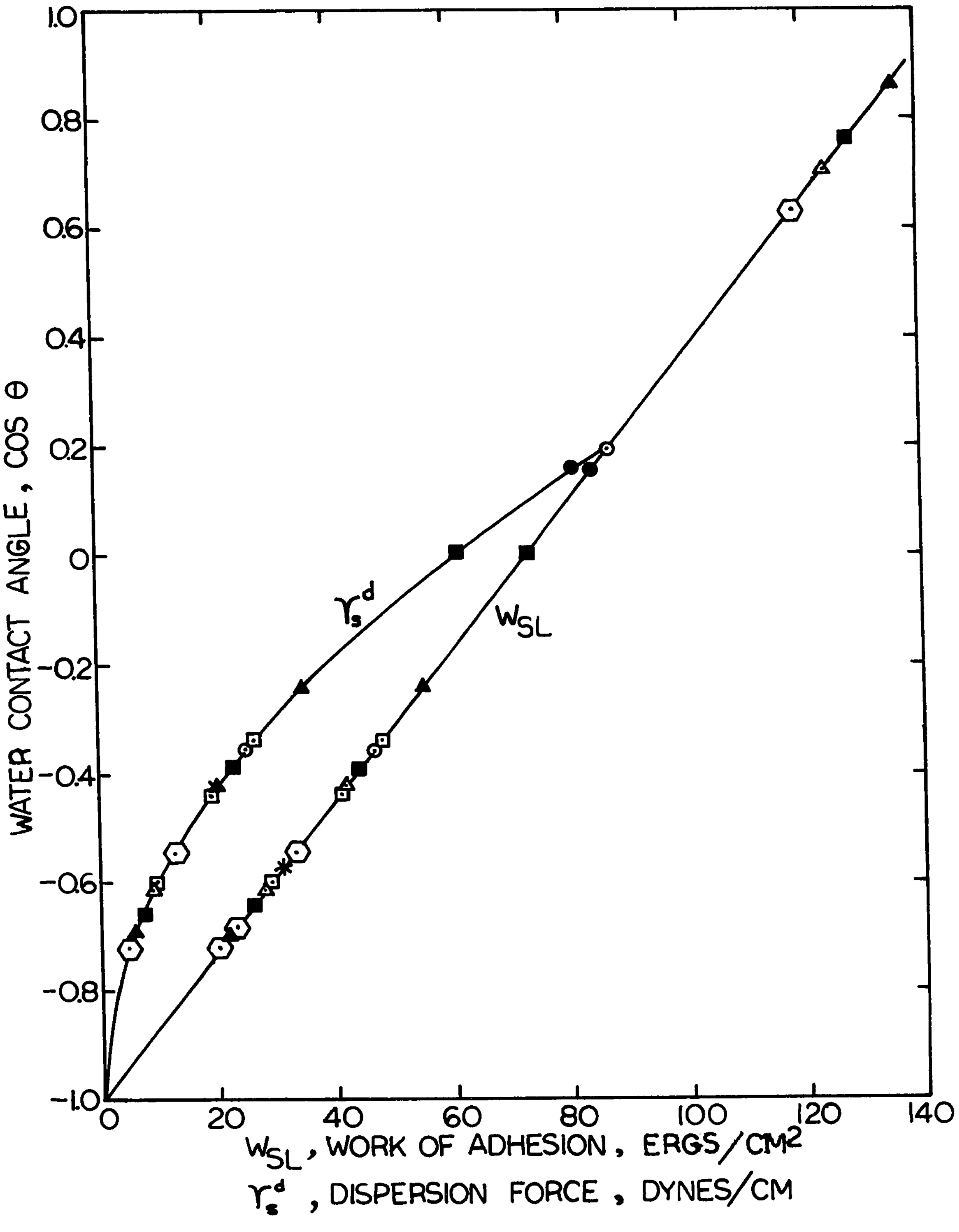
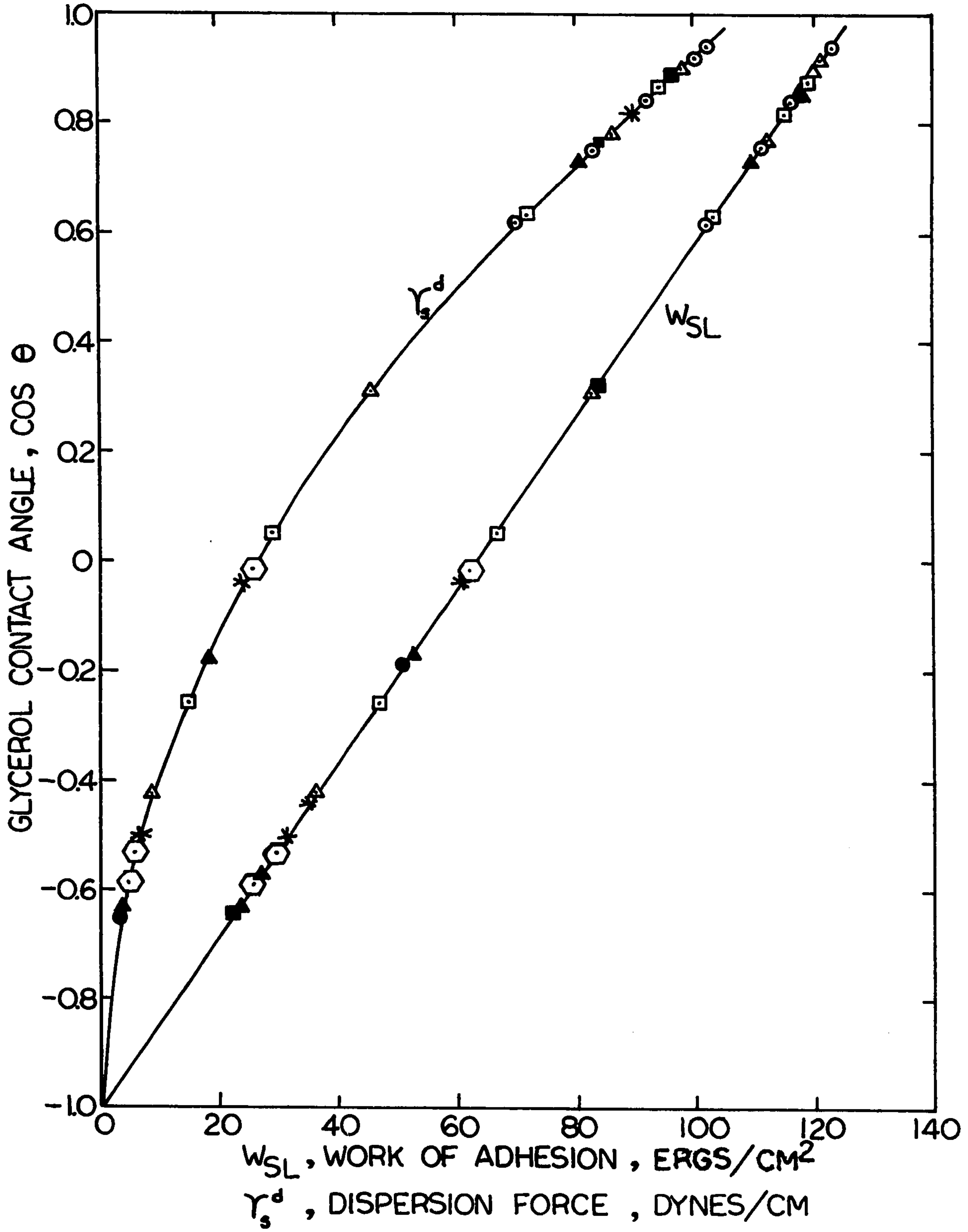

1.0
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1.0
WATER CONTACT ANGLE , COS Θ
0
20
40
60
80
100
120
140
γ_s^d
W_{SL}
W_{SL} , WORK OF ADHESION , ERGS/CM^2
γ_s^d , DISPERSION FORCE , DYNES/CM

Figure 2: Glycerol Contact Angle Versus the Work of Adhesion and Solid Dispersion Forces

Open: Alcohols treated surfaces

Closed: Silanes treated surfaces



1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
GLYCEROL CONTACT ANGLE, COS Θ
0
20
40
60
80
100
120
140
W_{SL}, WORK OF ADHESION, ERGS/CM^2
γ_s^d, DISPERSION FORCE, DYNES/CM
γ_s^d
W_{SL}

contact angle increased with decreasing work of adhesion. For one degree increase in the contact angle of water and glycerol, the work of adhesion of water and glycerol on the surface decreases by 1.213 and 1.056 dynes/cm respectively. When the work of adhesion is smaller than the liquid surface tension, the contact angle is larger than 90°.

To reduce the work of adhesion of a liquid on a solid surface, the solid surface can be adsorbed with substances of lower energy. The reduction of energy depends upon the amount of adsorption. Figures 3-6 show the relationships between the work of adhesion and the surface coverage of the adsorbates. The shape of the curves in Figures 3-6 are similar to that of the curves in Figures 7-10 (Chapter 3). Increasing the number of adsorbate groups per unit surface area, decreases the work of adhesion of a liquid on the solid surface. On the alcohol and silane treated silica surfaces (Figures 3-4), the data obtained with water show that the slope of the curve is steep at low surface coverage becoming horizontal below 20-30 ergs /cm^2.

Figures 5 and 6 show the work of adhesion data obtained with glycerol on alcohol and silane treated silica surfaces. The shapes of these plots are similar, i.e., the slope changes from small to large and small again as a

Figure 3: The Work of Adhesion of Water on Alcohol Treated Silica Surfaces as a Function of the Surface Coverage

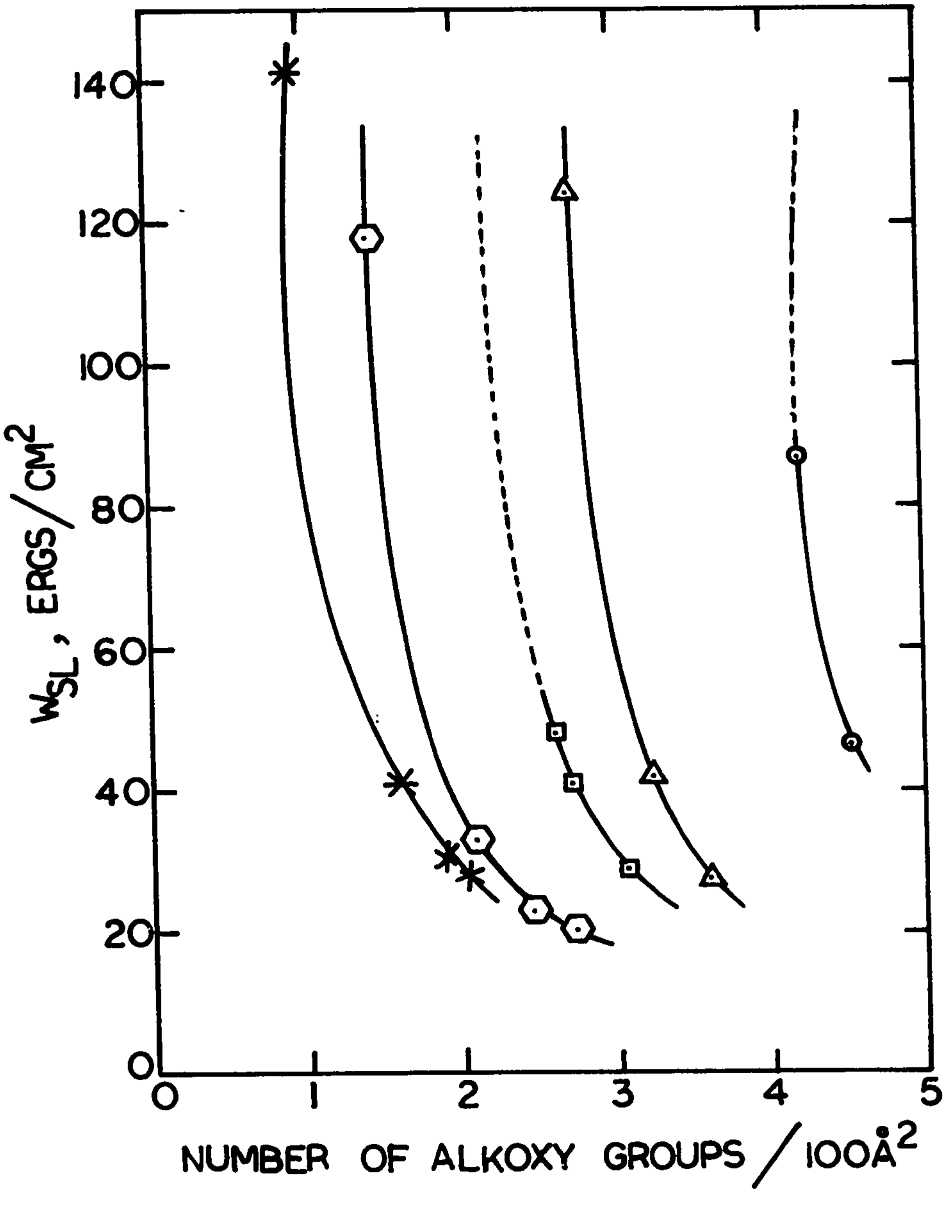
o Silica surface treated with methanol

△ Silica surface treated with ethanol

□ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



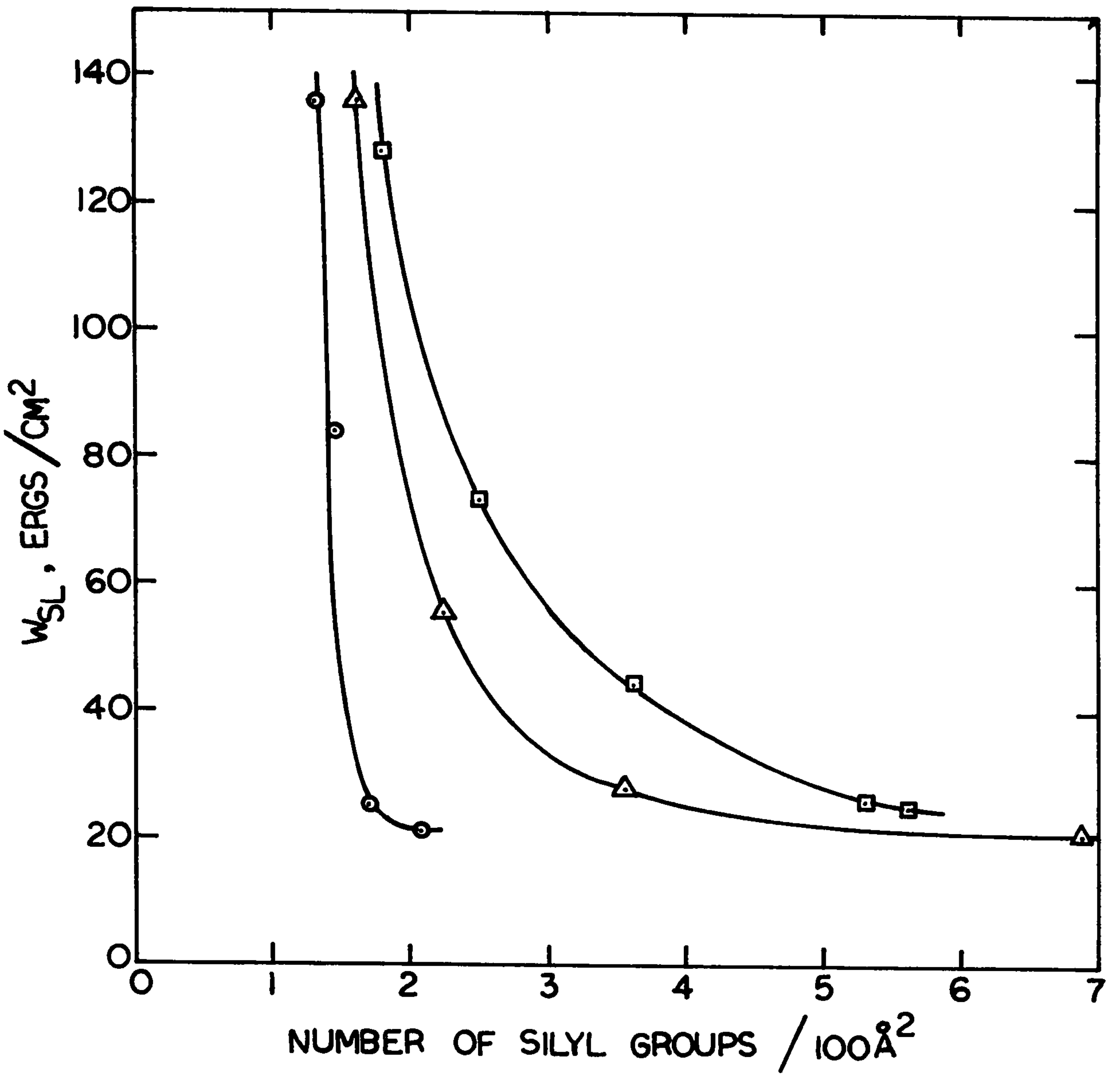
W_{SL}, ERGS/CM^2
140
120
100
80
60
40
20
0
0
1
2
3
4
5
NUMBER OF ALKOXY GROUPS / 100Å^2

