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# Adsorption from binary non-aqueous solutions on non-porous adsorbents

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ADSORPTION FROM BINARY NON-AQUEOUS  
SOLUTIONS ON NON-POROUS ADSORBENTS

by

Robert Douglas Hansen

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

Major Subject: Physical Chemistry

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## I. INTRODUCTION

Adsorption from solution has become increasingly important to chemists in recent years. This position of increased importance has emphasized the need for fundamental knowledge of the forces of adsorption. While a great amount of work has been done studying adsorption from solution, as can be evidenced by the large number of references in Dietz's Bibliography of Solid Adsorbents (1), very little has been accomplished towards understanding the processes of adsorption.

In order to obtain a better understanding of the nature of adsorption from solution, it is necessary to know something of the forces operating at the solid-solution interface and the distance from the solid surface over which these forces exert themselves. The great majority of the research studying adsorption from solution has been done with porous adsorbents such as charcoal. While many of these results are of interest with respect to the solution of a particular problem, they are of little or no use in formulating a general theory of adsorption from solution. In studies using porous adsorbents, the results have been complicated by the fact that the physical structures of the adsorbent were unknown and that the adsorption due to the forces operating at the solid-solution interface could not

be separated from the capillary condensation occurring simultaneously. In many cases, the adsorption due to capillary condensation undoubtedly makes up the greater part of the measurable adsorption. The only way to resolve these two modes of adsorption is to use adsorbents which are known to be non-porous. The results of the adsorption studies can then be attributed solely to forces operating at the solid-solution interface, and these results will not be dependent on the physical structure of the adsorbent.

Even if the physical structure of the adsorbent is known, it is necessary to know something of the nature of the surface of the adsorbent. The chemical constitution of the surface of the adsorbent is dependent largely upon the previous treatment. (c) The chemical constitution of the surface plays an important part in that it is the surface layer that influences the adsorption to a great extent. Studies of the chemical structure of various adsorbents have recently been made by Anderson and Emmett (2). Included in the adsorbents studied by them was a carbon black used in the present research. Such studies are sure to give great assistance in interpreting results of adsorption studies and in formulating satisfactory theories of adsorption from solution.

In order to formulate a general theory for adsorption from solution, it will be necessary to obtain data showing the effect of adsorbate parameters on adsorption, the effect

of solvent on adsorption, and the effect of the chemical nature of the surface of the adsorbent. While the present work cannot hope to provide all the required information, it is hoped that these results will show trends upon variation of chain length of the solute, variation of the solvent, and changes in the nature of the surface of the adsorbent. It is thus possible that this work can be considered with other experimental results of the same type in attempting to formulate a theory of adsorption from solution.

Recently an excellent review article was published by Kipling (3) concerning the adsorption of non-electrolytes from solution. Another good review can be found in the volume Adsorption and Chromatography by H. G. Cassidy (4). While these reviews trace the ideas developed concerning adsorption from solution, the more important developments will be discussed here in more detail. It is hoped that this discussion will enable the reader to become familiar with the problems of adsorption from solutions and the various attempts made by previous workers to explain the observed results.

It was first pointed out by Williams (5) that the adsorption isotherm obtained by measuring the change in concentration of solute after exposure to the adsorbent does not give a true measure of the amount of solute removed from solution. He developed an equation that took into

account the change in volume on adsorption, thus obtaining what may be referred to as apparent adsorption corrected for volume change. Williams also suggested that both solute and solvent were simultaneously adsorbed from solution. Ostwald and de Izaguirre (6) later indicated that both components of a binary liquid solution were adsorbed simultaneously. They pointed out that the isotherm obtained by measuring the change in concentration of solute brought about by adsorption was actually a composite of the individual isotherms representing the adsorption of solute and solvent respectively.

© There have been numerous attempts made to separate such a composite isotherm into its two individual isotherms. However, all of these attempts have been more or less unsatisfactory. Williams (5) attempted to obtain individual adsorption values by measuring adsorption on charcoal from the vapor phase above solutions of acetic acid in water. He also measured the adsorption on charcoal from the binary liquid solutions. By assuming that the same amounts of acetic acid and water were adsorbed from the vapor phase as from the liquid phase in equilibrium with the vapor, he was able to calculate values of the individual adsorption of acetic acid and water. Williams obtained the relationship

$$\frac{x}{x_{\infty}} + \frac{y}{y_{\infty}} = 1, \quad (1)$$

where  $x$  and  $y$  grams of acetic acid and water respectively were adsorbed at a given concentration, and  $x_{\infty}$  and  $y_{\infty}$  grams of acid and water respectively were adsorbed from the pure components. Although Williams did not comment on this relationship, a recent method by Kipling and Tester (7) makes use of such an equation.

Ostwald and de Izaguirre (6) applied an arithmetical analysis to the binary solution isotherms to establish the shapes of the composite isotherms when the individual isotherms have various forms. They showed that "negative" adsorption (preferential adsorption of the solvent) is only possible if the solvent is adsorbed. Ostwald and de Izaguirre developed the relation

$$\frac{n_0 \Delta x}{m} = n_1^s (1 - x) - n_2^s x \quad (2)$$

between the binary solution isotherm and the individual adsorption isotherms; here  $n_0$  is the total number of moles in the original solution,  $n_1^s$  and  $n_2^s$  are respectively the number of moles of components 1 and 2 adsorbed per gram of adsorbent, and  $x$  is the mole fraction of component 1 in the solution after adsorption. Bartell and Sloan (8) assumed that the individual isotherms obeyed the Freundlich equation, thereby obtaining the relation

$$\frac{n_0 \Delta x}{m} = k_1 x^a (1-x) - k_2 (1-x)^b x \quad (3)$$

by substituting the corresponding Freundlich expressions for  $n_1^S$  and  $n_2^S$  in the equation of Ostwald and de Izaguirre. Bartell and Sloan evaluated the four constants, and consequently obtained the individual isotherms, by a method of successive approximations. A similar method was used recently by Kipling and Tester (9) in which they assumed that the individual isotherms followed the Langmuir equation. Again, they were able to calculate the individual adsorption isotherms. Kipling and Tester, however, found that although both treatments gave isotherms which appeared reasonable, the two treatments gave isotherms which differed greatly. Furthermore, the limiting amounts adsorbed did not agree with results obtained by studying adsorption of the pure components. It thus appears that both of these methods are inadequate.

An attempt was made by Dobine (10) to determine the amount of solvent adsorbed by comparing isotherms obtained by treating aqueous solutions of acetic acid with dry and moist charcoal. Jones and Outridge (11) attempted to obtain individual isotherms by measuring the total volume of liquid adsorbed. They used two different methods, measuring the weight increase when the adsorbent was equilibrated with the vapor of the solution, and measuring the increase in weight of adsorbent after immersion in the solution. The first method is the technique used by Williams (5); the second

method is similar to the method of Bachmann (12), which consisted of immersing the adsorbent in the solution until equilibrium was reached, then withdrawing the adsorbent and removing excess solution by blotting before measuring the increase in weight. Knowing the total volume of adsorbate held by the adsorbent, he was able to calculate the individual isotherms from the composite binary isotherm.

Recently Kipling and Tester (7) obtained individual adsorption isotherms from the vapors in equilibrium with the binary solutions, using a steam-activated charcoal adsorbent. They then proposed a method for describing their results. Following the treatment of Elton (13) they assumed that the surface of the adsorbent was covered at all times by a unimolecular layer of adsorbate. Thus they wrote

$$n_1^s A_1 + n_2^s A_2 = A, \quad (4)$$

where  $A_1$  and  $A_2$  are the areas occupied by one mole of components 1 and 2, and  $A$  is the total surface area of one gram of adsorbent. This equation can also be written as

$$\frac{n_1^s}{(n_1^s)^0} + \frac{n_2^s}{(n_2^s)^0} = 1, \quad (5)$$

where  $(n_1^s)^0$  and  $(n_2^s)^0$  are the amounts adsorbed from the vapors of the pure components. This latter equation is identical to the expression which Williams (5) deduced



experimentally. Using Equations 2 and 5, Kipling and Tester obtained the individual isotherms, i.e.,  $n_1^S$  and  $n_2^S$  as functions of  $x$ , the equilibrium mole fraction. The calculated individual isotherms agreed rather well with the individual isotherms obtained experimentally by adsorption from the vapor phase.

The assumption made by Kipling and Tester that adsorption from solution is unimolecular is open to considerable question. They justify this assumption by noting that the isotherms for the pure vapors adsorbed separately on charcoal obey Langmuir's equation for unimolecular adsorption. The adsorption of gases and vapors by charcoal, though fairly well represented by Langmuir's equation, has nevertheless been shown to depend on a mechanism other than that proposed by Langmuir. Pierce, Wiley, and Smith (14) have stated that even at low relative pressures the assumption of monolayer adsorption is incorrect. Their reasons for assuming that capillary condensation occurs simultaneously with adsorption in the first layer are based on the following considerations: (1) excessively large surface areas are computed on the basis of monolayer adsorption; (2) the pore diameters that must be assumed if adsorption is monomolecular are quite small; (3) volumes of adsorbates held by a given charcoal are constant. Evidence which will be given later strongly suggests that all adsorption from

solution is multilayer in character, whether on porous or non-porous adsorbents.

What appears to be a more reasonable treatment and one more consistent with the known mechanism of vapor adsorption by porous adsorbents can be based on the assumption that the adsorption is constrained by the pore volume of the adsorbent. This can be expressed as

$$n_1^s V_1 + n_2^s V_2 = V, \quad (6)$$

where  $V_1$  and  $V_2$  are the respective molar volumes of components 1 and 2, and  $V$  is the pore volume of the adsorbent. This expression can be written as

$$\frac{n_1^s}{(n_1^s)^0} + \frac{n_2^s}{(n_2^s)^0} = 1. \quad (5)$$

This equation is identical with the expression obtained by Kipling and Tester. Thus, an analysis of a binary isotherm using Equations 2 and 5 will lead to individual isotherms which are identical with those calculated by the method of Kipling and Tester. As evidence that the pore-filling mechanism is more consistent with observed facts than the treatment by Kipling and Tester, molar volumes calculated from Equations 5 and 6 agree within one percent of the accepted literature values, whereas molecular areas calculated from Equations 4 and 5 are such that edgewise

adsorption of benzene must be postulated to account for the area of benzene in the system benzene-ethanol.

The limiting cases where this treatment fails to hold should be pointed out. Wherever the pore radii are the same order of magnitude as the molecular radii, the volume of adsorbate will cease to be constant, due to incomplete filling of the pores. The steric effects of these small pore radii have been discussed in detail by Brunauer (15). When the pore radii are small, Equation 6 no longer holds and this treatment breaks down. It should be borne in mind that adsorption from saturated vapors differs from adsorption from solution in an important respect. In the adsorption from saturated vapors, there is, in addition to the adsorption at the solid-liquid interface, adsorption at the liquid-vapor interface. Therefore, great caution must be exercised in comparing adsorption from solution with adsorption from saturated vapors. Only when the area of the liquid-vapor interface is negligibly small compared to the surface area of the adsorbent can the two modes of adsorption be considered the same. This condition is generally satisfied by porous adsorbents. However, when the pore radii become larger, the liquid-vapor interface can no longer be neglected and the effects of the adsorption at this interface must be considered.

If it were possible to measure the absolute amount of solute and solvent adsorbed, it would be possible to determine the distance from the surface that the adsorptive forces extended over. In the absence of such measurements, it is still possible in some instances to infer such distances. Until recently adsorption from solution was considered to be unimolecular. Investigation of immiscible binary systems on non-porous adsorbents have shown S-shaped isotherms. R. S. Hansen (16) has demonstrated the existence of multilayer adsorption in such systems. An argument has been presented by Fu, Hansen, and Bartell (17) to show that adsorption from the miscible system butyric acid-water on graphite is multimolecular. Their argument was based upon consideration of activity coefficients calculated for adsorbed layers in this system. They found a sharp break in the plot of the logarithm of the activity coefficient of the surface layer versus the logarithm of the surface molality, which they identified with completion of the first adsorbed layer. Recently Craig (18) has shown multilayer adsorption occurring with the miscible system butyric acid-water on the non-porous adsorbent Graphon. The adsorption of butyric acid exceeded the amount that could be placed in a close-packed monolayer of butyric acid molecules. This is the only instance where multilayer adsorption has been proven for miscible binary systems.