Figure 4: The Work of Adhesion of Water on Silane Treated Silica as a Function of the Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$



W_{SL}, ERGS/CM^2
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS /100Å^2

Figure 5: The Work of Adhesion of Glycerol on Alcohol Treated Silica as a Function of the Surface Coverage

o Silica surface treated with methanol

△ Silica surface treated with ethanol

▫ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

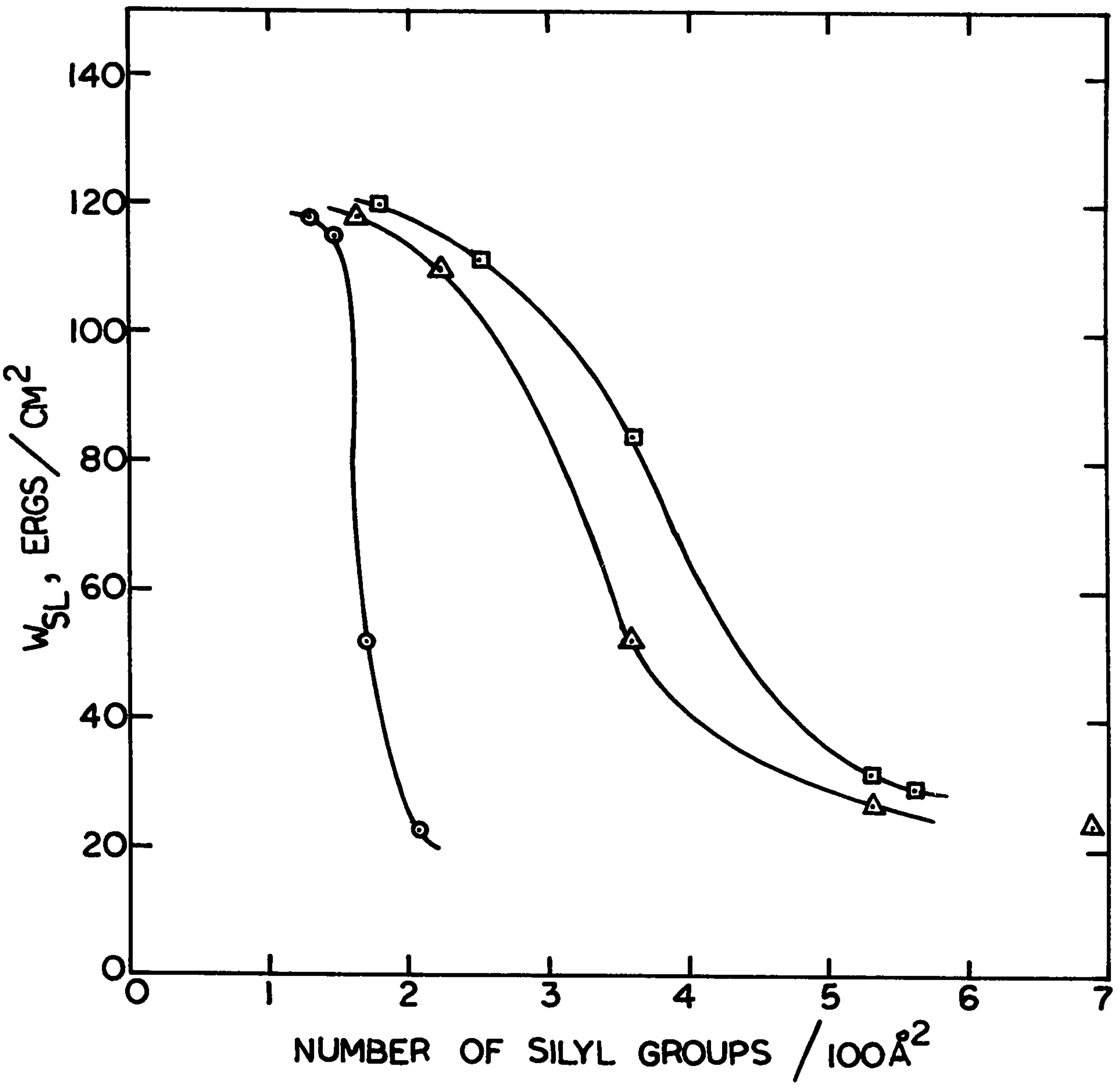
* Silica surface treated with decanol

Figure 6: The Work of Adhesion of Glycerol on Silane Treated Silicas as a Function of Surface Coverage

◻ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$



140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
W_{SL}, ERGS/CM^2
NUMBER OF SILYL GROUPS /100Å^2

function of the surface coverage. From the results of Figures 3 and 4 and Figures 5 and 6 it is clear that the work of adhesion depends not only upon the surface coverage, the type of adsorbed species, but also on the surface tension of the liquid.

b) Dispersion Forces and Contact Angle

Equation (9) shows the relationship between the work of adhesion and the dispersion forces. Since the surface tension of the liquid remains constant, the dispersion forces of the liquid would also be constant. Thus, the dispersion forces are proportional to the work of adhesion. Therefore, we would expect that the relationship between γ_s^d and the surface coverages would be similar to that obtained for $W_{s\ell}$. The plots relating γ_s^d with surface coverages for the two liquids are given in Figures 7 to 10.

c) The Heats of Adsorption and Contact Angle

The plots of contact angles for water and glycerol versus the net heat of adsorption of octamethylcyclotetrasiloxane (D_4) are shown in Figures 11-14. Decrease in the net heat of adsorption corresponds to increase in the contact

Figure 7: Dispersion Forces (Solid) Calculated from Water Contact Angle on Alcohol Treated Silicas as a Function of the Surface Coverage

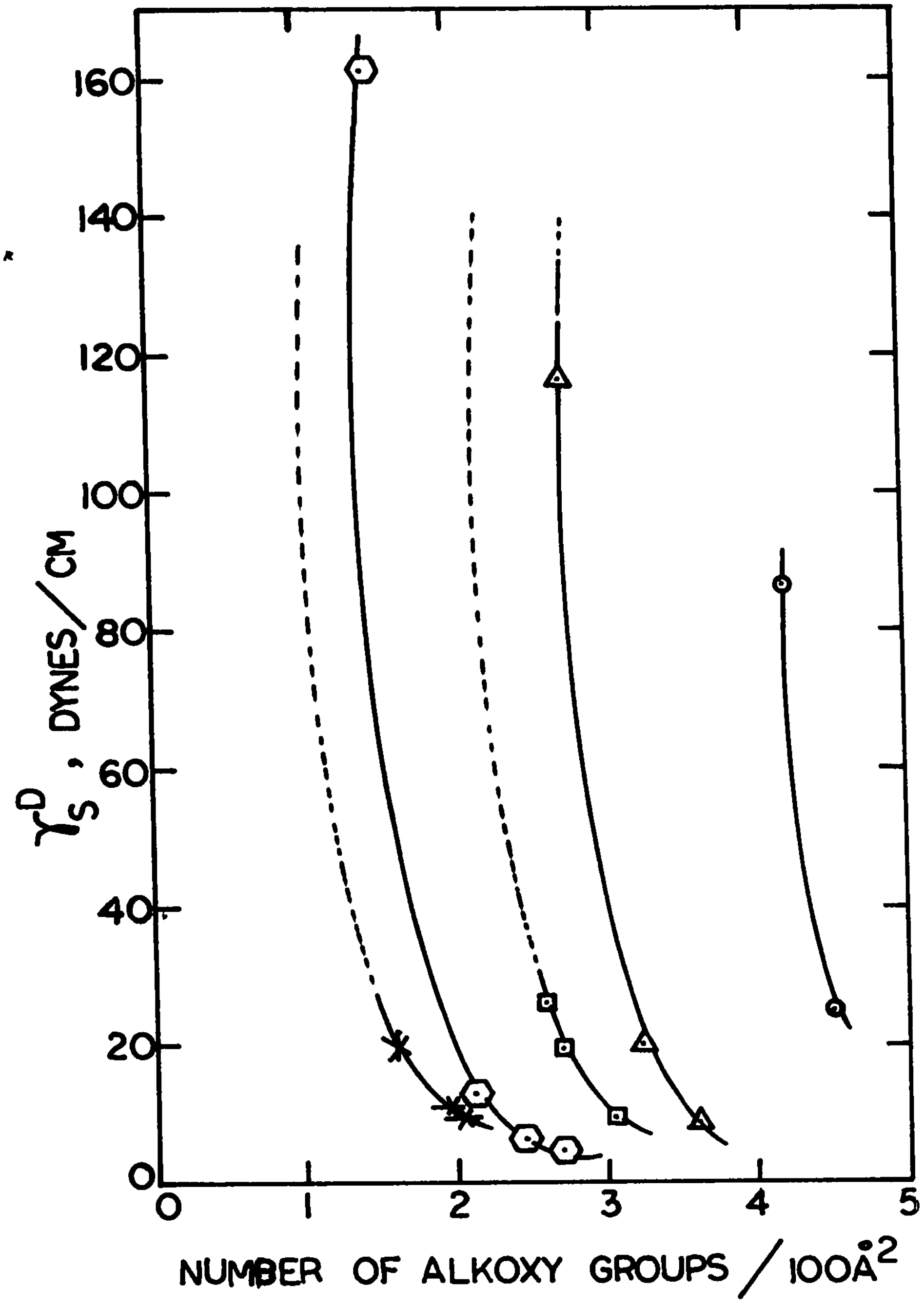
o Silica surface treated with methanol

Δ Silica surface treated with ethanol

□ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



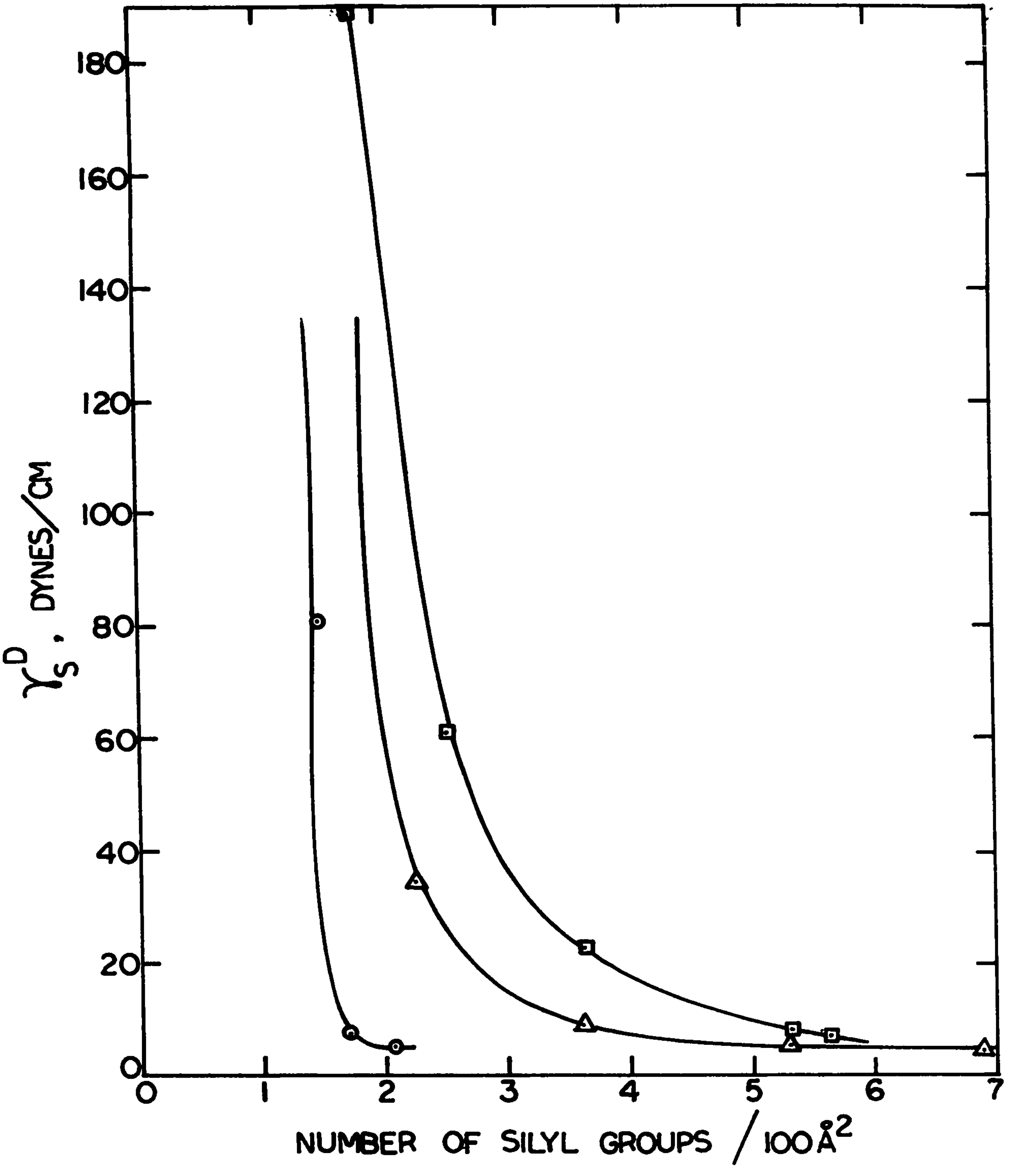
160
140
120
100
80
60
40
20
0
γ_S^D, DYNES/CM
0
1
2
3
4
5
NUMBER OF ALKOXY GROUPS / 100Å²

Figure 8: Dispersion Forces (Solid) Calculated from Water Contact Angle on Silane Treated Silica as a Function of the Surface Coverage

□ Silica Surface treated with CH_3HSiCl_2

△ Silica Surface treated with $(CH_3)_2SiCl_2$

○ Silica Surface treated with $(CH_3)_3SiCl$



γ_S^D , DYNES/CM
180
160
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS / 100 Å^2

Figure 9: Dispersion Forces (Solid) Calculated from Glycerol Contact Angle on Alcohol Treated Silicas as a Function of the Surface Coverage

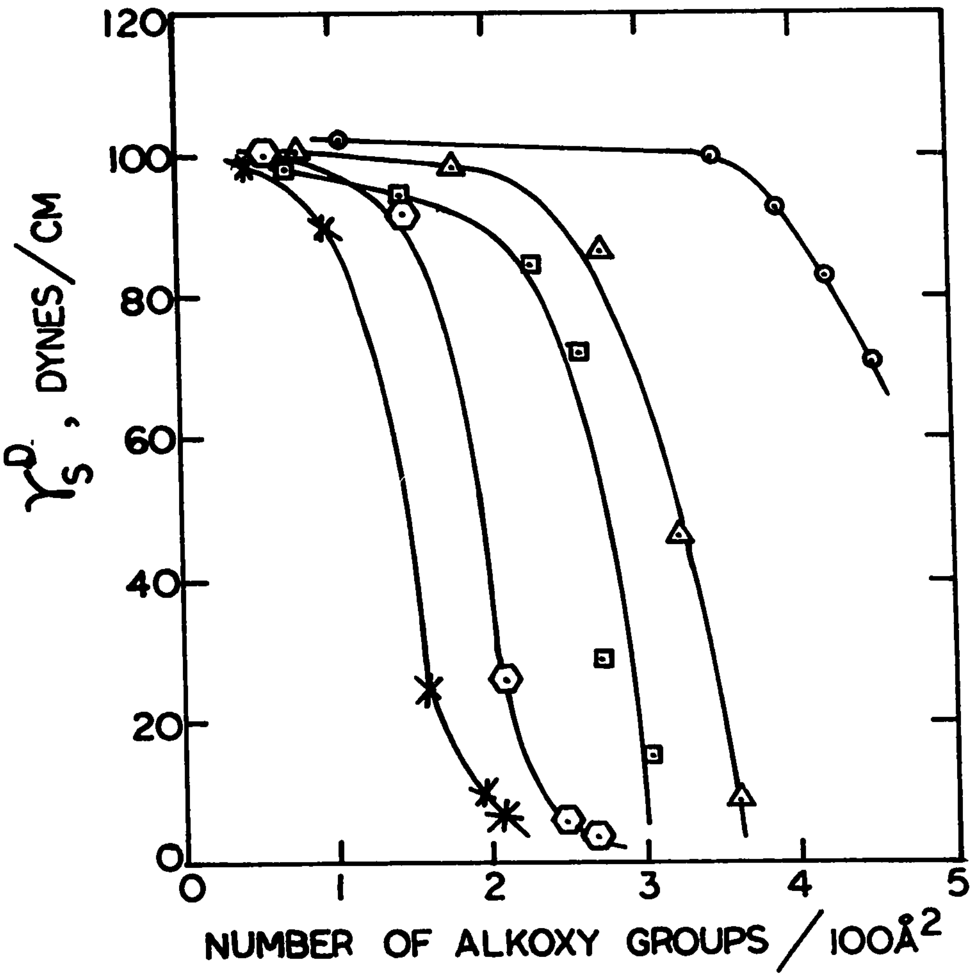
o Silica surface treated with methanol

Δ Silica surface treated with ethanol

□ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



γ_s^D , DYNES/CM
120
100
80
60
40
20
0
0
1
2
3
4
5
NUMBER OF ALKOXY GROUPS / 100Å^2

Figure 10: Dispersion Forces (Solid) Calculated from Glycerol Contact Angle on Silane Treated Silicas as a Function of the Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$

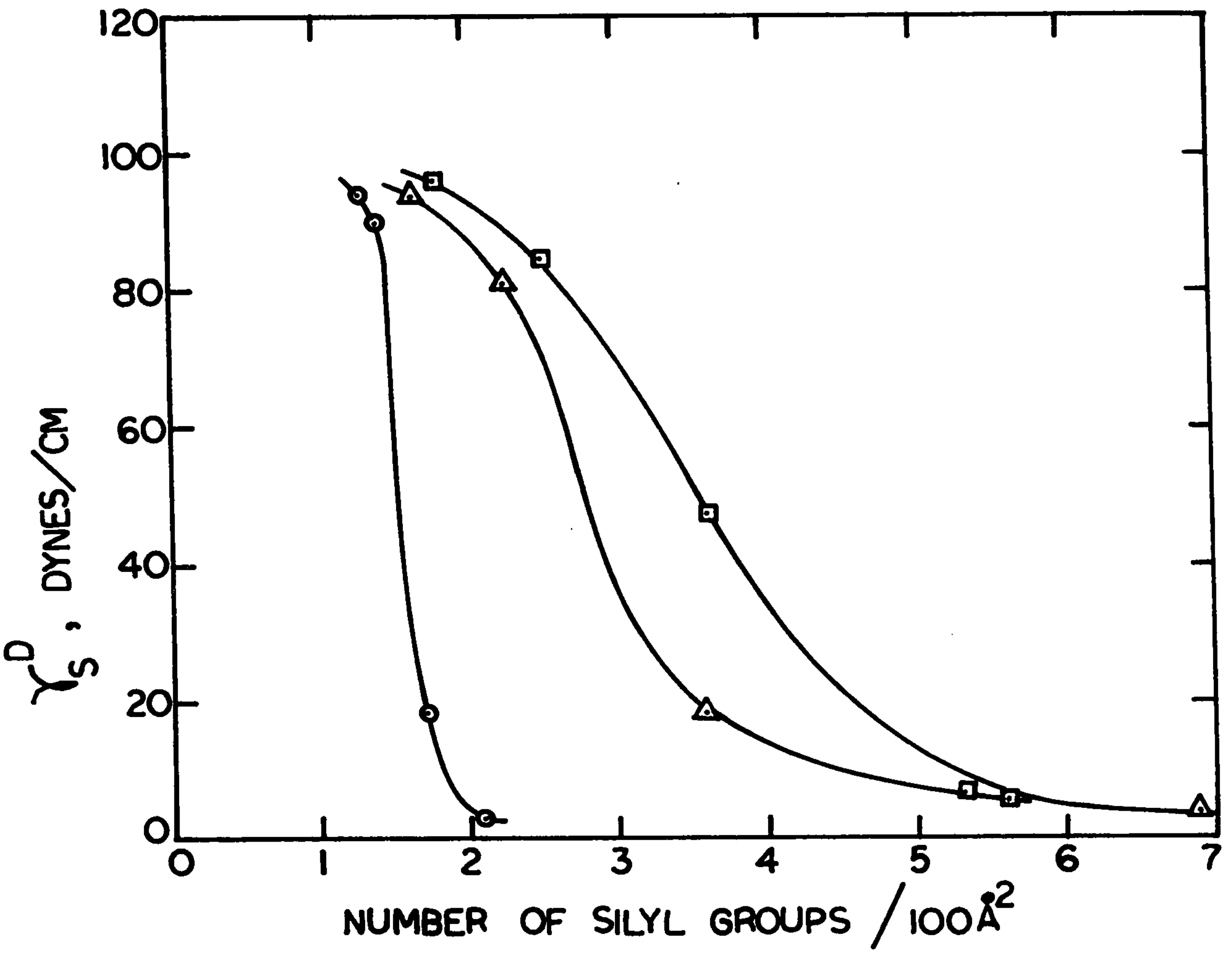

120
100
80
60
40
20
0
γ_S^D, DYNES/CM
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS / 100Å^2

Figure 11: Water Contact Angle Versus the Net Heat of Adsorption of Octamethyltetracyclosiloxane (D_4) on Alcohol Treated Silica Surfaces

o Silica surface treated with methanol

△ Silica surface treated with ethanol

◻ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol

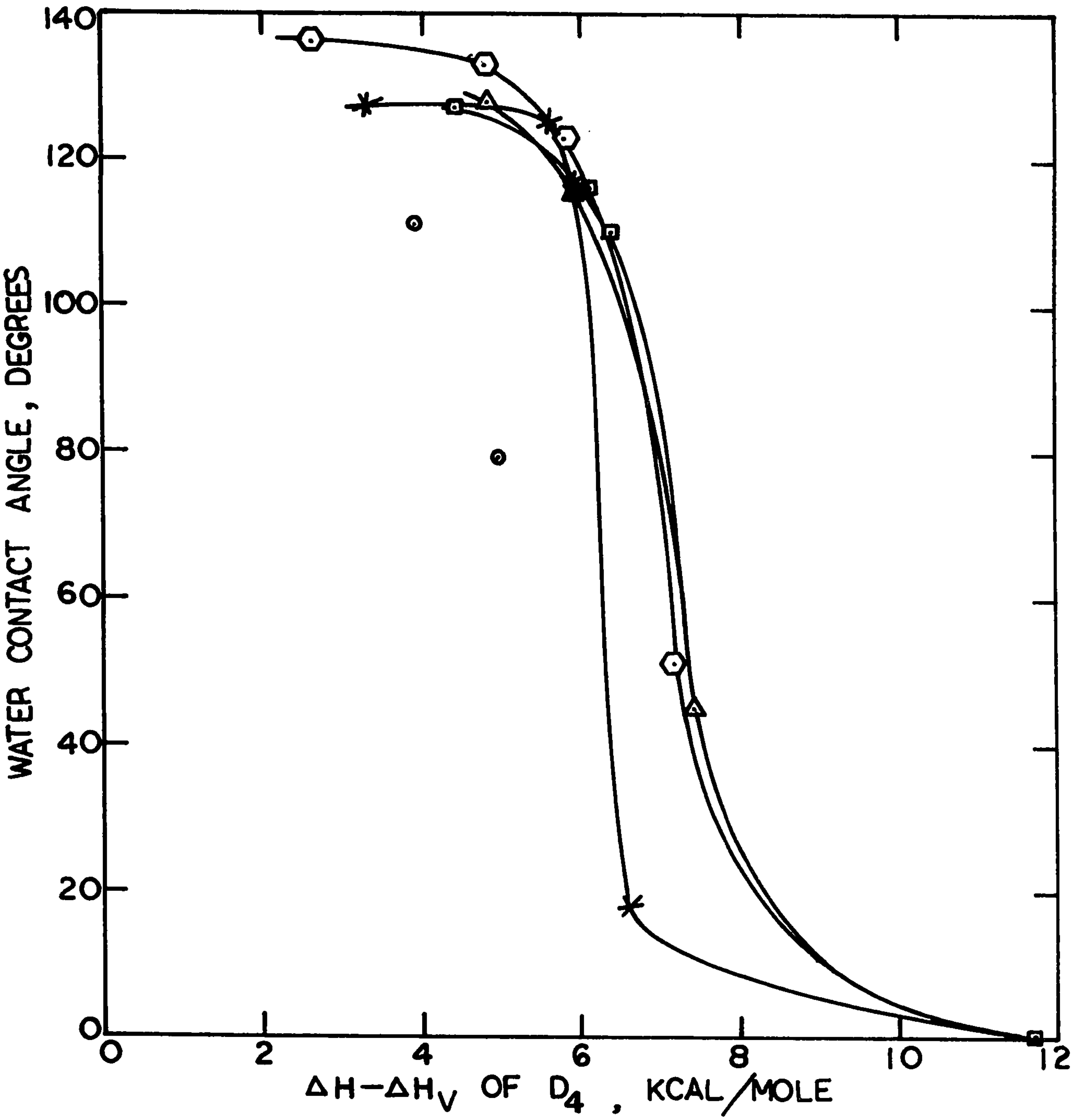

140
120
100
80
60
40
20
0
WATER CONTACT ANGLE, DEGREES
0
2
4
6
8
10
12
ΔH−ΔH$_V$ OF D$_4$, KCAL/MOLE

Figure 12: Water Contact Angle Versus the Net Heat of Adsorption of Octamethyltetracyclosiloxane (D_4) on Silane Treated Silica Surface

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$

Figure 13: Glycerol Contact Angle Versus the Net Heat of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Alcohol Treated Silica Surface