One of the most successful approaches in considering forces arising from the solid surface is the Polanyi potential theory (19) of adsorption. Polanyi assumed that surfaces of equipotential enclosed volume increments with the surface.  $\mathcal{E}_g$  and  $\mathcal{E}_1$ , the adsorption potentials for the solute and solvent respectively, are given by

$$\mathcal{E}_g = RT \ln \frac{p_g^0}{p_g}$$

and

$$\mathcal{E}_1 = RT \ln \frac{p_1^0}{p_1} ,$$

where  $p_g$  and  $p_1$  are the respective partial pressures of solute and solvent, and  $p_g^0$  and  $p_1^0$  are the respective saturated vapor pressures of solute and solvent at the temperature  $T$ . Thus,  $\mathcal{E}_g$  and  $\mathcal{E}_1$  can be determined from adsorption measurements on pure solute and pure solvent vapors. For slightly miscible binary systems, the adsorption potential is given by

$$\mathcal{E} = RT \ln \frac{C_0}{C} ,$$

where  $C$  is the concentration of solute and  $C_0$  is the saturation concentration of solute. The potential for displacement of solvent by solute is given by

$$\mathcal{E} = \mathcal{E}_g - \mathcal{E}_1 \frac{V_g}{V_1} ,$$

where  $V_g$  and  $V_1$  are the molar volumes of solute and solvent respectively. Thus, the adsorption of solute,  $g$ , from a binary liquid solution in solvent,  $l$ , can be calculated at any temperature from a knowledge of the pure gas isotherms of solute and solvent. The second term on the right is included because Polanyi realized that the solvent also had a positive adsorption potential and that solute could only be adsorbed at the expense of removing solvent from the adsorbent. The Polanyi treatment, as applied to adsorption from solution, is not general in that the equations are not symmetric to interchange of solute and solvent. This inconsistency has been pointed out by Hansen and Fackler (20).

The term  $C/C_0$ , called the reduced concentration, which appears in the term representing the work of removing solute from solution, has considerable significance in adsorption from slightly miscible binary solutions. The reduced concentration is a good approximation to the solute activity, and the amount adsorbed can be more easily correlated when considered as a function of the reduced concentration instead of the molar concentration. Craig (18) has shown that the adsorption isotherms of the aliphatic acids from aqueous solution are nearly congruent functions of the reduced concentration. This conclusion had previously been reached by Hansen (16) for the adsorption of valeric and caproic acids from water and also for the adsorption of aniline and phenol

from water.

A large portion of the investigations of adsorption from binary liquid systems covered only the very dilute concentration ranges. When these investigations were carried out over the entire concentration range for miscible systems, it was found that the adsorption reached a maximum and then decreased until it reached zero as the concentration approached that of pure solute. In many cases the isotherms crossed the concentration axis at some intermediate point, giving what is frequently called "negative" adsorption of the solute. Of course, in a binary miscible system the terms solute and solvent lose their usual meaning, as either component could be considered as solvent. It is customary to refer to the component as solute whose positive adsorption is being measured. Heymann and Boye (21) discussed two types of binary solution isotherms; one type being where one component showed positive adsorption over the entire concentration range, the other type being isotherms which crossed the concentration axis at an intermediate point, showing positive adsorption of one component at low concentration of that component and negative adsorption at high concentrations of that component. Bartell and Scheffler (22) studied the adsorption of the aliphatic alcohols from benzene solution. Using a silica adsorbent they found that methanol was positively adsorbed over the entire

concentration range, whereas the longer chain homologs gave sigmoid isotherms, the amount of alcohol adsorbed decreasing as the molecular weight increased. Using a charcoal adsorbent they found that benzene was preferentially adsorbed over the greater portion of the concentration range, the order of alcohol adsorption being the same as on silica. These results are in agreement with the conclusion that silica is a more polar adsorbent than charcoal. Bartell and Lloyd (23) demonstrated the effect of surface properties of the adsorbent upon the shape of the binary isotherms. They subjected a charcoal to different types of activation and then determined the isotherms for the system benzene-ethanol. Depending on the method of activation, they obtained isotherms which showed preferential adsorption of benzene, isotherms which showed preferential adsorption of ethanol, and isotherms with intermediate behavior. Elton (24) discussed the thermodynamic requirements for complete preferential adsorption and purported to show that if both components of a binary solution have positive adsorption potentials, complete preferential adsorption cannot occur. He also stated that negative adsorption potentials are unlikely from kinetic considerations, leading to the conclusion that sigmoid-shaped isotherms should almost invariably be found. The fact that isotherms showing complete preferential adsorption are frequently found indicates that Elton's explanation is incomplete.



Doss and Rao (25) have suggested that sigmoid-shaped isotherms are caused by the preferential adsorption of a complex of intermediate composition. The complex adsorbed should have the composition corresponding to the solution concentration at the point where the isotherm crosses the concentration axis. For pyridine-water solutions they found a complex corresponding to  $C_5H_5N \cdot H_2O$  and for acetone-water mixtures a complex corresponding to  $(CH_3)_2CO \cdot H_2O$ . Venkatanarasimhacher and Doss (26) studied adsorption from the miscible system pyridine-ethanol on silica gel. They obtained a sigmoid isotherm which cut the concentration axis at 78.5 weight per cent pyridine. They attributed this sigmoid isotherm to preferential adsorption of the complex corresponding to  $2C_5H_5N \cdot EtOH$ . The results of studies by Bartell and Lloyd (23) would indicate that this explanation is incorrect, as Bartell and Lloyd obtained isotherms which crossed the concentration axis at different points, depending upon the activation to which the charcoal was subjected. This point will be discussed further elsewhere in this thesis.

Rao and Jatkar (27) in further studies on binary liquid mixtures have identified the maxima and minima in the isotherms with complex formation. It seems reasonable that failure of complex formation as an explanation for the

inversion points would indicate failure of this argument as an explanation of maxima and minima. This point will also be discussed further elsewhere in this thesis.

## II. OBJECTIVES

The long range objective of this research was to assist in the formulation of a satisfactory general theory of adsorption from solution. With this in mind, the investigation of the adsorption of some normal paraffin hydrocarbons and cyclohexane from methanol and ethanol solutions by three non-porous carbon adsorbents was undertaken with the following immediate objectives:

To investigate whether the adsorption is determined only by the forces at the solid-solution interface, or whether the adsorption is affected by the work required to transfer the adsorbed molecules from the bulk solution to the surface phase.

To determine the effect of chain length on the adsorption of a homologous series, and to attempt to infer from this effect the orientation of the adsorbed molecules.

To examine the isotherms of the partly miscible binary systems for multilayer adsorption, and to determine if a treatment could be developed to indicate the thickness of the adsorbed layers and the nature of the adsorption potentials as a function of distance from the surface.

To examine the isotherms of the miscible systems for sigmoid character, and to determine if the intersection of the isotherms with the concentration axis may be due to the establishment of a preferred molecular structure, whether it can be attributed to certain areas of the adsorbent possessing properties different from the rest of the surface, or whether it can be due merely to the nature of the adsorption potentials of solute and solvent.

To examine the isotherms of the miscible systems for evidence that would indicate the existence of multilayer adsorption in these systems.

To compare the adsorption on the different adsorbents in an attempt to determine the effect of the chemical composition of the surface upon the adsorptive properties of these carbon adsorbents.

And, finally, to determine whether the generalizations developed from studying the adsorption of the aliphatic acids and alcohols from aqueous solutions were due to the peculiar nature of the solvent, or whether these generalizations have universal application to adsorption from solution.

### III. MATERIALS AND APPARATUS

#### A. Adsorbents

In order to avoid capillary condensation and other effects caused by porous adsorbents, the adsorbents chosen for this work were non-porous. In this way the results obtained could be expected to depend only upon the forces acting at the solid-liquid interface and not upon the physical structure of the adsorbent. The three carbon blacks selected had previously been shown to be non-porous by virtue of agreement between surface areas obtained by nitrogen adsorption and by electron microscopy.

The adsorbents were subjected to high temperature evacuation to remove volatile impurities. The adsorbents were placed in a quartz flask which was connected to a vacuum pump. The flask was then heated in an electric muffle furnace at a temperature of 1000°C. for a period of 24 hours. After treatment the adsorbents were stored in glass-stoppered flasks. Following is a description of the adsorbents used:

##### 1. Spheron-6

A pelletized medium-processing channel carbon black, obtained from Godfrey L. Cabot, Inc. The surface area of this adsorbent was 114.0 square meters per gram.

## 2. Graphon

A partially graphitized channel carbon black, prepared from Spheron-6 by heating in an induction furnace at 3200°C. The surface area was 78.7 square meters per gram.

## 3. DAG-1

A deflocculated artificial graphite, obtained from the Acheson Colloid Corporation. The surface area was 102.4 square meters per gram.

The surface areas listed for these adsorbents were determined by W. V. Fackler, Jr. and S. D. Christian. The determinations were made previous to this work, but since the adsorbents used in these studies were identical with the adsorbents on which the surface area determinations were made, it is felt that the values quoted are valid. The surface areas were determined by the low-temperature nitrogen adsorption method of Brunauer, Emmett, and Teller (28).

## B. Chemicals

### 1. Alcohols

Methanol, reagent grade, obtained from the General Chemical Company, New York, New York, was purified by distillation. Methanol was distilled in five different batches, the boiling range for each batch falling within the range 64.76-64.86°C., corrected to 760 mm Hg.

Ethanol, commercial grade absolute, was purified by the method of Lund and Bjerrum (29). Two batches of ethanol were purified, the two boiling ranges falling within 78.62-78.70°C., corrected to 760 mm. Hg.

## 2. Hydrocarbons

Octane, pure grade, was obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. The octane was shaken with portions of concentrated sulfuric acid until there was no coloration of the acid layer, then washed with redistilled water and sodium carbonate solution. Excess water was removed by shaking with sodium hydroxide pellets. The octane was then dried by storage over sodium and subsequently distilled. The boiling range, corrected to 760 mm. Hg was 125.88-126.00°C.

Decane, Eastman Kodak white label grade, was purified in the same manner as the octane. The decane used in the methanol solutions had a boiling range of 174.10-174.33°C., corrected to 760 mm. Hg. The decane used in the ethanol solutions was distilled over sodium and had a corrected boiling range of 174.33-174.34°C.

Dodecane, Eastman Kodak practical grade, was subjected to the same treatment as octane. The

dodecane was dried with sodium and then distilled over sodium. The corrected boiling range was 216.52-216.77°C.

Cyclohexane, commercial grade, was obtained from the DuPont Chemical Company. It was purified in the same manner as the other hydrocarbons. The cyclohexane was dried over sodium and distilled over sodium. The corrected boiling range was 80.72-80.85°C.

All distillations were carried out using a thirty-plate Oldershaw distilling column, operating at a reflux ratio of ten to one.

### C. Equipment

#### 1. Distilling Column

A thirty-plate, vacuum-jacketed, Oldershaw distilling column was used for all distillations. This was equipped with a liquid-dividing still head operated by a Flexopulse automatic timer. The characteristics of this type column have been determined by Collins and Lantz (30).

#### 2. Interferometer

A Rayleigh interference refractometer, obtained from Adam Hilger, Ltd., London was used for analyses. One-centimeter cells made of fused



quartz held the liquids. The cells were equipped with covers carved from Teflon. The covers were made in such a manner that mercury seals could be formed to prevent evaporation of the liquids. The interferometer was placed in an air-thermostated box, a temperature of  $25.0 \pm 0.1^{\circ}\text{C}$ . being maintained by a Precision Scientific Company "Merc-to-Merc" thermoregulator.

### 3. Shaker

The adsorption tubes were shaken by a motor driven shaker in an air-thermostated box. The temperature of the box was maintained at  $25.0 \pm 0.1^{\circ}\text{C}$ . by a Precision Scientific Company "Merc-to-Merc" thermoregulator.