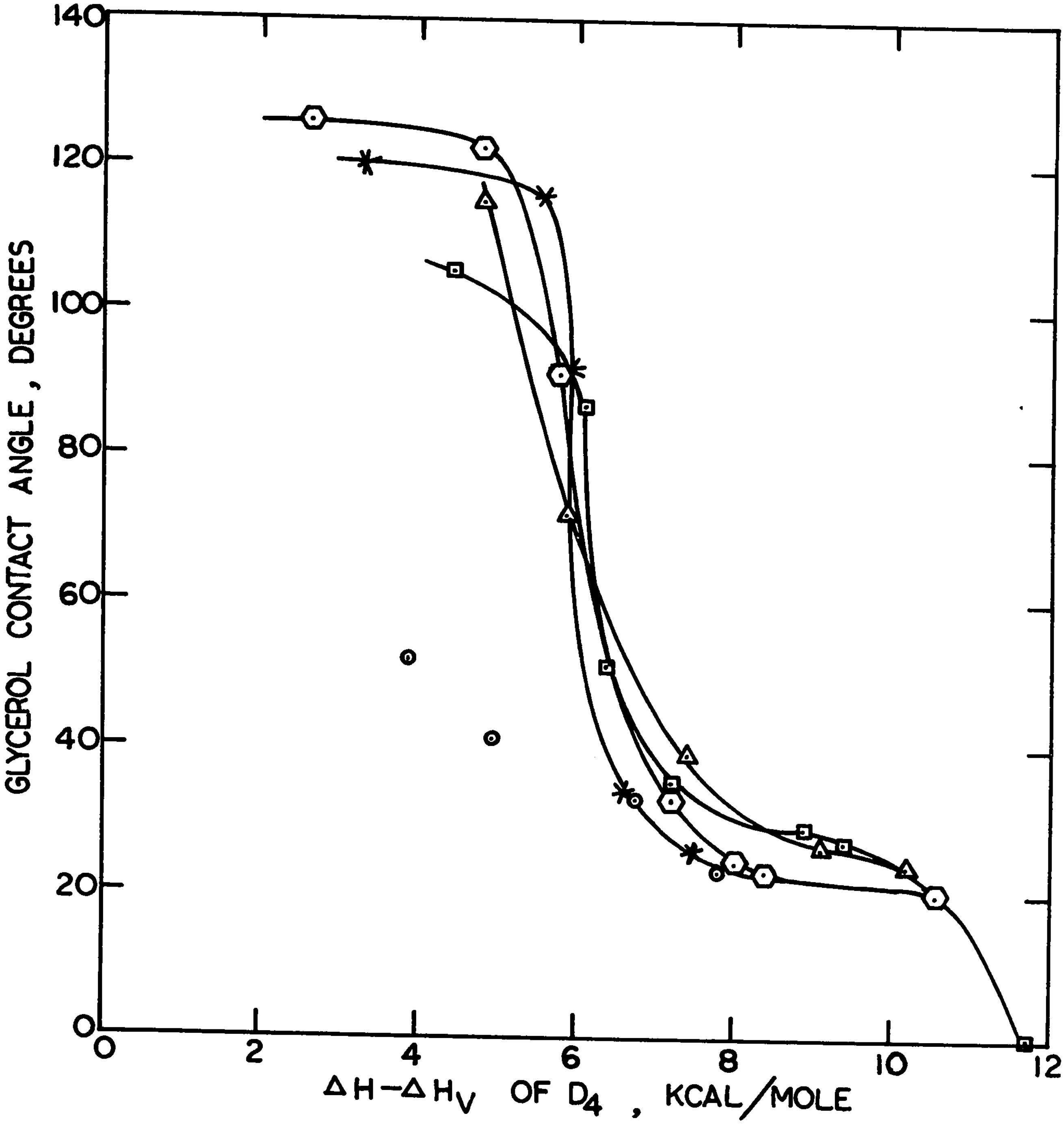
o Silica surface treated with methanol

△ Silica surface treated with ethanol

◘ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



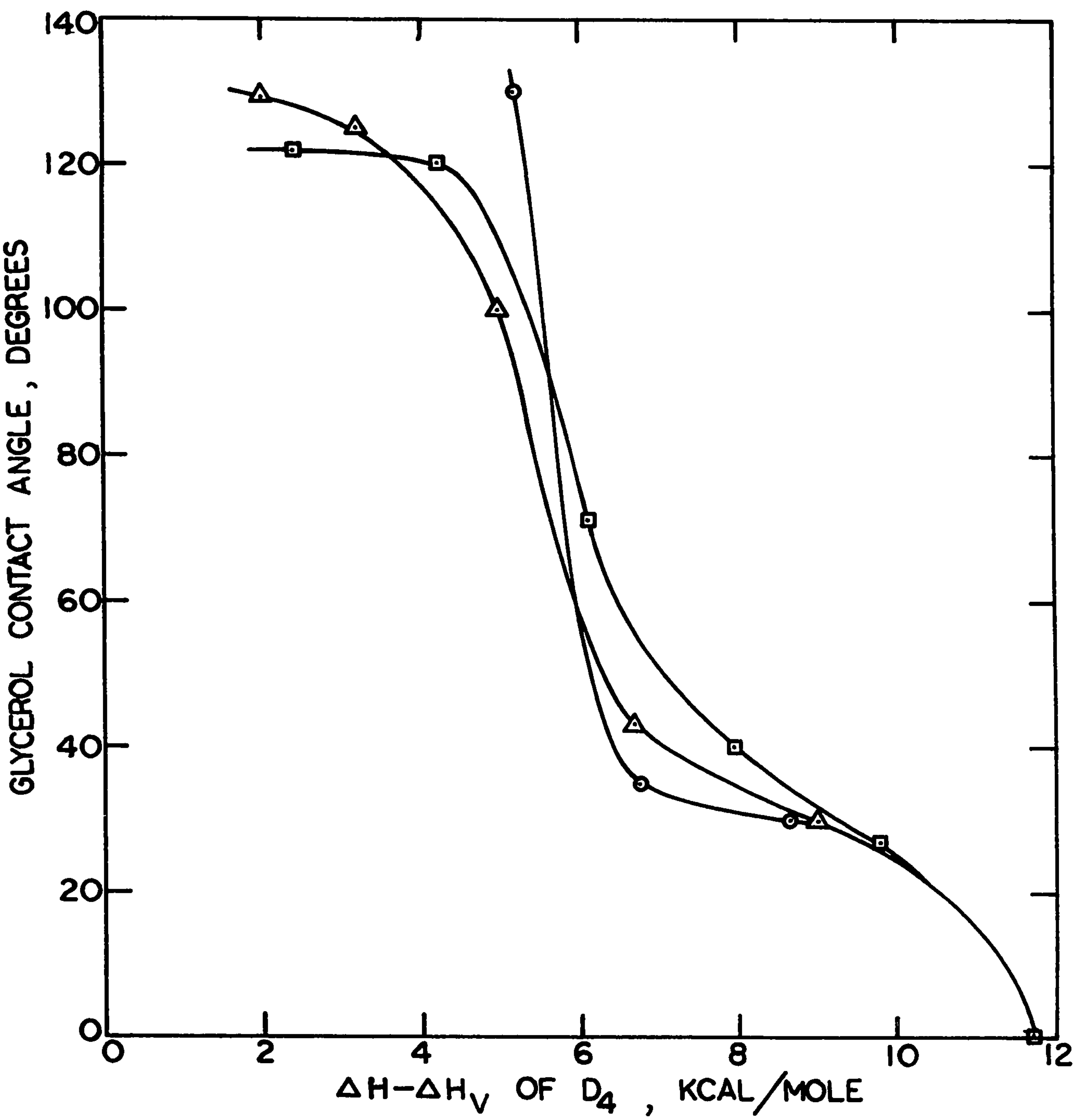
140
120
100
80
60
40
20
0
0
2
4
6
8
10
12
GLYCEROL CONTACT ANGLE, DEGREES
ΔH−ΔH_V OF D_4, KCAL/MOLE

Figure 14: Glycerol Contact Angle Versus the Net Heat of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Silane Treated Silica Surface

▫ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

o Silica surface treated with $(CH_3)_3SiCl$


GLYCEROL CONTACT ANGLE, DEGREES
0
20
40
60
80
100
120
140
0
2
4
6
8
10
12
$\Delta H - \Delta H_V$ OF D_4, KCAL/MOLE

angle. In general, the curves can be divided into three regions. For a value of the net heat of adsorption above 7-8 Kcal/mole, the contact angle is below about 40^{o}. For values below 5-6 Kcal/mole, the contact angle is above 120^{o}. This region is equi-valent to the flat or the limiting contact angle region as described in Figures 7-10 (Chapter 3). In the range of 6-7 Kcal/mole, the contact angle is very sensitive to the net heat of adsorption values.

The results of Figures 11-14 are summarized in Figures 15 and 16, plotted in terms of Cosine of the contact angle. These plots can also be divided into three regions. For a net heat of adsorption of 9 Kcal/mole, the contact angle is less than 30^{o}. For a net heat of adsorption values between 9 and 6 Kcal/mole, the contact angle value increased abruptly from 30^{o} to 120^{o}. Below 6 Kcal/mole, the slope of the $\cos\theta$ versus ΔH plot decreased.

Since zero value of the net heat of adsorption signifies that the heat of adsorption equals heat of condensation, it corresponds to a maximum change in the surface energy due to the adsorption of alkoxy or silyl groups on the silica surfaces. If we were therefore, to extend the plots of Figures 15 and 16 to zero net heat of adsorption, the contact angle value obtained ought to be close to the maximum possible values. The values obtained in this fashion

Figure 15: Water Contact Angle Versus the Net Heat of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Alcohol and Silane Treated Silica Surfaces

White Dots: Alcohols treated surfaces

Black Dots: Silanes treated surfaces

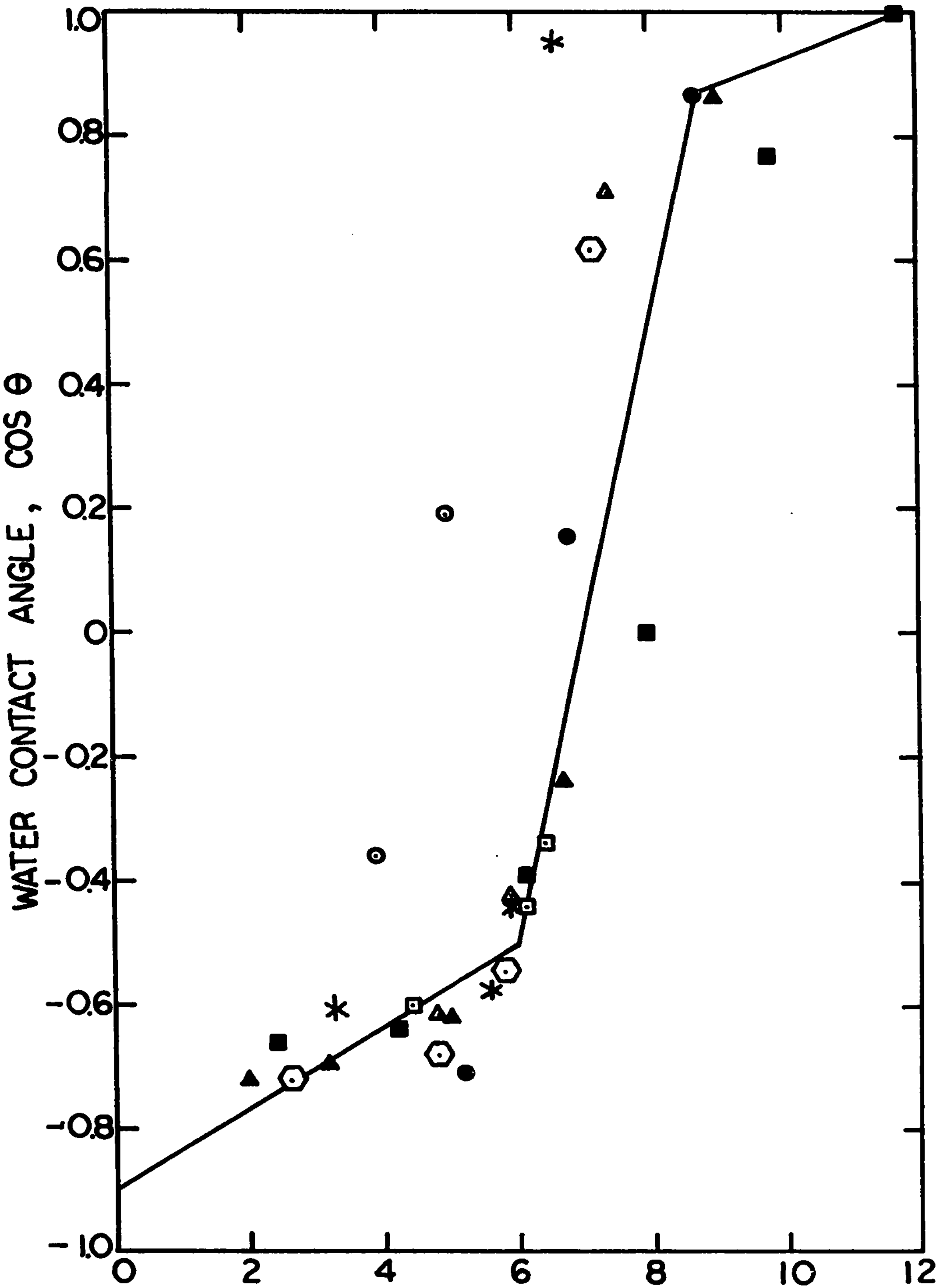
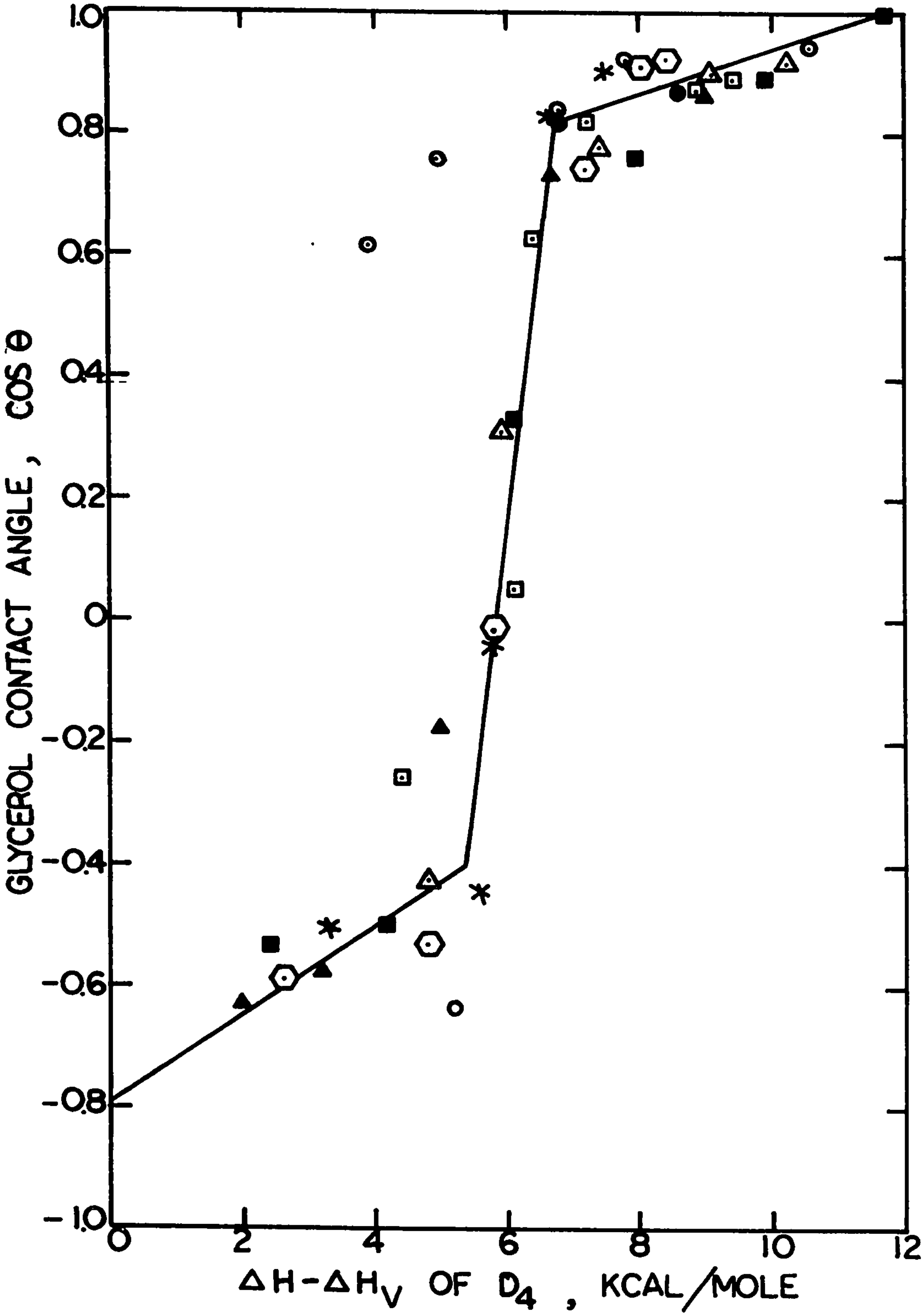

1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
WATER CONTACT ANGLE, COS Θ
0
2
4
6
8
10
12
ΔH−ΔH_V OF D_4, KCAL/MOLE

Figure 16: Glycerol Contact Angle Versus the Net Heat of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Alcohol and Silane Treated Silica Surfaces

White Dots: Alcohols treated surfaces

Black Dots: Silanes treated surfaces


GLYCEROL CONTACT ANGLE , COS θ
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
12
ΔH - ΔH_V OF D_4 , KCAL/MOLE

are 154° and 143° for water and glycerol respectively. The value for water compares favorably with the value of 156° reported by Zisman (4).