### 4. Adsorption Tubes

Adsorption tubes were made from 15 x 125 mm. Pyrex test tubes. The test tubes were heated and drawn to a fine tip after introduction of adsorbent into the tubes. Pipets with drawn out tips were used to fill the adsorption tubes. After the liquid was added the adsorption tubes were sealed off by means of a micro torch. In some cases, 10 ml. glass-stoppered volumetric flasks were used, these being sealed by painting the tops with paraffin wax.

#### IV. METHOD OF PROCEDURE

##### A. Preparation of Solutions

All solutions were prepared at 25°C. in 50 cc. glass-stoppered volumetric flasks. Each solution was made up by weight and by volume, all concentrations being given as moles per liter at 25°C. The procedure in making up solutions consisted of weighing the amount of hydrocarbon, then adding alcohol to the mark while the solution was kept at 25°C. in a water bath. The solution was then weighed so that the weights of both solute and solvent were known in addition to the total volume of the solution. All weights were corrected to the weight in vacuo before the concentrations were calculated.

In general, from eight to thirteen solutions were prepared for each system studied, more solutions being used for the miscible systems. In determining the interferometric calibration curve for each system, pairs of solutions were required whose indices of refraction were very nearly the same since only small refractive index differences could be measured on the interferometer. For certain systems this required solutions in addition to those prepared for the adsorption studies; in these cases the solutions were made up by weight only, 10 cc. volumetric

flasks being used for these solutions.

#### B. Determination of Interferometric Calibration Curves

In order to measure concentration changes with the interferometer it was necessary to construct a calibration curve for each system. The calibration curve related the measured refractive index change,  $\Delta R$ , to the corresponding concentration change,  $\Delta C$ . The  $\Delta R$  values were obtained by subtracting from the observed interferometer readings the interferometer readings obtained when pure solvent was in both sides of the cell. A pair of solutions was compared in the interferometer and the ratio of  $\Delta R$  to difference of weight per cent solute was plotted against the average weight per cent of the solutions. This procedure was followed using pairs of solutions covering the entire concentration range. A plot was then made of weight per cent hydrocarbon against the molar concentration of hydrocarbon. Slopes were obtained from this graph for every point of the calibration curve. Each point on the calibration curve was then multiplied by the corresponding slope of the weight per cent versus concentration curve. This procedure gave the desired  $\Delta R/\Delta C$  against molar concentration graph. This rather lengthy procedure was followed because the weight per cent concentrations were known more accurately than the molar concentrations of the solutions.

### C. Procedure for Measuring Adsorption

The general procedure for adsorption measurements consisted of adding a measured volume of solution to a weighed amount of adsorbent and then shaking the adsorption tubes in a mechanical shaker at 25°C. for a period of at least 24 hours. Some of the determinations were made using a 10 cc. glass-stoppered volumetric flask as an adsorption tube, this being sealed by painting around the stopper with paraffin wax. The flasks were weighed before and after adding the adsorbent, the solutions added by a volumetric pipet. This type of adsorption tube was satisfactory for dilute solutions of hydrocarbons in alcohols.

A more satisfactory type of adsorption tube was made by heating a 15 x 125 mm. Pyrex test tube and drawing it out to a fine tip after the adsorbent had been weighed into the tube. The solution was added by means of a pipet with the tip drawn out so that it could be inserted into the drawn out neck of the adsorption tube. These pipets were calibrated before use. After the solution was added to the adsorption tube the neck of the tube was heated to seal off the tube. The tubes were then shaken in the mechanical shaker.

After the adsorption tubes had been shaken for a period of at least 24 hours, the tubes were centrifuged and the

supernatant liquid withdrawn with a syringe. This solution was then placed in one side of the interferometer cell. The original solution was placed in the other side of the cell and the two solutions compared in the interferometer. By means of the calibration curve the interferometer reading was converted to a concentration change. The amount of either component adsorbed, as surface excess of that component, could then be calculated from the change in concentration brought about by adsorption. If the slope of the calibration curve at any point was so great that different values were obtained at initial and final concentrations, after the first approximate change in concentration had been determined a second value was read from the calibration curve at the mean concentration, so that the  $\Delta R/\Delta C$  value used in the final calculation of the concentration change was the mean value of the solutions being compared.

The 24 hour period of shaking was chosen in accord with studies on rates of equilibrium made by Craig (18) on adsorption from aqueous solutions of acids and alcohols. His studies showed that a period of 24 hours was more than sufficient for the attainment of equilibrium. The amount of adsorbent used in each determination varied widely, ranging from 0.1 gram to 1 gram. The amount of adsorbent used depended upon the amount adsorbed and the calibration

curve for the system. In general, interferometer readings of 100 to 200 were sought in order to obtain greater accuracy. The amount of adsorbent used was chosen in an attempt to keep the interferometer reading within this range. The volume of solution added in most cases was five milliliters, although a volume of ten milliliters was used several times with solutions near the solubility limit.

The results were calculated as  $V\Delta C/m$  versus some function of the concentration, where  $V$  is the volume of the solution in milliliters,  $\Delta C$  is the measured change in concentration in moles per liter, and  $m$  is the weight of adsorbent in grams. For the slightly miscible systems reduced concentrations were used as ordinates, reduced concentrations being the concentration of solute in the equilibrium solution divided by the concentration of solute in a saturated solution. The abscissa values were expressed as millimoles adsorbed per gram of adsorbent.

#### D. Method of Determining Solubilities

In the course of this work it was necessary to measure the saturation solubilities of the various hydrocarbons in methanol. The general procedure was to prepare a saturated solution of hydrocarbon in alcohol and to compare this satu-

saturated solution interferometrically with a solution of known concentration. The saturated solutions were prepared in two different ways. In one method methanol was shaken with an excess of hydrocarbon in an air bath thermostated at 25.0°C. In the other method a slight excess of hydrocarbon was shaken with methanol at an elevated temperature until miscibility occurred; the solution was then placed in a water bath at 25.0°C. until phase separation occurred. After equilibration in the water bath, the methanol phase was removed with a capillary syringe and placed in one side of an interferometer cell; a solution of known concentration was placed in the other side of the cell and the  $\Delta R$  determined.

From an extrapolation of the interferometric calibration curve the concentration of the saturated solution could be calculated. The interferometric calibration curves for the normal aliphatic hydrocarbons in methanol were all straight lines so that no difficulty was encountered in extrapolating to higher concentrations. The calibration curve for the system cyclohexane-methanol had slight curvature in the vicinity of the saturation solubility of cyclohexane in methanol; for this reason a different technique was used in analysis of the saturated solution. A portion of the methanol phase was withdrawn and weighed, then the saturated solution diluted with a weighed

amount of methanol. The resulting solution was then compared interferometrically with a standard solution of known concentration. As a check on this method, the dilutions were carried out such that the resulting solutions were quite far apart in concentration. Each of these solutions was compared with a different standard solution, the agreement being better than one part in three hundred. All solubility determinations were made in triplicate except in the case of octane-methanol where duplicate determinations gave agreement to one part in a thousand.



## V. EXPERIMENTAL RESULTS

### A. Adsorption of Aliphatic Hydrocarbons from Methanol Solutions

The results of measurements of adsorption of three normal aliphatic hydrocarbons and one cyclic aliphatic hydrocarbon from methanol solutions are presented in Tables 1A through 4C. The results for the normal hydrocarbons are given in Tables 1 - 3; the results for the cyclic hydrocarbons are given in Table 4. The letters A, B, and C given with the table numbers refer to the three adsorbents used in these measurements, these being Spheron-6, Graphon, and DAG-1 respectively.

In these tables,  $C$  is the concentration of hydrocarbon in moles per liter at 25°C.,  $V$  is the volume of solution in milliliters equilibrated with  $m$  grams of adsorbent. The  $VAC/m$  values, in millimoles of hydrocarbon per gram of adsorbent, represent surface excesses of hydrocarbon per gram of adsorbent. The  $\sqrt{2}^{(v)}$  values, in millimoles of hydrocarbon per square centimeter of surface area, represent surface excesses of hydrocarbon per unit area of surface, obtained from the  $VAC/m$  values by dividing by the surface area of the adsorbent. These  $\sqrt{2}^{(v)}$  surface excesses are of the type discussed by Guggenheim and Adam (31).

Table 1A

Adsorption of Octane from Methanol on Spheron-6

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0457	0.036	0.035	0.031
.1126	.088	.076	.067
.2379	.186	.136	.119
.3496	.273	.186	.163
.4691	.366	.221	.194
.5851	.456	.251	.220
.7174	.560	.313	.275
.8411	.656	.339	.297
.9635	.752	.441	.387
1.080	.842	.536	.470
1.232	.961	1.42	1.25

Table 1B

Adsorption of Octane from Methanol on Graphon

c (moles/l.)	c/c <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0453	0.035	0.048	0.061
.1074	.084	.080	.102
.2319	.181	.156	.198
.2355	.184	.162	.206
.3449	.269	.201	.255
.4694	.366	.264	.335
.5822	.454	.296	.376
.7157	.558	.343	.436
.8374	.653	.415	.527
.9557	.745	.461	.585
1.086	.847	.709	.900
1.232	.961	1.25	1.59

Table 1C

Adsorption of Octane from Methanol on DAG-1

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0684	0.053	0.033	0.032
.1113	.087	.059	.058
.1117	.087	.059	.058
.2383	.186	.120	.117
.4035	.315	.183	.179
.5867	.458	.218	.213
.7565	.590	.247	.241
.9572	.747	.291	.284
1.068	.833	.332	.324
1.214	.947	.469	.458
1.240	.967	.544	.531

Table 2A

Adsorption of Decane from Methanol on Spheron-6

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0176	0.031	0.034	0.030
.0542	.096	.080	.070
.0904	.161	.116	.102
.1932	.344	.172	.151
.2784	.496	.236	.207
.3699	.659	.318	.279
.4708	.839	.455	.399
.4920	.877	.527	.462
.5407	.963	1.21	1.06

Table 2B

Adsorption of Decane from Methanol on Graphon

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles cm. <sup>2</sup> )
0.0128	0.023	0.032	0.041
.0489	.087	.099	.126
.0934	.166	.146	.185
.1892	.337	.187	.237
.2966	.528	.240	.305
.4073	.726	.350	.445
.4739	.844	.463	.588
.4977	.887	.582	.739
.5382	.959	1.19	1.52

Table 2C

Adsorption of Decane from Methanol on DAG-1

c (moles/l.)	c/c <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0158	0.028	0.034	0.033
.0554	.099	.074	.072
.0957	.170	.101	.099
.1914	.341	.138	.135
.2908	.518	.182	.178
.4142	.738	.268	.262
.4886	.870	.338	.330
.5079	.905	.394	.385
.5380	.958	.560	.547

Table 3A

Adsorption of Dodecane from Methanol on Spheron-6

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0137	0.051	0.048	0.042
.0141	.052	.049	.043
.0258	.096	.087	.076
.0452	.168	.121	.106
.0610	.226	.140	.123
.0963	.357	.173	.152
.1269	.471	.209	.183
.1586	.588	.242	.212
.1969	.730	.291	.255
.2294	.851	.397	.348
.2474	.918	1.01	.888



Table 3B

Adsorption of Dodecane from Methanol on Graphon

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\frac{\sqrt{v}}{2} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0074	0.027	0.058	0.074
.0154	.057	.106	.135
.0185	.069	.118	.150
.0226	.084	.122	.155
.0269	.100	.126	.160
.0543	.201	.167	.212
.0944	.350	.194	.246
.1293	.479	.211	.268
.1655	.614	.252	.320
.1934	.717	.324	.411
.2238	.830	.433	.550
.2386	.885	.505	.641
.2438	.904	.565	.718
.2522	.935	.787	.999

Table 3C

Adsorption of Dodecane from Methanol on DAG-1

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0102	0.038	0.045	0.044
.0265	.098	.096	.094
.0271	.101	.102	.100
.0440	.163	.117	.114
.0627	.232	.135	.132
.1116	.414	.168	.164
.1756	.651	.232	.227
.1764	.654	.222	.217
.2117	.785	.298	.291
.2279	.845	.328	.320
.2482	.921	.391	.382
.2512	.932	.401	.392
.2614	.970	.502	.490

Table 4A

Adsorption of Cyclohexane from Methanol on Spheron-6

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.3590	0.108	0.047	0.041
.7207	.217	.102	.089
1.263	.381	.181	.159
1.797	.542	.277	.243
2.334	.704	.415	.364
2.709	.817	.546	.479
3.062	.923	.881	.773
3.195	.963	1.60	1.41

Table 4B

Adsorption of Cyclohexane from Methanol on Graphon

C (moles/l.)	C/C <sub>0</sub>	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.3584	0.108	0.043	0.055
.7222	.218	.098	.124
1.265	.381	.174	.221
1.781	.537	.293	.372
2.333	.703	.530	.673
2.665	.803	.741	.941
3.067	.925	1.32	1.67
3.210	.968	2.20	2.79

Table 4C

Adsorption of Cyclohexane from Methanol on DAG-1

$C$ (moles/l.)	$C/C_0$	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.3613	0.109	0.023	0.022
.3619	.109	.026	.025
.7249	.219	.077	.075
1.270	.383	.140	.137
1.805	.544	.200	.195
2.344	.707	.327	.319
2.724	.821	.416	.406
3.089	.931	.598	.584
3.275	.987	.961	.938

To define  $\sqrt{2}^{(v)}$  it is necessary to consider two portions of solution of exactly the same volume; the first portion contains unit area of surface, the second portion is in the interior of the solution.  $\sqrt{2}^{(v)}$  is then the number of moles of component 2 in the first portion in excess of the number of moles of component 2 in the second portion.

No activity data were available for these systems; however, the absolute activity of the hydrocarbon is approximated by the  $C/C_0$  value. Because the activity of the hydrocarbon in a saturated solution of hydrocarbon in methanol is not equal to the activity of pure hydrocarbon, but instead equal to the activity in a solution of hydrocarbon saturated with methanol, the less soluble methanol is in hydrocarbon the better approximation  $C/C_0$  is to the hydrocarbon activity.

#### B. Adsorption of Aliphatic Hydrocarbons from Ethanol Solutions

The results of measurements of adsorption of two normal aliphatic hydrocarbons and one cyclic aliphatic hydrocarbon from ethanol solutions are presented in Tables 5A through 7C. The results for the normal hydrocarbons are given in Tables 5 and 6; the results for the cyclic hydrocarbon are given in Table 7. The letters A, B, and C refer

Table 5A

Adsorption of Decane from Ethanol on Spheron-6

C (moles/l.)	Mole Fraction Decane	$\frac{V\Delta C}{m}$ (millimole/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimole/cm. <sup>2</sup> )
0.1928	0.012	0.075	0.066
.3917	.025	.128	.112
.7912	.053	.182	.160
1.207	.086	.220	.193
1.602	.122	.246	.216
1.994	.163	.258	.226
2.402	.213	.254	.223
2.821	.272	.232	.204
3.233	.347	.190	.167
3.662	.439	.129	.113
4.056	.549	.058	.051
4.475	.694	.011	.010
4.894	.886	-.013	-.011

Table 5B

## Adsorption of Decane from Ethanol on Graphon

C (moles/l.)	Mole Fraction Decane	$\frac{VAC}{m}$ (millimole/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimole/cm. <sup>2</sup> )
0.1933	0.012	0.093	0.118
.3887	.024	.147	.187
.7845	.052	.209	.265
1.188	.084	.239	.306
1.600	.121	.266	.338
2.004	.165	.286	.363
2.411	.215	.287	.364
2.821	.273	.275	.349
3.234	.347	.227	.288
3.661	.437	.167	.212
4.059	.542	.090	.114
4.472	.734	.032	.041
4.891	.883	.004	.005



Table 5C

Adsorption of Decane from Ethanol on DAG-1

C (moles/l.)	Mole Fraction Decane	$\frac{V\Delta C}{m}$ (millimole/g.)	$\frac{1}{\sqrt{2}}(v) \times 10^6$ (millimole/cm. <sup>2</sup> )
0.1963	0.012	0.063	0.062
.3975	.025	.096	.094
.7995	.054	.145	.142
1.211	.086	.160	.156
1.612	.123	.165	.161
2.019	.167	.174	.170
2.426	.216	.171	.167
2.846	.278	.148	.145
3.254	.351	.115	.112
3.668	.439	.059	.058
4.065	.549	.030	.029
4.475	.694	.005	.005
4.893	.878	-.009	-.009

Table 6A

Adsorption of Dodecane from Ethanol on Spheron-6

C (moles/l.)	Mole Fraction Dodecane	$\frac{VAC}{m}$ (millimole/g.)	$\frac{1}{\sqrt{2}}(v) \times 10^6$ (millimole/cm. <sup>2</sup> )
0.0728	0.004	0.062	0.054
.1544	.009	.101	.089
.1545	.009	.102	.089
.3165	.020	.146	.128
.6806	.046	.210	.184
1.002	.071	.262	.230
1.718	.143	.372	.326
2.050	.186	.385	.338
2.418	.244	.359	.315
2.757	.306	.300	.263
2.772	.309	.286	.251
3.119	.392	.178	.156
3.650	.571	.031	.027
4.197	.863	-.018	-.016

Table 6B

Adsorption of Dodecane from Ethanol on Graphon

C (moles/l.)	Mole Fraction Dodecane	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}^{(v)} \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0649	0.004	0.087	0.110
.1439	.010	.128	.163
.1460	.010	.132	.168
.3045	.019	.162	.206
.6742	.046	.238	.302
.989	.070	.283	.359
1.362	.105	.350	.444
1.713	.143	.402	.511
2.009	.180	.420	.533
2.375	.236	.380	.483
2.385	.237	.369	.469
2.729	.301	.313	.398
3.101	.388	.194	.246
3.107	.390	.195	.248
3.639	.567	.060	.076
3.643	.569	.059	.075
3.645	.571	.066	.084
4.194	.861	.002	.003
4.194	.861	.002	.003

Table 6C

Adsorption of Dodecane from Ethanol on DAG-1

C (moles/l.)	Mole Fraction Dodecane	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.0777	0.004	0.070	0.068
.1579	.009	.097	.095
.1660	.010	.097	.095
.3356	.021	.121	.118
.6910	.047	.149	.146
.6893	.047	.154	.150
1.022	.073	.193	.188
1.029	.074	.190	.186
1.377	.106	.214	.209
1.725	.144	.216	.211
2.083	.191	.193	.188
2.785	.312	.127	.124
3.653	.572	.015	.015
4.196	.863	-.016	-.016

Table 7A

Adsorption of Cyclohexane from Ethanol on Spheron-6

C	Mole Fraction		$\frac{V_{AC}}{m}$	$\sqrt{2}^{(v)} \times 10^6$
(moles/l.) Cyclohexane	A*		(millimoles/g.)	(millimoles/cm. <sup>2</sup> )
0.3588	0.022	0.120	0.012	0.011
.3658	.022	.120	.010	.008
.7203	.044	.233	.028	.025
1.444	.092	.493	.056	.049
2.177	.145	.696	.088	.077
2.182	.146	.699	.072	.063
2.192	.203	.805	.097	.085
3.632	.264	.862	.111	.097
4.377	.333	.900	.100	.088
5.113	.408	.924	.085	.075
5.852	.491	.940	.059	.052
6.591	.582	.949	.015	.013
7.346	.688	.955	-.029	-.025
8.078	.802	.962	-.063	-.055
8.817	.931	.978	-.051	-.045
8.814	.931	.978	-.048	-.042

\*Activity of cyclohexane calculated from data of Washburn and Handorf (32).

Table 7B

## Adsorption of Cyclohexane from Ethanol on Graphon

C (moles/l.)	Mole Fraction Cyclohexane	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)	$\sqrt{2}(v) \times 10^6$ (millimoles/cm. <sup>2</sup> )
0.3593	0.022	0.120	0.012	0.015
.3653	.022	.120	.013	.017
.7230	.045	.241	.025	.032
1.449	.093	.498	.046	.058
2.184	.146	.699	.066	.084
2.910	.203	.805	.088	.112
2.916	.203	.805	.081	.103
3.624	.263	.861	.092	.117
3.636	.264	.864	.091	.116
4.370	.332	.899	.103	.131
4.378	.333	.900	.113	.144
5.105	.407	.924	.121	.154
5.841	.490	.940	.121	.154
6.577	.581	.949	.105	.133
6.580	.581	.949	.100	.127
7.335	.687	.955	.061	.077
8.066	.799	.961	.020	.025
8.806	.929	.977	.004	.005

\*Activity of cyclohexane calculated from data of Washburn and Handorf (32).

Table 7C

Adsorption of Cyclohexane from Ethanol on DAG-1

C	Mole Fraction		$\frac{V\Delta C}{m}$	$\sqrt{2}^{(v)} \times 10^6$
(moles/l.) Cyclohexane	A*	(millimoles/g.)	(millimoles/cm. <sup>2</sup> )	
0.3659	0.022	0.120	0.007	0.007
.7259	.045	.241	.013	.013
2.190	.147	.700	.052	.051
2.920	.203	.805	.066	.064
3.642	.265	.864	.065	.063
4.389	.334	.901	.071	.069
5.124	.410	.925	.061	.060
5.857	.491	.940	.057	.056
5.855	.491	.940	.030	.029
6.593	.584	.949	.015	.015
7.343	.687	.955	-.014	-.014
8.073	.801	.961	-.054	-.053
8.813	.931	.978	-.058	-.057

\*Activity of cyclohexane calculated from data of Washburn and Handorf (32).

to the three adsorbents used in these measurements, these being Spheron-6, Graphon, and DAG-1 respectively.

In these tables,  $C$  is the concentration of hydrocarbon in moles per liter at 25°C.,  $A$  is the activity of hydrocarbon referred to the pure component at 25°C. As in the previous section, the  $V\Delta C/m$  values are surface excesses of hydrocarbon in millimoles per gram of adsorbent and the  $\sqrt{2}^{(v)}$  values are surface excesses of hydrocarbon in millimoles per square centimeter of surface.

Activity data were not available for the decane and dodecane systems; activity data for the system cyclohexane-ethanol system were calculated from partial pressure data of Washburn and Handorf (32).

### C. Solubilities

The solubilities of the aliphatic hydrocarbons in methanol that were determined during the course of the work are listed in Table 8.

Values for the solubility of decane and cyclohexane in methanol were not recorded in the literature.



Table 8

## Solubility of Hydrocarbons in Methanol

Solute	Temperature	Molarity	Weight %	Solute Mole Fraction
Octane	25.0	1.282	19.25	0.0627 <sup>a</sup>
Decane	25.0	0.5613	10.25	.0251
Dodecane	25.0	0.2696	5.883	.0116
Cyclohexane	25.0	3.317	36.05 <sup>b</sup>	.177 <sup>c</sup>

<sup>a</sup>Value of 0.06 + .005 interpolated from data of L. Sieg, Chem.-Ing.-Tech. 23, 112 (1951).

<sup>b</sup>Value of 36.75 interpolated from data of D. C. Jones and S. Amstell, J. Chem. Soc. 1930, 1316.

<sup>c</sup>Value of 0.18 + 0.005 interpolated from data of L. Sieg, Chem.-Ing.-Tech. 23, 112 (1951).

## VI. DISCUSSION

## A. Evaluation of Experimental Data

One of the sources of error in the present work was the uncertainty in the interferometric analyses. While the interferometer can be read with a reproducibility of about one scale division with aqueous systems, the reproducibility was considerably poorer with the solutions used in the present work. The solutions used here were characterized by having large temperature coefficients of the indices of refraction. These large temperature coefficients caused the interferometer readings to fluctuate as the temperature of the air bath varied within the limits of the temperature control. The precision of reading the interferometer was about three scale divisions.

A source of error often found in interferometric analyses is caused by shifts in the coloration of the interference fringes. These band shifts are due to optical dispersion and occur only at large  $\Delta R$  values. The presence of these band shifts was usually detected when the interferometric calibration curve was being determined, since the  $\Delta R$  values were frequently quite large in these determinations. It is believed that no error in this work was the result of band shifts. In determining the isotherms the  $\Delta R$  values were usually kept below 300; band shifts in the systems

used were absent with  $\Delta R$  values of less than 400 or 500.

The values of the interferometer readings with the pure components in both sides of the cells, called the zero readings, were another source of uncertainty. As stated by Craig (18), the zero readings varied too greatly to be explainable on the basis of the different indices of refraction of the various components. With the partly miscible systems the zero readings for pure solvent were used at all concentrations. For the miscible systems the zero readings were determined for both pure components, and the zero readings for the intermediate points were calculated on the basis of linear variation of zero readings with concentration of solute.