4.4 CONCLUSION

The work of adhesion of water and glycerol on silica surfaces modified with alcohols and chlorosilanes was related to the surface coverages. The work of adhesion decreased with increasing surface coverage. The contact angle values were also related to the net heat of adsorption of octamethylcyclotetrasiloxane (D_4). As the net heat of adsorption decreased, the contact angle increased only slowly at first followed with a very marked increase. As the heat of adsorption of D_4 approached the value of its heat of condenstation, the contact angle again increased only slightly. The extrapolated value of the contact angle of water to zero net heat of adsorption was 154° which is in excellent agreement with the predicted value of 156°.

4.5 REFERENCES

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CHAPTER 5

FLOTATION

5.1 INTRODUCTION

Mineral dressing was defined as the process of mechanically separating and saving valuable minerals from the valueless material of an ore, whereby the valuable minerals are concentrated into smaller bulk and weight by discarding some of the waste (1). In most mineral dressing processes, the mineral surfaces have to be conditioned before conducting the separation process. For example, in order to increase the selectivity in separating quartz from other beach sand minerals, and saline minerals from each other (2), the minerals are conditioned with nitric acid, hydrofluoric acid (3), fatty amines (4), and fatty acids (5) before undergoing electrodynamic separation. Separation of sulfide from non-sulfide minerals requires conditioning with collectors, frothers and modifiers before introducing bubbles to bring the valuable minerals to the surface of the flotation cell (6-8).

The conditioning may be done in the dry state or in an aqueous solution. Dry conditioning has received considerable attention in the field of electrostatic separation. But in the field of flotation, wet conditioning is widely used. Conditioning in aqueous solutions represents a complex situation. Whenever a mineral particle with aged or fresh surface is immersed in the flotation solution, there may be complicated reactions occurring at the liquid-solid interface. It is, therefore, difficult to control some of the variables which are important to floatability. In order to minimize the complications of the flotation system, dry conditioning has been investigated.

Morey, Parks and Gibson (9) have found that it is sufficient to expose dry quartz to the vapor of octyl alcohol at 100°C to render the quartz hydrophobic for flotation. Under the same conditions iron oxides become hydrophobic to a much less extent. For the flotation of sand from an artificial sand-copper oxide mixture, Iskra (10) conditioned the mixture in the dry state with alkyl chlorosilanes. Scheu (11) was able to float sand from a mixture containing sand, metallic silver and metallic tungsten by conditioning the mixture with alkyl chlorosilanes in the vapor phase.

The purpose of this investigation was to correlate the floatability of silicas to contact angles, surface energy and heats of adsorption. Silica surfaces were modified by reaction with alcohols and chlorosilanes before flotation. The changes in the surface energies thus affected were measured in terms of the heats of adsorption, and contact angle (Chapters 2 to 4). In this section we will attempt to correlate the flotation data in terms of the surface properties.

5.2 EXPERIMENTAL

Silicas used for flotation tests were described in Chapter 2. Surface modification with alkyl chlorosilanes and normal alcohols was also described in Chapter 2. In addition, silica surfaces were modified by adsorbing alkyl amines from their solutions in acetone.

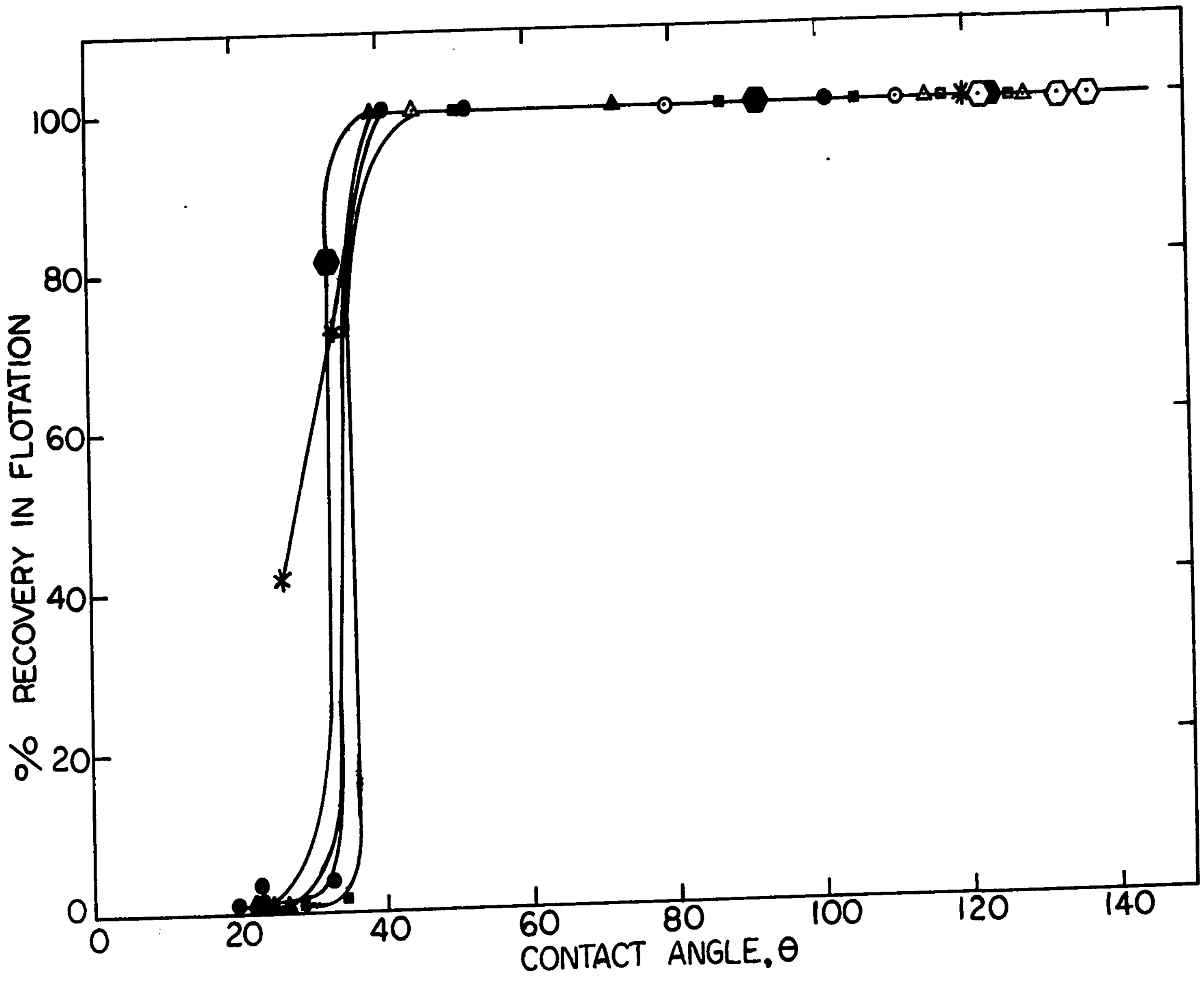
One gram samples were used for flotation tests. Modified Hallimond tube (12), with an 8 inch column and medium porosity glass filter was used. Nitrogen gas at a flow rate of 60 cc/min. was introduced through the disc to produce bubbles. Distilled water at a PH of 6.5 was used as the medium. Flotation time was three minutes.

5.3 RESULTS AND DISCUSSION

a) Contact Angle and Flotation

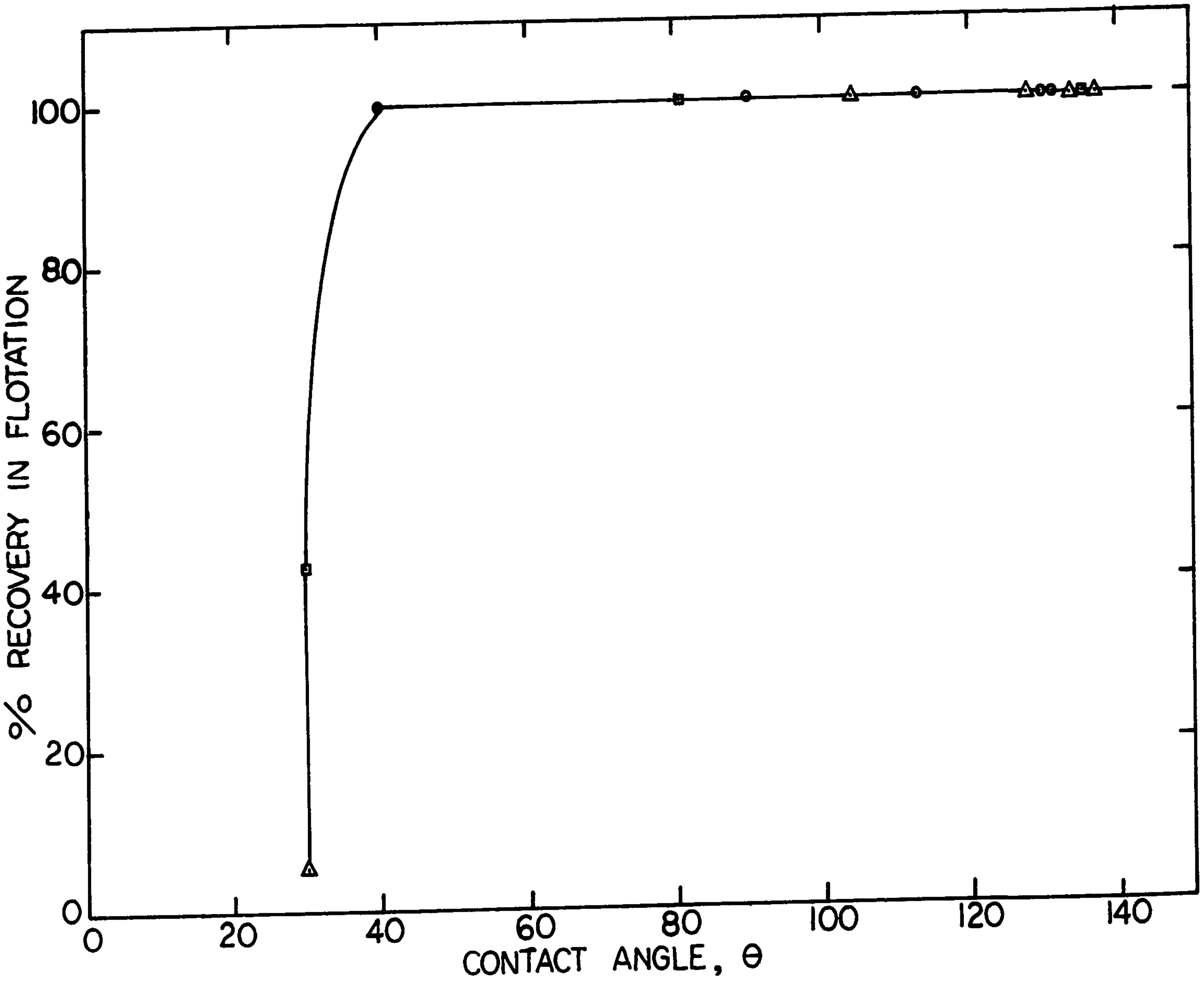
In Figure 1, percentage flotation of silicas treated with normal alcohols has been plotted as a function of the water contact angle. The results for silicas treated with chlorosilanes are shown in Figure 2. Percent

Figure 1: Percent Recovery of Alcohol Treated Silica Surfaces as a Function of Contact Angle of Water



% RECOVERY IN FLOTATION
0
20
40
60
80
100
CONTACT ANGLE, θ
0
20
40
60
80
100
120
140

Figure 2: Percent Recovery of Silane Treated Silica Surfaces as a Function of Contact Angle of Water


% RECOVERY IN FLOTATION
0
20
40
60
80
100
CONTACT ANGLE, θ
0
20
40
60
80
100
120
140

recovery is virtually zero when the contact angle is below about 30°, but increases markedly with contact angle above 30°. One hundred percent flotation recovery is obtained when the contact angle is above 40°.

The two cases discussed above suggest that there is a critical angle value (40°) for hundred percent recovery in flotation. Below this critical value, flotation decreases rapidly. This result is in agreement with that of Smith and Lai (13,14) who studied flotation of quartz with amines. Fuerstenau (15,16) reported 50% flotation recovery with a contact angle of 40°. This difference may be due to the different methods of measurements. Floatability of a solid mineral may change due to the buoyance force of a bubble, the specific gravity and the size of the mineral particles. Thus, the actual functional relationship between contact angle and floatability may depend on several factors.

In Figures 3 and 4 percent recovery in flotation has been plotted as a function of the number of alkoxy or silyl groups per 100 $\mathring{A}^2$ area. Floatability is essentially zero up to a certain surface coverage and then quickly increases with surface coverage. The plots due to the various functional groups are arranged toward increasing surface coverages as the size of the alkyl groups becomes smaller.

Figure 3: Percent Recovery of Silicas Treated with Alcohols Versus Surface Coverage

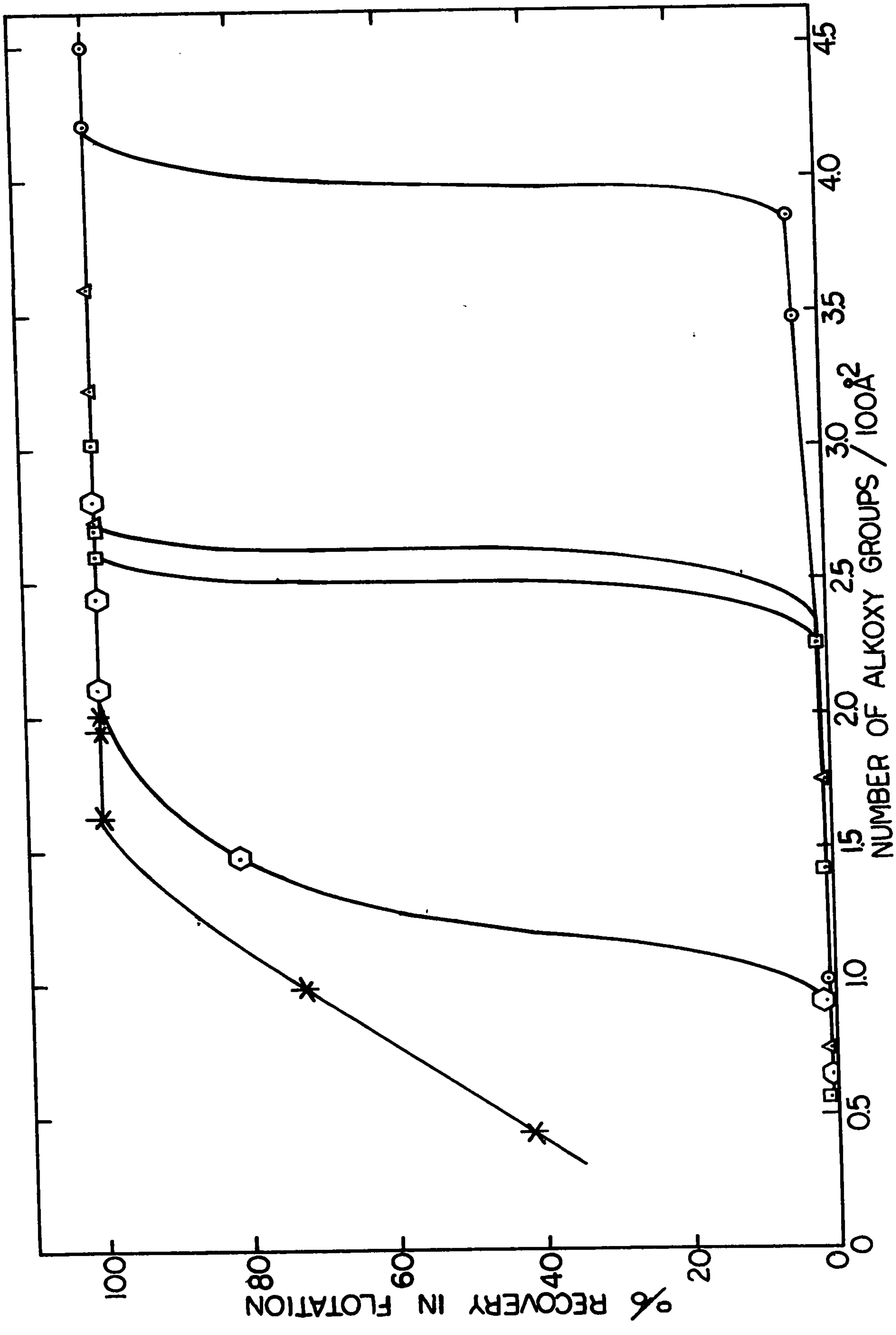
o Silica surface treated with methanol

△ Silica surface treated with ethanol

□ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol



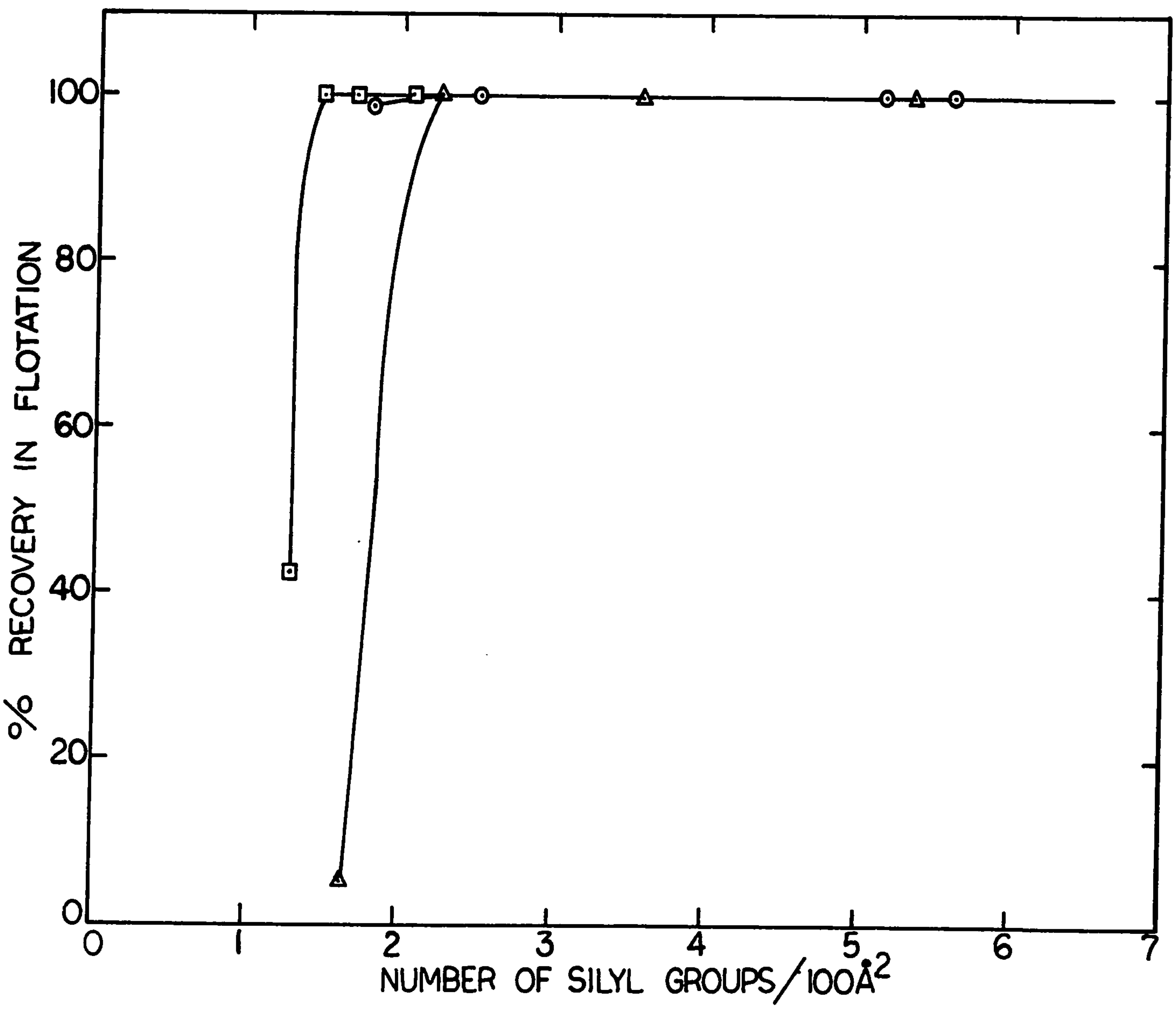
% RECOVERY IN FLOTATION
0
20
40
60
80
100
NUMBER OF ALKOXY GROUPS / 100Å²
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5

Figure 4: Percent Recovery of Silicas Treated with Silanes Versus Surface Coverage

□ Silica surface treated with CH_3HSiCl_2

△ Silica surface treated with $(CH_3)_2SiCl_2$

○ Silica surface treated with $(CH_3)_3SiCl$


% RECOVERY IN FLOTATION
100
80
60
40
20
0
0
1
2
3
4
5
6
7
NUMBER OF SILYL GROUPS/100Å²

The surface coverage at which flotation becomes significant increases as the number of carbon atoms in the alkoxy groups decreases. The various plots are essentially parallel to each other and could therefore be superimposed by shifting them along the horizontal axis.

b) The Work of Adhesion and Flotation

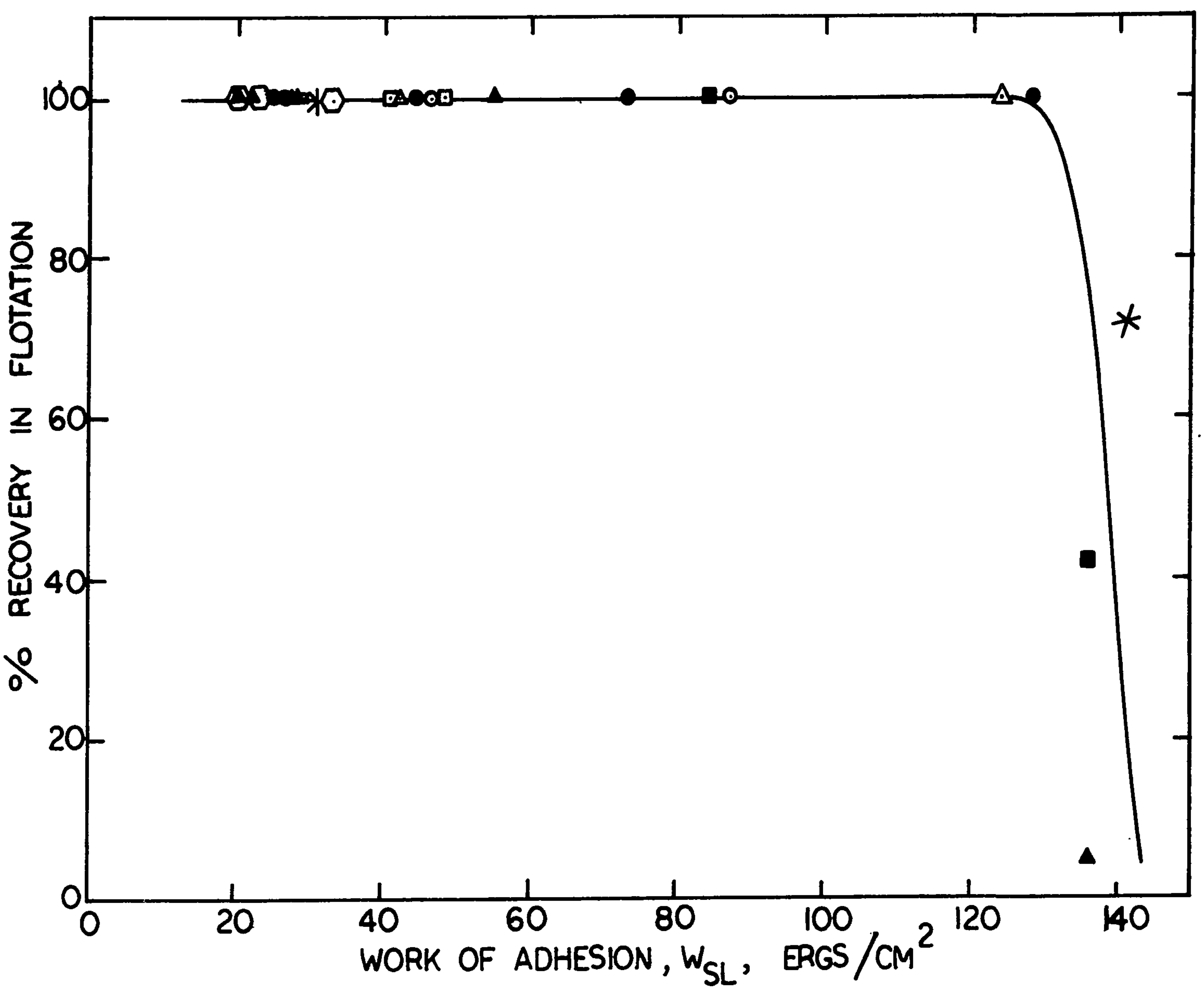
Since contact angle and the work of adhesion are related (equations 3a and 7 in Chapter 4), then flotation must be related to the work of adhesion. Figure 5 shows the plot of percent recovery in flotation versus the work of adhesion for water on the silica surface treated with alcohols and silanes. It is obvious that for the work of adhesion below 125 ergs/cm^2, 100% recovery in flotation is obtained. As the work of adhesion increases over 125 ergs/cm^2, the floatability decreases abruptly.

These results are in agreement with the predictions. Equation 4(a) of Chapter 4 states that if $W_{s\ell} \geq 2 \cdot \gamma_{\ell a}$, solid surface will be wetted by the liquid. Since the surface tension of water is 72.8 dynes/cm at 20^{o}C, work of adhesion of 145.6 ergs/cm^2 represents a state where the solid will be completely wetted giving zero floatability. Thus roughly a 14% reduction in the work of adhesion for water on silica surfaces is required to obtain 100% recovery in flotation.

Figure 5: Percent Recovery in Flotation Versus the Work of Adhesion for Alcohol and Silane Treated Surfaces

Open: Alcohol treated Surface

Closed: Silane treated surface


% RECOVERY IN FLOTATION
0
20
40
60
80
100
0
20
40
60
80
100
120
140
WORK OF ADHESION, W_{SL}, ERGS/CM^2

c) Heats of Adsorption and Flotation

Although the work of adhesion is a good criteria of floatability, its determination is quite complex. Since the heat of adsorption is related to the work of adhesion, it should be possible to correlate floatability with heats of adsorption of the model compounds on silica surfaces. Figure 6 shows the relationship between percent recovery in flotation and the heat of adsorption of octamethylcyclotetrasiloxane (D_4) on silica surfaces treated with alcohols. Figure 7 shows the same relationship for silicas treated with chlorosilanes. The heats of adsorption measurements were made with a gas chromatograph (17). For the alcohol treated surfaces the floatability is virtually zero when the heat of adsorption is above about 19 Kcal/mole. One hundred per cent recovery in flotation is obtained when the heat of adsorption is below about 18 Kcal/mole. Similar results were obtained with surfaces treated with chlorosilanes.