Since the interferometric calibration curves for the various systems are not shown, it is desirable to indicate the sensitivity of the systems to interferometric analysis. The sensitivity is directly proportional to the value of  $\Delta R/\Delta C$ . The range of these  $\Delta R/\Delta C$  values, in scale divisions of the interferometer per millimole change in hydrocarbon concentration, are given below for the various binary systems:

Octane - Methanol	3.9 - 4.6
Decane-Methanol	5.7 - 6.2
Dodecane - Methanol	7.7
Decane - Ethanol	3.6 - 5.0
Cyclohexane - Methanol	3.8 - 4.4
Dodecane - Ethanol	5.4 - 6.8
Cyclohexane - Ethanol	2.5 - 3.9

It is apparent that the sensitivity varied considerably from system to system.

Probably one of the chief sources of error in this work was the concentration change resulting from evaporation of solution. This difficulty arose from the fact that no suitable stopcock greases were available for use with hydrocarbon-alcohol mixtures. The best method for sealing the standard solutions consisted of inverting a test tube over the neck of the volumetric flask, then painting paraffin wax around the body of the flask where the test tube rested.

While it was previously stated that the temperature of the air bath enclosing the mechanical shaker was maintained at  $25.0 \pm 0.1^{\circ}\text{C}.$ , the temperature inside the adsorption tubes has been found (18) to be up to  $0.5^{\circ}\text{C}.$  higher. This higher temperature is presumably due to friction of the liquid and adsorbent being shaken against the walls of the adsorption tubes. It is probable that if a water bath had been used instead of an air bath this temperature differential could have been considerably lessened and possibly eliminated entirely. After removal of the adsorption tubes from the mechanical shaker the tubes were placed in a centrifuge for a period of about one minute. While the temperature of the room was fairly constant at  $24.5^{\circ}\text{C}.$ , this short exposure to room temperature added some

uncertainty to the temperature at which the adsorption equilibrium was reached.

The surface areas used in the calculation of the  $\sqrt{2}^{(v)}$  surface excesses were determined by the low-temperature nitrogen adsorption method of Brunauer, Emmett, and Teller (28). Surface area values obtained by this technique are considered precise to about two percent.

#### B. Significance of Reduced Concentrations

The isotherms for partly miscible binary systems can be conveniently compared when the amount adsorbed is plotted as a function of  $C/C_0$ , the reduced concentration. When the nature of the surface phase is considered, two pictures appear to be reasonable. One may consider the adsorbed solute molecules to be concentrated at the surface as pure solute; the other alternative would be to consider the adsorbed solute saturated with solvent. If the adsorbate is concentrated as solute saturated with solvent, then the work required to transfer one mole of solute from bulk solution to the surface phase is given by  $RT \ln C_0/C$ . In this case, it can be seen that the reduced concentration is directly related to the work of adsorption. At large reduced concentrations the work necessary to transfer solute from bulk solution to the surface phase is relatively small, which makes the steep rise of the isotherms at these large reduced

concentrations reasonable. If the solute is concentrated at the surface as pure solute, instead of solute saturated with solvent, then the work required to transfer solute from bulk solution to surface phase is  $-RT \ln a$ , where  $a$  is the absolute activity of the solute in bulk solution. As previously stated, the lower the solubility of solvent in solute, the better approximation  $C/C_0$  is to the absolute activity of the solute.

Craig (18) has found that the adsorption of the normal aliphatic acids from dilute aqueous solution on several non-porous adsorbents was dependent only upon the reduced concentration for the slightly miscible acids and the activity for the miscible acids. For the normal aliphatic alcohols he found a slight, but systematic, deviation from congruency when the adsorption was plotted against  $C/C_0$ , or the activity. The isotherms obtained in the present research were not congruent functions of the reduced concentration, but instead showed systematic deviations from congruency.

### C. The Form of the Isotherms of the Partly Miscible Systems

When the adsorption of the hydrocarbons from methanol solution is plotted as a function of the reduced concentration, it is noted that in all cases the isotherms rise

rather steeply as the reduced concentration approaches unity. This rapid rise suggests that the adsorption is strongly dependent upon the work required to remove the solute from bulk solution and transfer it to the solid-solution interface; since the work required to transfer solute from bulk solution to the surface phase is proportional to the logarithm of the reduced concentration as the reduced concentration approaches unity the work required decreases rapidly.

Assuming the cross-sectional area of a normal hydrocarbon molecule to be 20.5 square Angstroms, the quantity of hydrocarbon required to fill a close-packed monolayer of hydrocarbon with the longitudinal axis of the molecule perpendicular to the surface would be 0.924 millimoles per gram on Spheron-6, 0.638 millimoles per gram on Graphon, and 0.830 millimoles per gram on DAG-1. This cross-sectional area is that found for the normal aliphatic acids (33); it is believed that this value is a good approximation to the area of the normal hydrocarbon molecules if oriented perpendicular to the surface. This area then represents the minimum area which could be occupied by a hydrocarbon molecule. Since these are maximum amounts of normal hydrocarbon that could be placed in a monolayer, these values will also serve as maximum values for cyclohexane, which would undoubtedly have a larger cross-sectional area.

Comparing these maximum amounts of solute with the measured surface excesses as tabulated in Tables 1 to 4, it can be seen that these maxima are exceeded by the measured values for the following systems:

<u>Spheron-6</u>	<u>Graphon</u>	<u>DAG-1</u>
Cyclohexane-Methanol	Cyclohexane-Methanol	Cyclohexane-Methanol
Octane-Methanol	Octane-Methanol	
Decane-Methanol	Decane-Methanol	
Dodecane-Methanol	Dodecane-Methanol	

While the measured surface excesses of the normal hydrocarbons have not exceeded the maxima on the adsorbent DAG-1, the isotherms on DAG-1 show the same steep rise as with the other adsorbents, and the surface excesses would probably exceed the calculated maxima at higher reduced concentrations. For the systems enumerated above multilayer adsorption is definitely proven, while multilayer adsorption of the normal hydrocarbons on DAG-1 is strongly suggested.

Many previous workers have explained adsorption measurements in terms of the Langmuir equation. The equation, proposed by Langmuir (34) in 1915 on the assumption that the gaseous molecules were non-interacting and that the adsorption was unimolecular, is of the form

$$\theta = \frac{b_p}{1 + b_p} \quad (1)$$



where  $\theta$  is the fraction of the surface covered at the pressure  $p$ , and  $b$  is a constant related to the molecular heat of adsorption and the temperature. The isotherms for the hydrocarbon-methanol systems were found to fit the Langmuir equation quite well up to  $C/C_0=0.3$ . In this case the Langmuir equation was used in the slightly modified form

$$n = \frac{a \beta \frac{C}{C_0}}{1 + \beta \frac{C}{C_0}} \quad (2)$$

where  $n$  is the amount adsorbed,  $a$  is the amount in a complete monolayer,  $\beta$  has the same significance as  $b$  in Equation 1. This agreement suggested that the data could be treated with a Langmuir equation to cover the adsorption up to the completion of the first layer.

To describe adsorption beyond this first layer, it was thought reasonable to employ the Polanyi treatment, using the analytical form of the Polanyi potential derived by Hill (35). The potential energy of interaction induced by a temporary dipole in a polarizable molecule is of the form

$$E = \frac{k}{r^6} ,$$

where  $k$  is proportional to the product of the polarizabilities of the interacting molecules, and  $r$  is the intermolecular distance. If this interaction exists between a molecule in the adsorption region and all the molecules in

a semi-infinite slab of adsorbent, integration over the slab gives

$$\Delta\mu = \frac{k'}{Z}$$

for the change in chemical potential of a pure liquid component brought about by introduction of a semi-infinite slab of adsorbent at a distance  $Z$  from the liquid component.  $k'$  is proportional to the product of the polarizability of the liquid and the difference in polarizability between the liquid component and the solid adsorbent.

In the adsorption of single component gases, these considerations lead immediately to an adsorption isotherm of the form

$$RT \ln \frac{P^0}{P} = \frac{K}{n^3} \quad (3)$$

where  $n$  is the number of moles adsorbed at the pressure  $P$ , and  $P^0$  is the saturated vapor pressure. The left hand side of Equation 3 is simply  $\Delta\mu$ , and  $n = ZA/v$ , where  $A$  is the surface area of the adsorbent and  $v$  the molar volume of the liquified adsorbate. The adsorbed material is assumed to be in the liquid state.

In adsorption from solution the corresponding transition to the adsorption isotherm is not so clear cut. Consider a solid adsorbent in equilibrium with a binary liquid solution. Let  $\Delta\phi$  be a volume increment between two

equipotential surfaces  $\vartheta$  and  $\vartheta + \Delta\vartheta$ . If  $\Delta\vartheta$  is assumed invariant, the conditions for equilibrium between material in bulk solution and in  $\Delta\vartheta$  follow from the invariance of the total free energy under constrained infinitesimal mass transfer. These conditions lead to

$$\delta F = 0 = (\mu_{1\vartheta} - \mu_{1b}) \delta n_{1\vartheta} + (\mu_{2\vartheta} - \mu_{2b}) \delta n_{2\vartheta}$$

subject to the condition that

$$\delta \Delta\vartheta = 0 = \bar{V}_{1\vartheta} \delta n_{1\vartheta} + \bar{V}_{2\vartheta} \delta n_{2\vartheta} .$$

Using the Lagrangian multiplier treatment, it follows that

$$\frac{\mu_{1\vartheta} - \mu_{1b}}{\bar{V}_{1\vartheta}} = \frac{\mu_{2\vartheta} - \mu_{2b}}{\bar{V}_{2\vartheta}} = -\lambda, \quad (4)$$

where  $\mu_{i\vartheta}$  and  $\bar{V}_i$  are the chemical potential and partial molar volume of component  $i$  at the position  $\vartheta$ , and  $\mu_{ib}$  is the chemical potential of component  $i$  in bulk solution.

The activity of component  $i$  is defined by

$$\mu_i = \mu_i^0 + RT \ln a_i ,$$

which leads to

$$\mu_{i\vartheta} - \mu_{ib} = \mu_{i\vartheta}^0 - \mu_{ib}^0 + RT \ln \frac{a_{i\vartheta}}{a_{ib}} , \quad (5)$$

where  $a_{i\vartheta}$  is referred to the pure liquid component  $i$  at  $\vartheta$  and  $a_{ib}$  is referred to pure liquid component  $i$  in bulk solution. From Equations 4 and 5, it follows that

$$\mu_{1\vartheta}^0 - \mu_{1b}^0 + RT \ln \frac{a_{1\vartheta}}{a_{1b}} = \frac{\bar{V}_{1\vartheta}}{\bar{V}_{2\vartheta}} \left( \mu_{2\vartheta}^0 - \mu_{2b}^0 + RT \ln \frac{a_{2\vartheta}}{a_{2b}} \right)$$

and

$$\frac{a_{1\vartheta}}{a_{2\vartheta}} = \frac{a_{1b}}{a_{2b}} e^{-\frac{(\mu_{1\vartheta}^0 - \mu_{1b}^0) - \alpha(\mu_{2\vartheta}^0 - \mu_{2b}^0)}{RT}}, \quad (6)$$

where  $\alpha = \bar{V}_{1\vartheta} / \bar{V}_{2\vartheta}$ . The following assumption is now made:

$\mu_{1\vartheta}^0 - \mu_{1b}^0 = -\mathcal{E}_1(\vartheta)$ , the Polanyi potential of component 1 at  $\vartheta$ . Equation 6 can now be written as

$$\frac{a_{1\vartheta}}{a_{2\vartheta}} = \frac{a_{1b}}{a_{2b}} e^{-\frac{\mathcal{E}_1(\vartheta) - \alpha \mathcal{E}_2(\vartheta)}{RT}}. \quad (7)$$

The quantity  $\mathcal{E}_1(\vartheta) - \alpha \mathcal{E}_2(\vartheta)$  is known as the effective potential and will be denoted by  $\mathcal{E}$ . The previous treatment was outlined by Hansen and Fackler (20).

$$\text{Let } \psi = \frac{a_{1\vartheta}}{a_{2\vartheta}} = \frac{a_{1b}}{a_{2b}} e^{-\frac{\mathcal{E}_1(\vartheta) - \alpha \mathcal{E}_2(\vartheta)}{RT}}. \quad (8)$$

$\psi$  is a monotonically increasing function of  $a_{1b}$  for fixed  $\vartheta$ ;  $C_{1\vartheta}$ , the concentration of component 1 at  $\vartheta$ , is a monotonically increasing function of  $a_{1\vartheta}$ , hence of  $\psi$  and  $a_{1b}$ . The nature of the functional dependence of  $C_{1\vartheta}$  on  $a_{1\vartheta}$  and  $x_{1\vartheta}$  is important; if the ratio  $\alpha = \bar{V}_{1\vartheta} / \bar{V}_{2\vartheta}$  is large (as in the cases under discussion),  $C_{1\vartheta}$  varies but slightly with  $x_{1\vartheta}$  and  $a_{1\vartheta}$  when these quantities are larger than 0.7.

If  $C_1^0$  is the concentration of hydrocarbon saturated with alcohol and  $a_1^0$  the corresponding hydrocarbon activity, then for  $a_1\phi > a_1^0$ ,  $C_1\phi$  may be approximated with only slight error by  $C_1^{0'}$ .

At a given  $a_{1b}$ , let  $\phi^*$  be that value of  $\phi$  for which  $a_1\phi = a_1^0$ . If  $\mathcal{E}/RT$  is of the form  $K/\phi^3$  (35), then  $a_1\phi$  is a monotonically decreasing function of  $\phi$ , so that for  $\phi \leq \phi^*$ ,  $a_1\phi \geq a_1^0$ ,  $C_1\phi \approx C_1^{0'}$ . For  $\phi > \phi^*$ ,  $a_1\phi < a_1^0$ ,  $C_1\phi < C_1^0$ , where  $C_1^0$  is the concentration of hydrocarbon in alcohol saturated with hydrocarbon. If the mutual solubilities are small,  $C_1^0$  may be assumed negligible compared to  $C_1^{0'}$ , and the adsorption (subject to approximations outlined is

$$\frac{V\Delta C}{m} = C_1^{0'} \phi^* .$$

Rearranging Equation 8 and setting  $\phi = \phi^*$ ,  $a_1\phi = a_1^0$ ,  $a_2\phi = a_2^0$ , we obtain (after taking logarithms)

$$\ln a_1^0 = \ln a_{1b} + a \ln \frac{a_2^0}{a_{2b}} + \frac{\mathcal{E}(\phi^*)}{RT} .$$

Now if the mutual solubility is small,  $a_2^0/a_{2b} \approx 1$ . Therefore,  $\ln(a_2^0/a_{2b})$  may be neglected in first approximation. Further,  $\mathcal{E}(\phi)/RT$  is assumed of the form  $K/\phi^3$  (35). Hence, to first approximation

$$\ln \frac{a_1^0}{a_{1b}} = \frac{K}{\phi^{*3}} \quad (9)$$

permitting calculation of  $\phi^*$ . It was found that the potential of the form  $K/\phi^3$  did not satisfactorily describe the adsorption in the immediate vicinity of the surface. It was this failure that led to the use of the Langmuir equation in attempting to describe the adsorption in the first layer.

In the treatment used here, it was assumed that the adsorption inside the volume  $\phi_0$ , enclosed by an equipotential surface, was governed by Equation 2. It was further assumed that outside the volume  $\phi_0$  the adsorption was governed by Equation (9), which was used in the form

$$\ln \frac{C_0}{C} = \frac{K}{\phi^3} \quad , \quad (10)$$

where  $\phi$  is the total volume adsorbed at the reduced concentration  $C/C_0$ . If  $n_H^i$  is the number of moles of hydrocarbon between  $\phi_0$  and  $\phi$  then we have the relationship

$$\phi = \phi_0 + n_H^i \bar{v}_H + n_H^i \frac{X_A^s}{1-X_A^s} \bar{v}_A \quad , \quad (11)$$

where  $\bar{v}_H$  and  $\bar{v}_A$  are the partial molar volumes of hydrocarbon and alcohol respectively, and  $X_A^s$  is the mole fraction of alcohol in the volume between  $\phi_0$  and  $\phi$ . If it is further assumed that the hydrocarbon is concentrated at the surface as hydrocarbon saturated with alcohol, then the last term in Equation 11 can be dropped because of the low solubilities

of methanol in the hydrocarbons studied. The values of  $n_H^i$  were obtained from the relation

$$n_H^i = \frac{V\Delta C}{m} - n_H'' , \quad (12)$$

where  $n_H''$  was obtained from Equation 2, and  $V\Delta C/m$  is the measured surface excess.

The values of  $\alpha$  and  $\beta$  from Equation 2 were evaluated by plotting  $\frac{C/C_0}{V\Delta C/m}$  against  $C/C_0$  for reduced concentrations ranging from 0 to 0.35. The values of  $\alpha$  and  $\beta$  were obtained from the slopes and intercepts of the straight line plots. Evaluation of these two constants allowed the calculation of  $n_H''$  from Equation 2. Substituting the value of  $\beta$  obtained from Equation 11 into Equation 10 led to the expression

$$\ln \frac{C_0}{C} = \frac{K}{\left[ \beta_0 + n_H \frac{V}{V_H} \right]^3} , \quad \beta_0 < \beta. \quad (12)$$

This equation expresses the adsorption for  $\beta > \beta_0$ , Equation 2 governing the adsorption for  $\beta < \beta_0$ . To evaluate  $K$  and  $\beta_0$  for a given system,  $n_H \frac{V}{V_H}$  was plotted against  $\ln^{-1/3} \left( \frac{C_0}{C} \right)$ . The best straight line was drawn; the slope was equal to  $K^{1/3}$  and the intercept was  $-\beta_0$ . This procedure was followed to obtain values for  $\alpha$ ,  $\beta$ ,  $K$  and  $\beta_0$  for the normal hydrocarbon systems. The values of these constants are shown in Table 9.

Table 9

Constants Obtained from Analytical Treatment of Isotherms  
of the Partly Miscible Systems

System	$K(\text{cm.}^3/\text{g.}^3)$	$\phi_0(\text{cc./g.})$	$\alpha(\text{m.moles/g.})$	$\beta$
Octane-Spheron-6	$0.062 \times 10^{-3}$	0.0430	0.565	1.75
Decane-Spheron-6	$.165 \times 10^{-3}$	.0550	.316	3.57
Dodecane-Spheron-6	$.181 \times 10^{-3}$	.0607	.262	5.19
Octane-Graphon	$.099 \times 10^{-3}$	.0425	.415	3.44
Decane-Graphon	$.242 \times 10^{-3}$	.0662	.281	6.05
Dodecane-Graphon	$.295 \times 10^{-3}$	.0710	.229	13.65
Octane-DAG-1	$.010 \times 10^{-3}$	.0243	.350	3.00
Decane-DAG-1	$.035 \times 10^{-3}$	.0330	.240	4.88
Dodecane-DAG-1	$.096 \times 10^{-3}$	.0515	.221	7.07



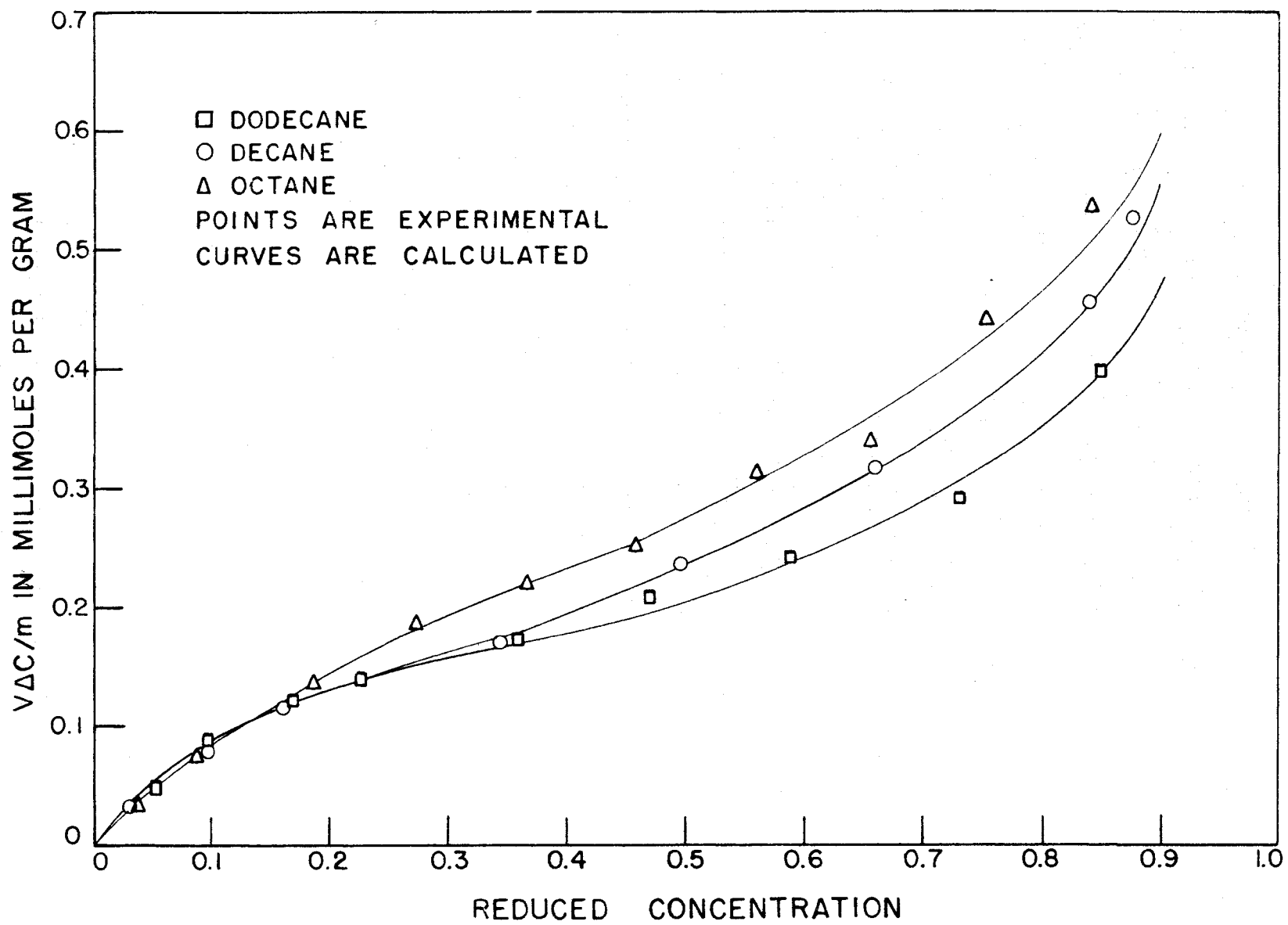
The graphs showing the agreement between the calculated isotherms and the experimental results are shown in Figures 1 to 3.