Both the natural mineral silica and Cab-O-Sil were treated with amines and tested for heats of adsorption and floatability. The results of flotation for the mineral silica adsorbed with maximum coverages of several amines along with the heats of adsorption of dioxane on these surfaces are given in Figure 8. It is obvious that while the heats of adsorption of dioxane on these surfaces decreased monotonically

Figure 6: Percent Recovery Versus Heats of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Alcohol Treated Surfaces

o Silica surface treated with methanol

Δ Silica surface treated with ethanol

◘ Silica surface treated with butanol

⬡ Silica surface treated with hexanol

* Silica surface treated with decanol

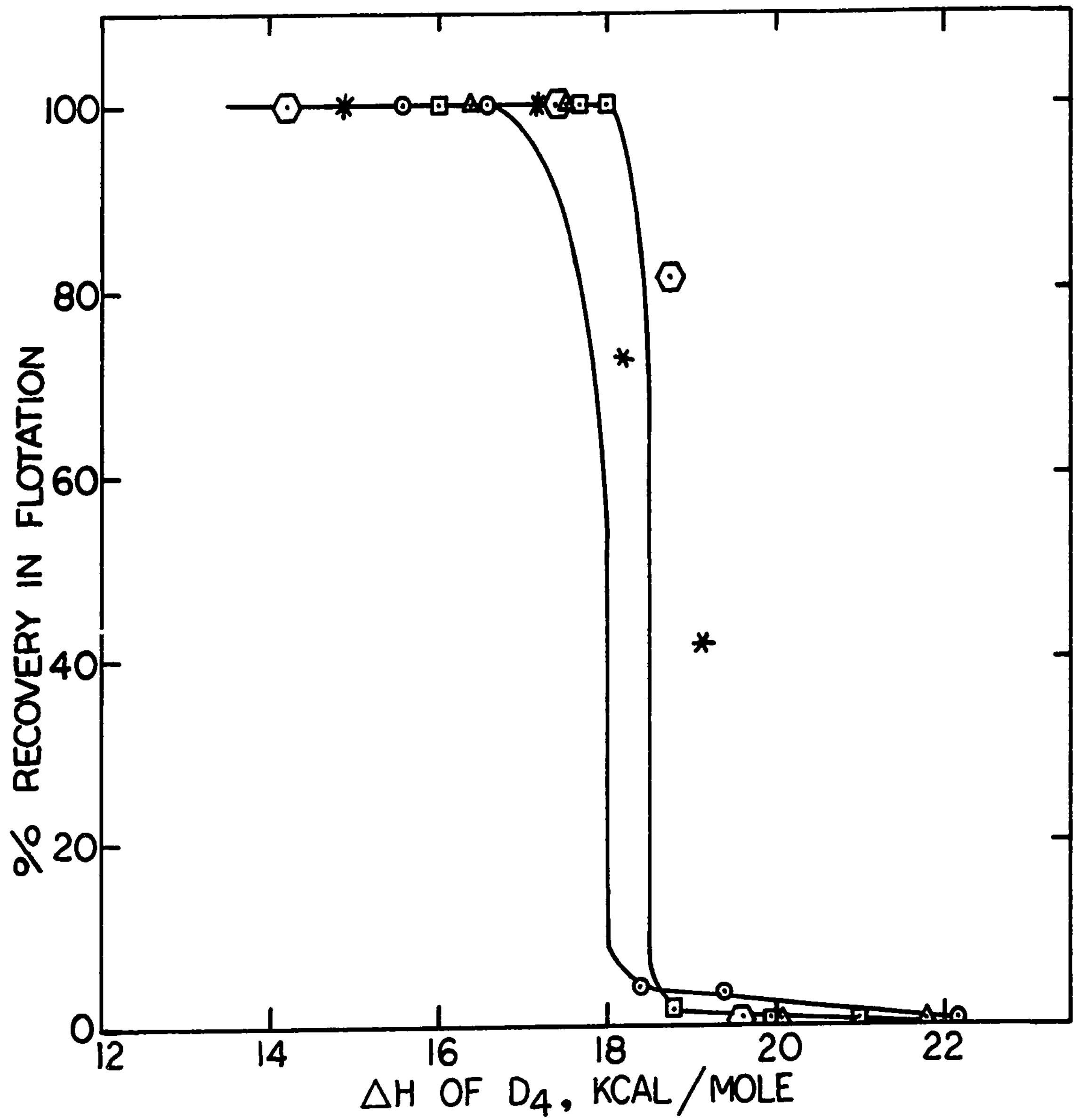
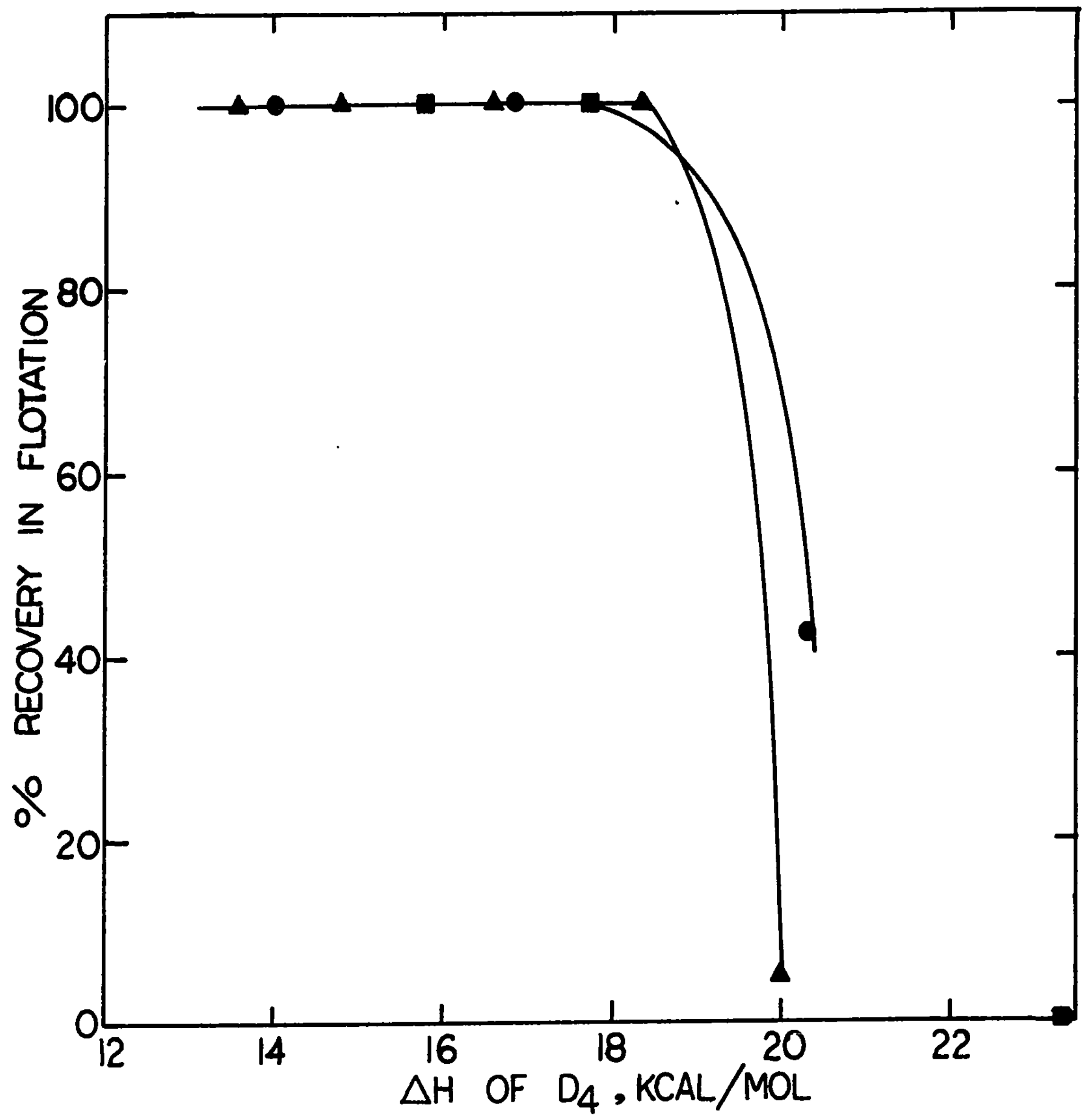

100
80
60
40
20
0
% RECOVERY IN FLOTATION
12
14
16
18
20
22
ΔH OF D4, KCAL/MOLE

Figure 7: Percent Recovery Versus Heats of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Silane Treated Surfaces

■ Silica surface treated with CH_3HSiCl_2

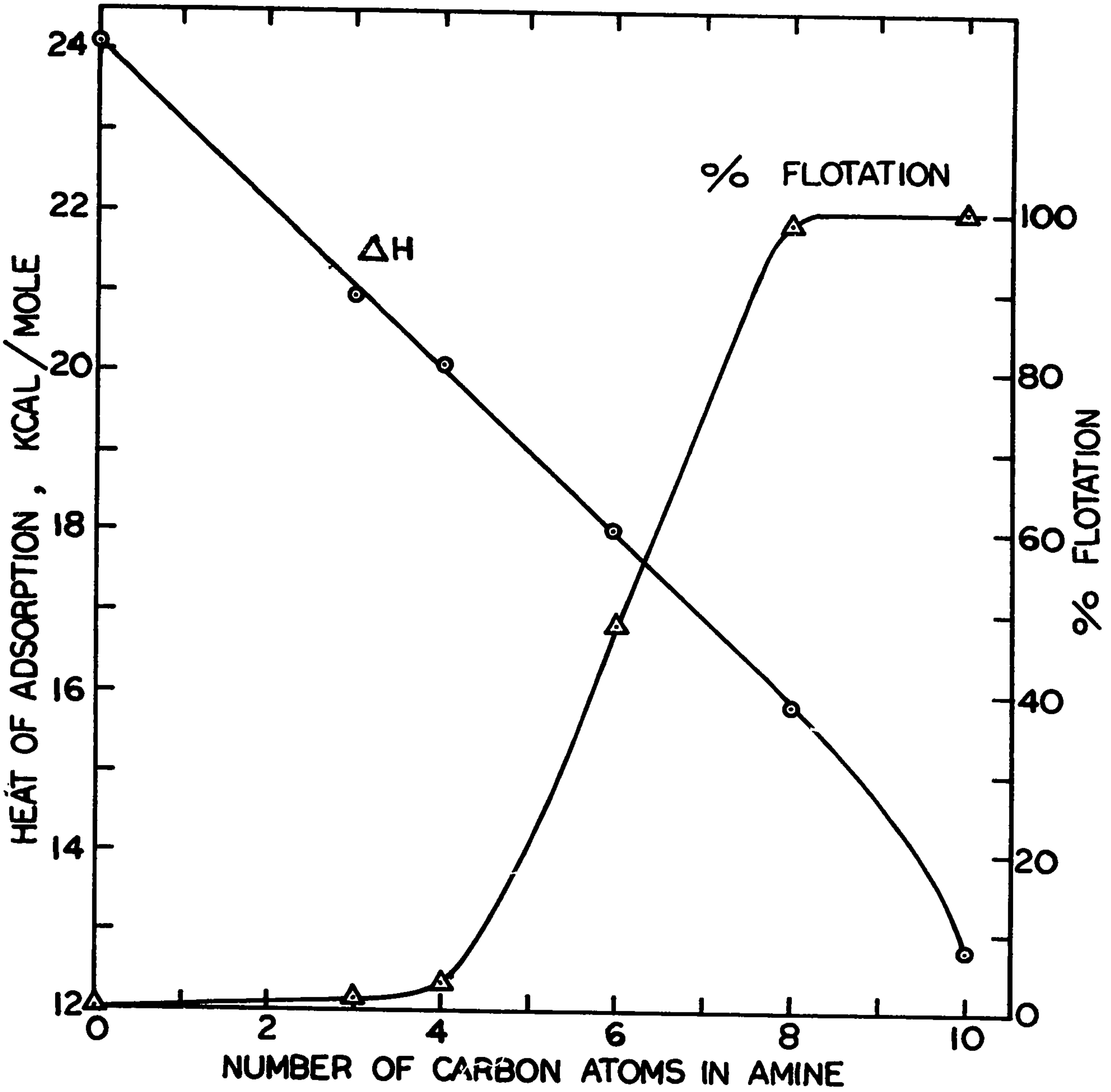
▲ Silica surface treated with $(CH_3)_2SiCl_2$

● Silica surface treated with $(CH_3)_3SiCl$



100
80
60
40
20
0
% RECOVERY IN FLOTATION
12
14
16
18
20
22
ΔH OF D4, KCAL/MOL

Figure 8: Floatability and Heats of Adsorption of Dioxane on the Mineral Silica Adsorbed with Amines (Maximum Coverages) as a Function of the Number of Carbon Atoms in the Amines


24
22
20
18
16
14
12
HEAT OF ADSORPTION , KCAL/MOLE
ΔH
% FLOTATION
100
80
60
40
20
0
% FLOTATION
0
2
4
6
8
10
NUMBER OF CARBON ATOMS IN AMINE

(about 1 Kcal/mole per carbon atom), with increase in the number of carbon atoms of the adsorbed amine molecules, the flotation behaviour was not as simple. The flotation of the mineral increased only slightly as a function of the size of the amine molecules up to butyl amine followed by a sharp increase in flotation. Flotation was essentially complete with the adsorption of octyl amine. Flotation results similar to these were also obtained with Cab-O-Sil. In this case, however, propyl and butyl amines were relatively more effective giving up to 10-15% flotation as compared to 2-4% for the mineral silica. The reason for the lack of effectiveness of propyl and butyl amines in flotation may be due to their solution or partial displacement from the surface by water. The long chain amines on the other hand may be more difficult to be dislodged from the surface.

In order to examine whether the desorption of the low molecular weight amines caused the results of Figure 8, flotation of Cab-O-Sil silica modified by adsorbing different amounts of octylamine or by chemical reaction with various alcohols was investigated. It was found, that flotation of Cab-O-Sil modified with octylamine when plotted as a function of the surface coverage (number of octyl amine molecules/100 $\mathring{A}^2$) resulted in a plot of the same general form as the one obtained with Cab-O-Sil or the mineral silica modified with amines of different molecular weights, Figure 8.

Figure 9 shows the results of flotation of Cab-O-Sil silica chemically reacted with alcohols to give two surface coverages as a function of the number of carbon atoms in the alkoxy groups. The heats of adsorption of octamethylcyclotetrasiloxane (D_4), on these surfaces are also included (17,18). These results are obviously similar, both in respect to the heats of adsorption as well as flotation, to those obtained with Cab-O-Sil or the mineral silica modified by adsorbing amines of different molecular weights, Figure 8. It is to be noted that as the surface coverage by the alkoxy groups increased, the flotation of silica treated with a given alcohol improved markedly while the heat of adsorption decreased. The shape of the flotation curves, nevertheless, remained unchanged. It is, therefore, clear that the flotation data obtained with amines of different molecular weights were not affected by the desorption or solution of the adsorbed molecules.