In determining the constants for the isotherms of cyclohexane, a different method was used to obtain the values of  $\alpha$  and  $\beta$ . These isotherms were nearly linear at low reduced concentrations, making determination of the constants  $\alpha$  and  $\beta$  in the usual manner difficult. At low reduced concentrations, the Langmuir equation can be reduced to

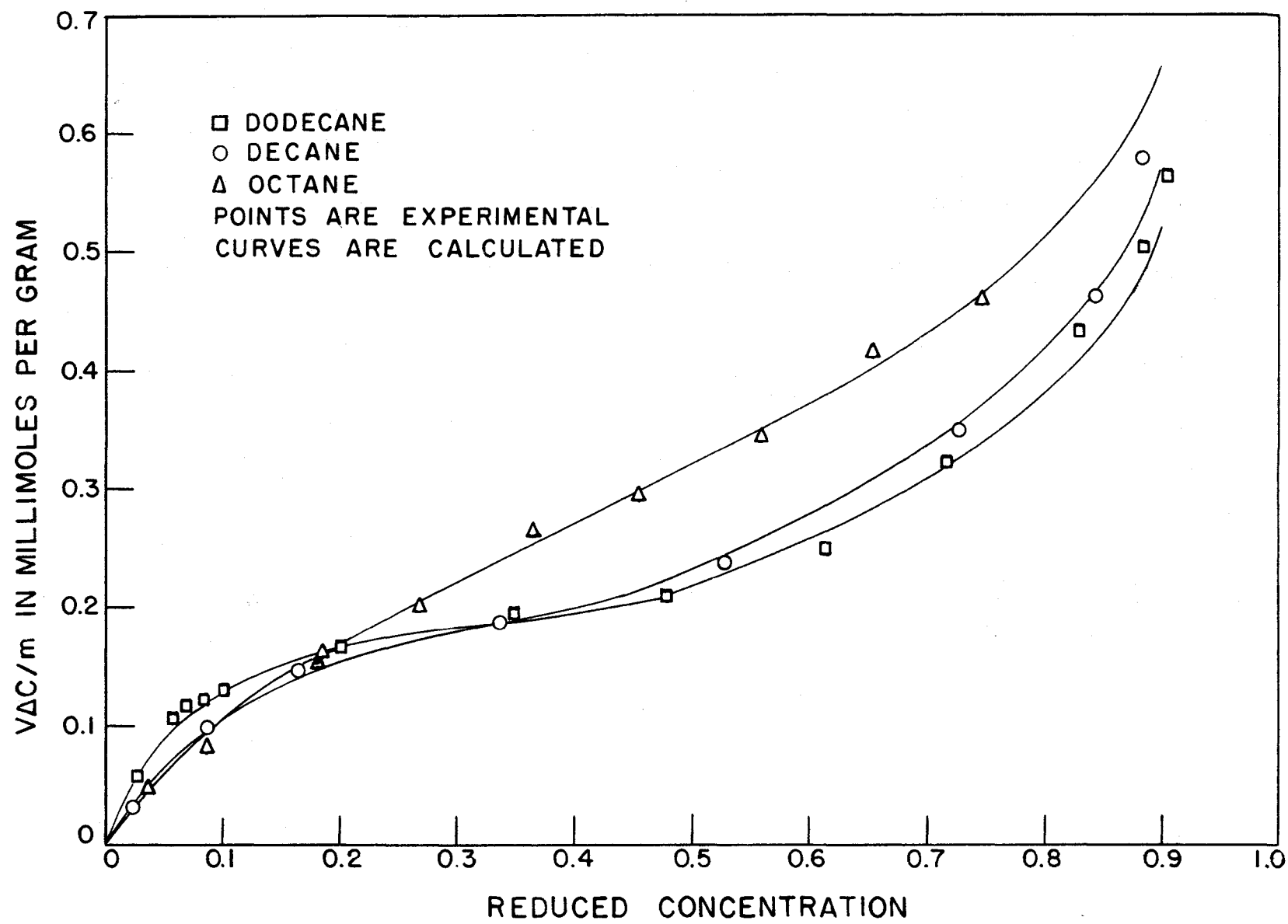
$$n = \alpha \beta \frac{C}{C_0} \quad , \quad (13)$$

the quantity  $\beta(C/C_0)$  in the denominator of the usual expression being negligibly small compared to unity. Therefore, to obtain values for  $\alpha$  and  $\beta$ , the limiting slopes of the isotherms as the reduced concentration approaches zero were determined. From Equation 13 it can be seen that the limiting slope is equal to the product  $\alpha\beta$ . The value of  $\beta$  was arbitrarily selected as one,  $\alpha$  being equal to the slope. The smaller the value of  $\beta$  chosen, the more nearly linear is the initial portion of the calculated isotherm. However, if  $\beta$  is chosen too small, the value of  $\alpha$  becomes quite large. It was found that setting  $\beta = 1$  gave values of  $\alpha$  in line with values of  $\alpha$  for the normal hydrocarbon. The constants  $K$  and  $\theta_0$  were determined in the usual manner. The values

Figure 1. Comparison of Calculated Isotherms and Experimental Results for the Adsorption of the Normal Hydrocarbons from Methanol Solution on Spheron-6

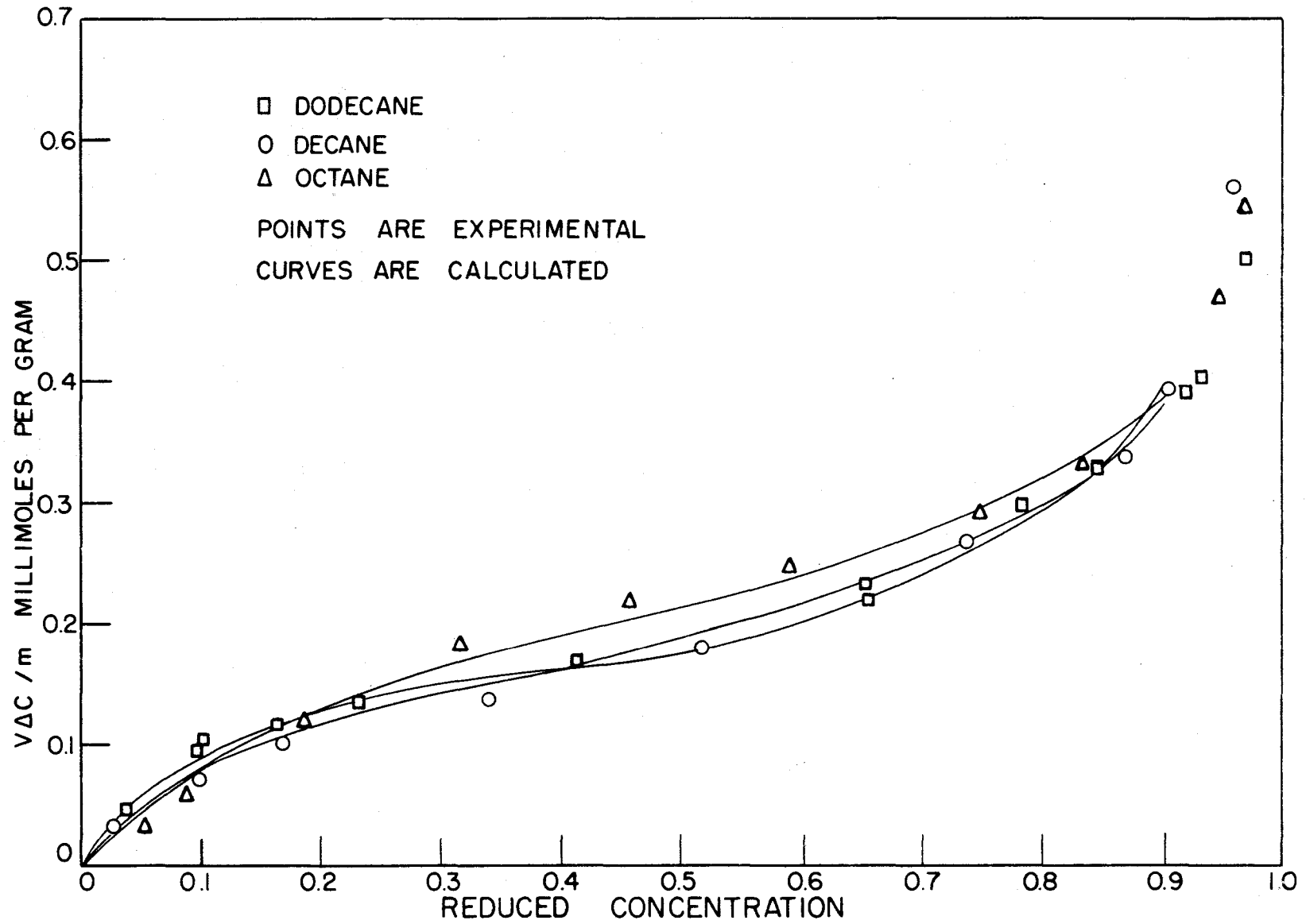


**Figure 2. Comparison of Calculated Isotherms and Experimental Results for the Adsorption of the Normal Hydrocarbons from Methanol Solution on Graphon.**



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Figure 3. Comparison of Calculated Isotherms and Experimental Results for the Adsorption of the Normal Hydrocarbons from Methanol Solution on DAG-1.



of the constants for cyclohexane isotherms are shown in Table 10.

Table 10  
 Constants Obtained from Analytical Treatment  
 of Cyclohexane Isotherms

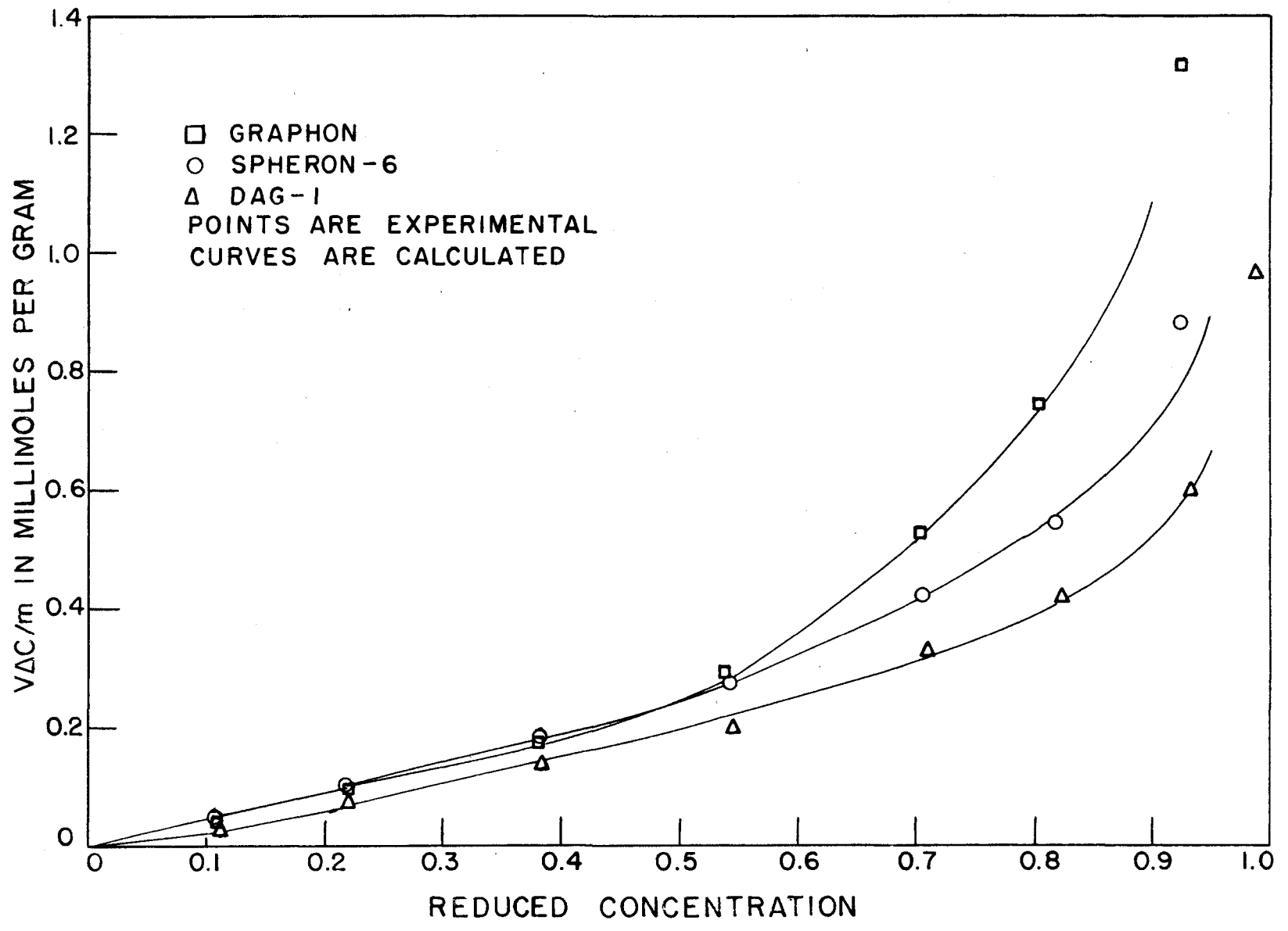
Adsorbent	$K(\text{cm.}^3/\text{g.}^3)$	$\phi_0(\text{cc./g.})$	$a(\text{m.moles/g.})$	$\beta$
Spheron-6	$0.0895 \times 10^{-3}$	0.0400	0.477	1.0
Graphon	$0.348 \times 10^{-3}$	0.0665	0.444	1.0
DAG-1	$0.0281 \times 10^{-3}$	0.0238	0.240	1.0

The graph showing the agreement between the calculated isotherms for cyclohexane and the experimental results is shown in Figure 4. It should be pointed out that while the treatment used here leads to continuous isotherms, there is a discontinuity in the first derivative at  $\phi_0$ , that is, where the values of  $n_H'$  calculated from Equation 12 begin to contribute to the isotherms.