In Figure 10, flotation of Cab-O-Sil silica treated with alcohols and amines are plotted against the net heat of adsorption, $\Delta H - \Delta H_v$ (heat of adsorption - heat of vaporization), of octamethylcyclotetrasiloxane (D_4) and benzene respectively. Flotation of the mineral silica modified with amines and alcohols as a function of the net heat of adsorp-

Figure 9: Floatability and Heats of Adsorption of Octamethylcyclotetrasiloxane (D_4) on Cab-O-Sil as a Function of the Number of Carbon Atoms in the Alkoxy Groups

Open: Heats of Adsorption Closed: Flotation

o and ● 1.2 alkoxy groups/100 A^2

Δ and ▲ 2.5 alkoxy groups/100 A^2

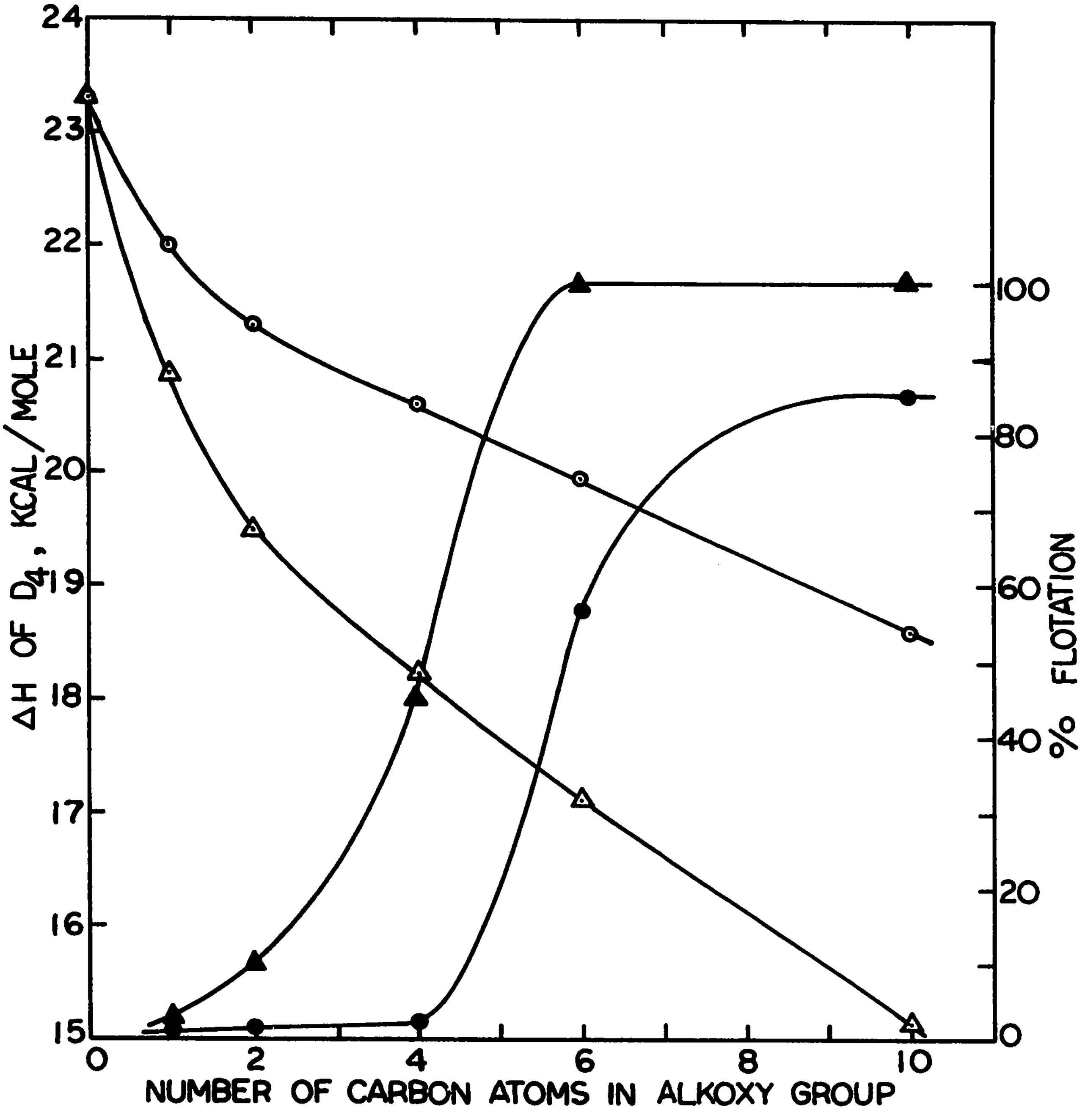

24
23
22
21
20
19
18
17
16
15
ΔH OF D_4, KCAL/MOLE
0
2
4
6
8
10
NUMBER OF CARBON ATOMS IN ALKOXY GROUP
100
80
60
40
20
0
% FLOTATION

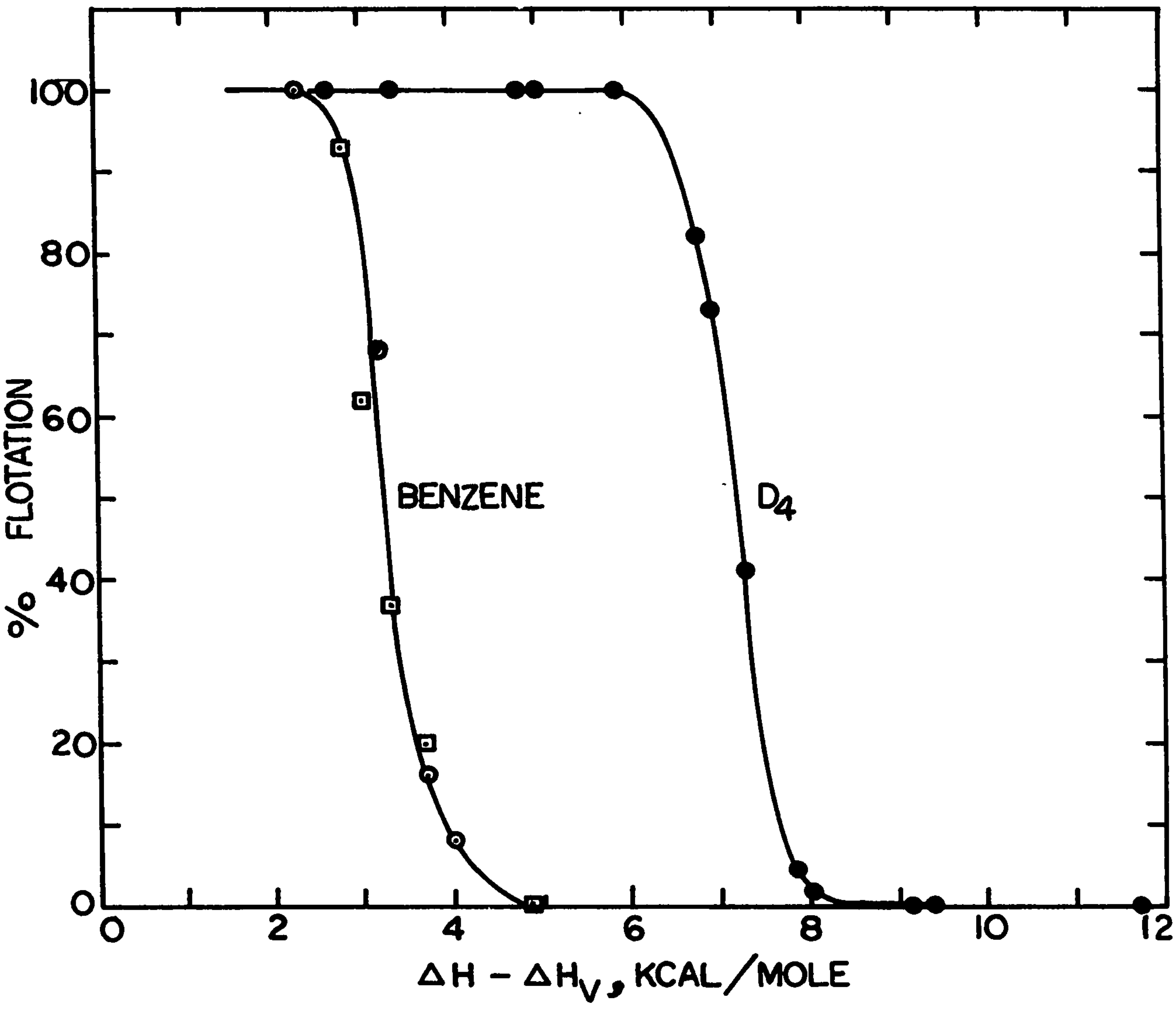
Figure 10: Flotation of Cab-O-Sil as a Function of the Net Heat of Adsorption of Octamethylcyclotetrasiloxane (D_4) and Benzene

Treatment of Silica:

○ Amines of different molecular weights at 0.6 of a monolayer

□ Octylamine at different surface coverage

● Alcohols at different surface coverage



100
80
60
40
20
0
% FLOTATION
0
2
4
6
8
10
12
ΔH − ΔHV, KCAL/MOLE
BENZENE
D4

tion of dioxane is given in Figure 11. Flotation with amines include the results obtained with amines of different molecular weights at maximum surface coverage and at different surface coverages of octyl-amine. The following points are worth noting:

1. The results of flotation of silicas modified with various alcohols and amines fall on a common line when plotted against the net heat of adsorption for each adsorbate. Thus, the type of the surface treatment used to effect changes in the surface energy is less important.

2. There appears to be a critical value for the surface energy above which flotation is negligible and increases to 100% with one Kcal/mole decrease in the heat of adsorption.

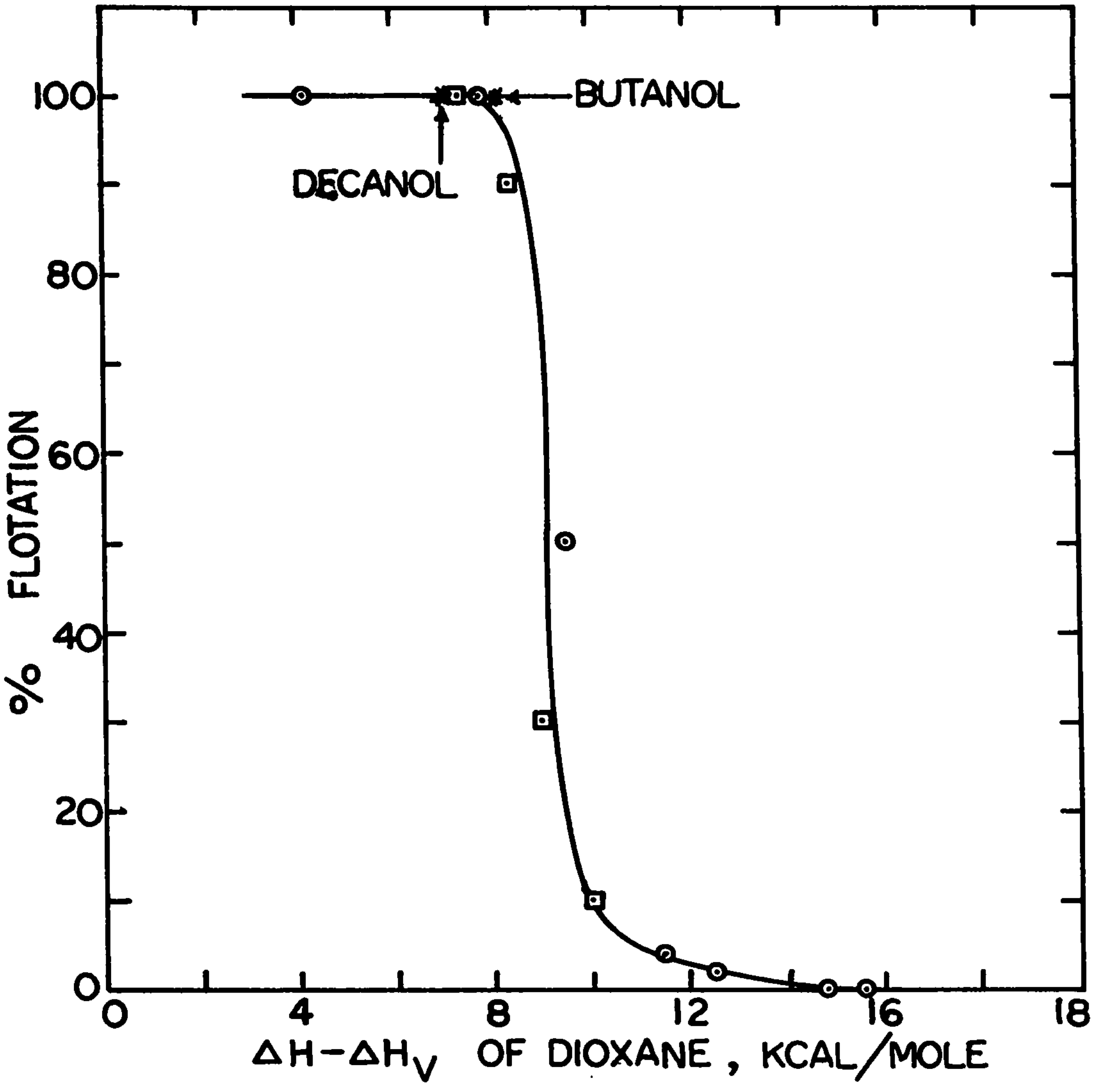
3. The value of the critical surface energy depends on the nature of the adsorbate molecule. This is hardly surprising since the net heat of adsorption on a particular surface depends on the chemical nature of the adsorbate. The value of the critical surface energy for silicas corresponds to approximately 60% of the net heat of adsorption of a compound on the untreated or unmodified surface.

Figure 11: Flotation of the Mineral Silica Treated with Amines and Alcohols as a Function of the Net Heat of Adsorption of 1,4-Dioxane

o Amines of diffferent molecular weights at maximum surface coverages

□ Octylamine at different surface coverages

* Alcohols at maximum surface coverages



100
80
60
40
20
0
% FLOTATION
0
4
8
12
16
18
ΔH-ΔH_V OF DIOXANE, KCAL/MOLE
BUTANOL
DECANOL

5.4 CONCLUSION

Flotation of Cab-O-Sil and mineral silica modified with alcohols, chlorosilanes and alkyl amines were correlated in terms of the contact angles of water or glycerol, the work of adhesion for water and the heats of adsorption of three model compounds. The results suggest that there is a critical contact angle or heat of adsorption value at which floatability changes from essentially zero to 100%. The nature of the surface treatment, used to effect changes in the contact angle or the surface energy appears to be unimportant.

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CHAPTER 6

CLAIMS TO ORIGINAL RESEARCH AND SUGGESTIONS FOR FURTHER WORK

6.1 CLAIMS TO ORIGINAL RESEARCH

1. Gas chromatography was used to investigate the nature of the interaction between the model compounds and the silica surfaces. Higher heats of adsorption values were obtained for all the adsorbates on the mineral quartz as compared with the synthetic silica, Cab-O-Sil.

2. Heats of adsorption values were diminished when the silica surfaces were reacted with alcohols and chlorosilanes. The extent of the diminition depended upon the molecular structure and the surface coverage of adsorbate.

3. Contact angle of water on clean silica surfaces is zero. Silica surfaces treated with alcohols and chlorosilanes on the other hand gave finite contact angle values.

4. The contact angle is a function of the surface coverage of the adsorbed species. The following equation was used to describe the contact angle on the treated silica surfaces:

$$\text{Cos } \theta = \text{Cos } \theta_1 - (\text{Cos } \theta_1 - \text{Cos } \theta_2) \frac{qa}{100}$$

where θ is the contact angle on the modified silica surfaces.

θ_1 is the contact angle on the unmodified silica surfaces.

θ_2 is the contact angle on the silica surface covered with a maximum amount of adsorbate.

q is the number of the adsorbed molecule per 100 $\mathring{A}^2$.

a is the area covered by one adsorbate molecule.

5. The cross-sectional area of the adsorbed species was calculated by superimposing the plots of contact angle versus surface coverage. The values thus obtained agreed very well with the calculated values.

6. It was found that a decrease in the net heat of adsorption by about one third is required to obtain stable finite contact angle values. The contact angle increased sharply with further decrease in the heat of adsorption.

7. Floatability was correlated in terms of the contact angles, surface coverages, and the heats of adsorption. The main findings are:

a) Floatability increased with increasing surface coverage and the carbon chain length of adsorbate molecule.

b) Hundred per cent flotation was obtained when the contact angle was above 40 or the work of adhesion was below 125 ergs/cm^2.

c) There is a critical value for the surface energy above which flotation is negligible and increases to 100% within one Kcal/mole decrease in the heat of adsorption. The critical value of surface energy for silicas corresponds to approximately 60% of the net heat of adsorption of a compound on the unmodified surface.

6.2 SUGGESTIONS FOR FURTHER WORK

1. The heats of adsorption measurements should be extended to larger surface coverages.
2. More work should be done with surfaces modified with amines and fatty acids.
3. Reaction of alcohols and chlorosilanes with other minerals should be investigated from the point of view of affecting selective flotation.