To indicate the sensitivity of the calculated isotherms to variation of the constants, four isotherms were calculated to show how individual variation of each constant would affect the calculated isotherm. These isotherms are



Figure 4. Comparison of Calculated Isotherms and Experimental Results for the Adsorption of Cyclohexane from Methanol Solution.



shown in Figure 5. The reference isotherm is the isotherm calculated for octane on Graphon, using the constants in Table 9. Each of the other isotherms represents a 20 per cent increase in one of the constants; for instance, isotherm a was calculated with  $K'$  greater than  $K$  by 20 per cent, the other three constants being the same as those used in the reference isotherm. It can be seen that the isotherms are most sensitive to the constants  $a$  and  $\beta_0$ .

Since variations of the individual constants affect the calculated isotherms in different ways, it is obviously possible to partially offset these changes by simultaneous variation of several of the constants. To demonstrate this, and to see how well a given isotherm can be fit by simultaneous variation of several of the constants, the constant  $a$  in the reference isotherm was increased by 20 per cent and the other constants varied by trial and error until the reference isotherm was most closely approximated. The resulting isotherm is compared with the reference isotherm in Figure 6. The legend indicates the variations in the other constants necessary to approximate the reference isotherm. The greatest deviation from the reference isotherm was 8 per cent.

If the adsorbed hydrocarbon molecules were coiled in a spherical shape, then  $a$ , the monolayer concentration, would be expected to vary as  $v^{-2/3}$ , where  $v$  is the molar

**Figure 5. Effect of Variation of Constants Upon  
Calculated Isotherms.**

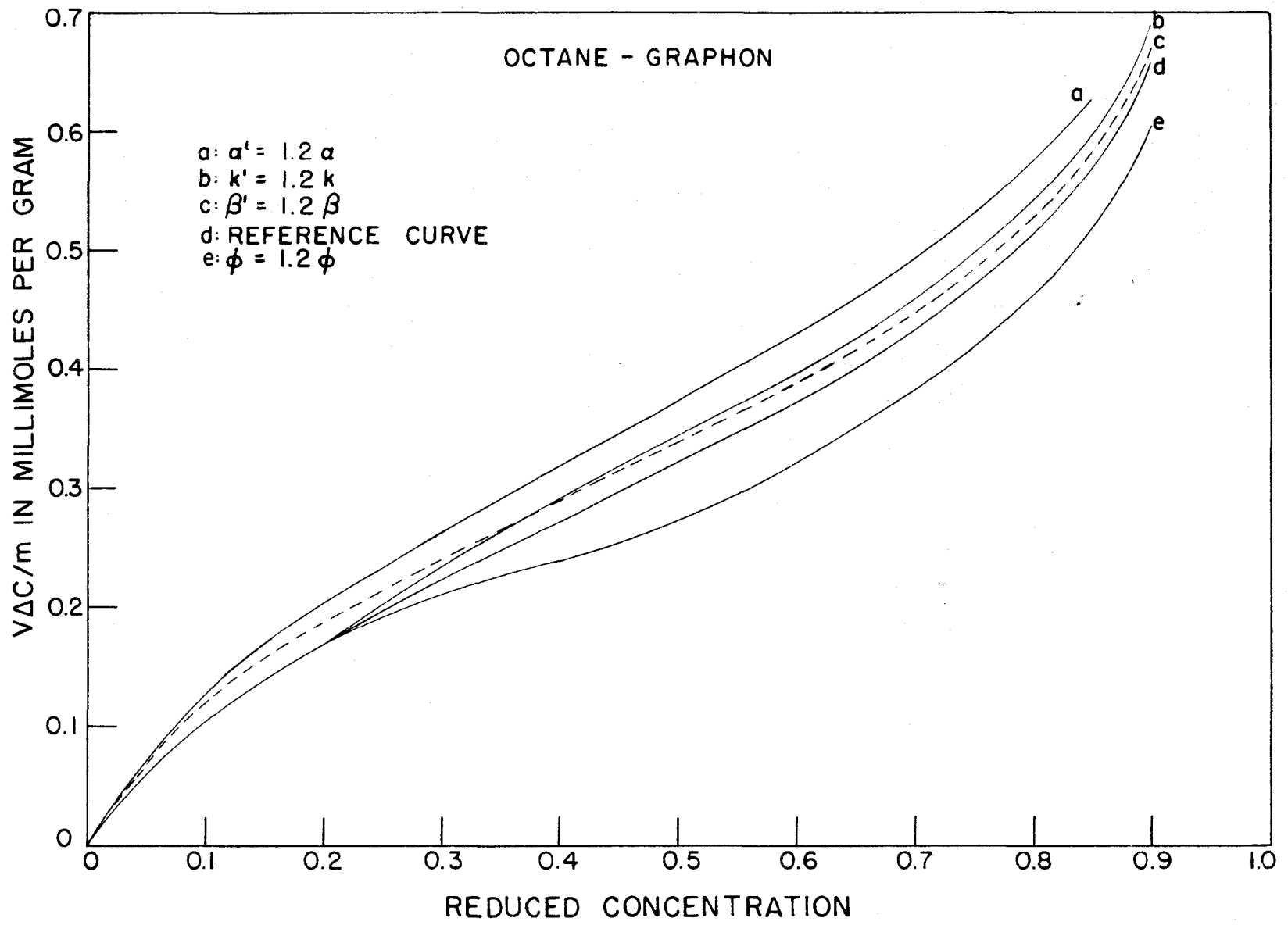
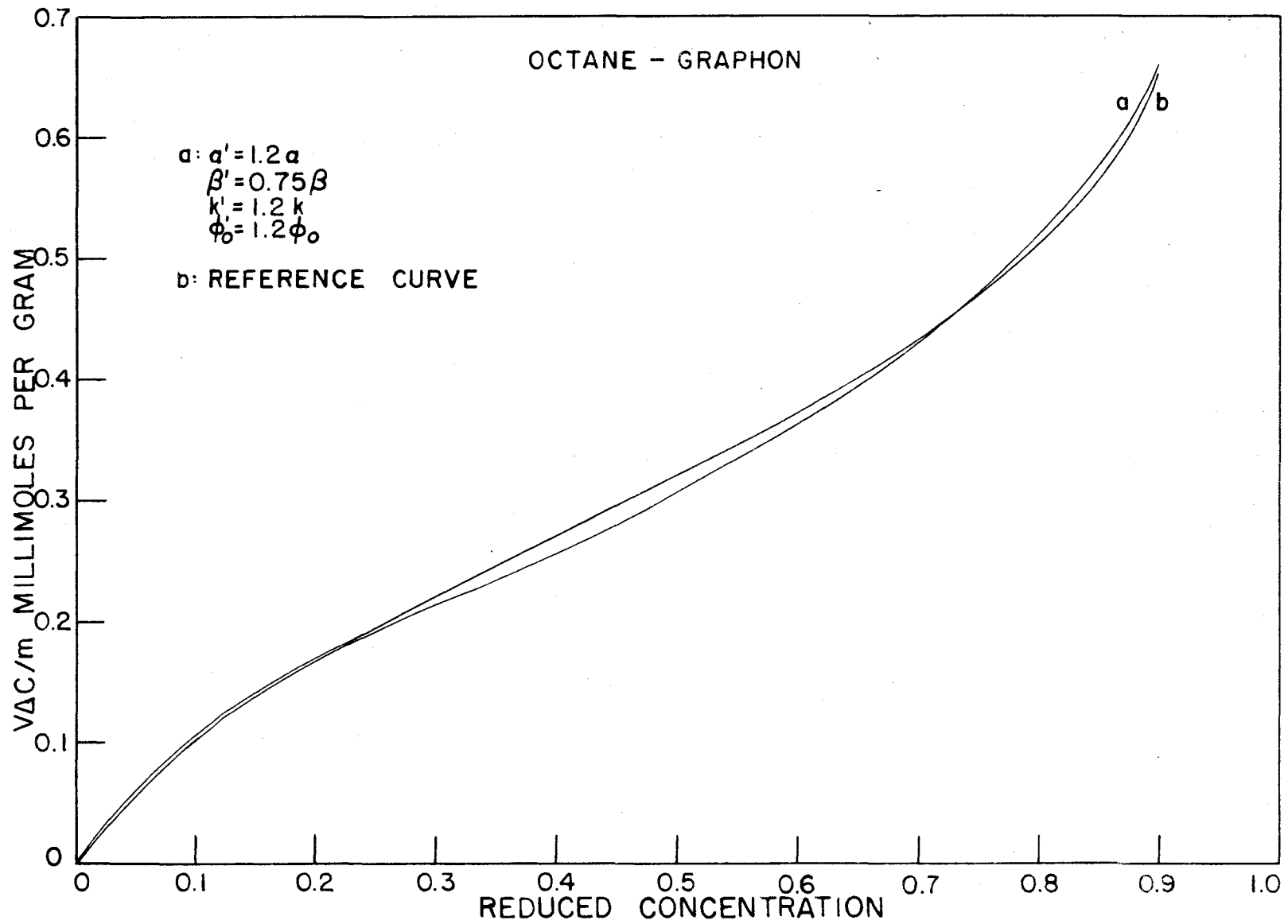


Figure 6. Effect of Variation of Constants Upon  
Calculated Isotherm.



volume of hydrocarbon. Correspondingly  $\rho_0$  would be expected to vary as  $v^{1/3}$  or as  $av$ .  $K$  might be expected to be proportional to the difference in polarizabilities of the hydrocarbon and alcohol molecules, as  $K$  reflects the interaction between the adsorbent and the adsorbed molecules. To test such a model, the isotherms on Spheron-6 were studied. The isotherms were first plotted against the solute activity, based on the standard state of solute saturated with methanol. The following method was used to calculate these activities. The equation  $\ln \gamma_H = B(1-x_H)^2$  was used to express the hydrocarbon activity coefficient,  $\gamma_H$ , in terms of the hydrocarbon mole fraction,  $x_H$ . The activity is given by

$$a = \frac{\gamma_H x_H}{\gamma_H^0 x_H^0}, \quad (14)$$

where the superscript zeroes refer to methanol saturated with hydrocarbon. Substituting the expression for  $\ln \gamma$  into Equation 14 and simplifying, we get

$$a = \frac{x_H}{x_H^0} e^{B(x_H^0 - x_H)(2 - x_H - x_H^0)}. \quad (15)$$

Since  $x_H$  and  $x_H^0$  are negligibly small compared to two, they can be neglected; then, using the exponential expansion the



expression

$$a = \frac{X_H^0}{X_H} \left[ 1 + 2B(X_H^0 - X_H) \right] \quad (16)$$

is obtained by neglecting higher terms in the expansion.

The values of B were obtained from the expression

$$\gamma_H^0 X_H^0 = \gamma_H^1 X_H^1 \quad (17)$$

obtained by considering the fact that the activity of hydrocarbon in a saturated solution of methanol is the same as the activity of hydrocarbon saturated with methanol; here  $\gamma_H^1$  and  $X_H^1$  are the activity coefficient and mole fraction of hydrocarbon in a solution of hydrocarbon saturated with methanol. Substituting  $e^{B(1-X)^2}$  for  $\gamma$  in Equation 17 leads to the expression

$$X_H^0 e^{B(1-X_H^0)^2} = X_H^1 e^{B(1-X_H^1)^2},$$

which can be solved for B if the solubilities of the components in each other are known. The solubility of methanol in octane was found in the literature (36). It was found that the mole fraction solubility of methanol in the hydrocarbons was a linear function of the hydrocarbon chain lengths for hexane, heptane, and octane. Therefore, the solubilities of methanol in decane and dodecane were obtained by extrapolation.

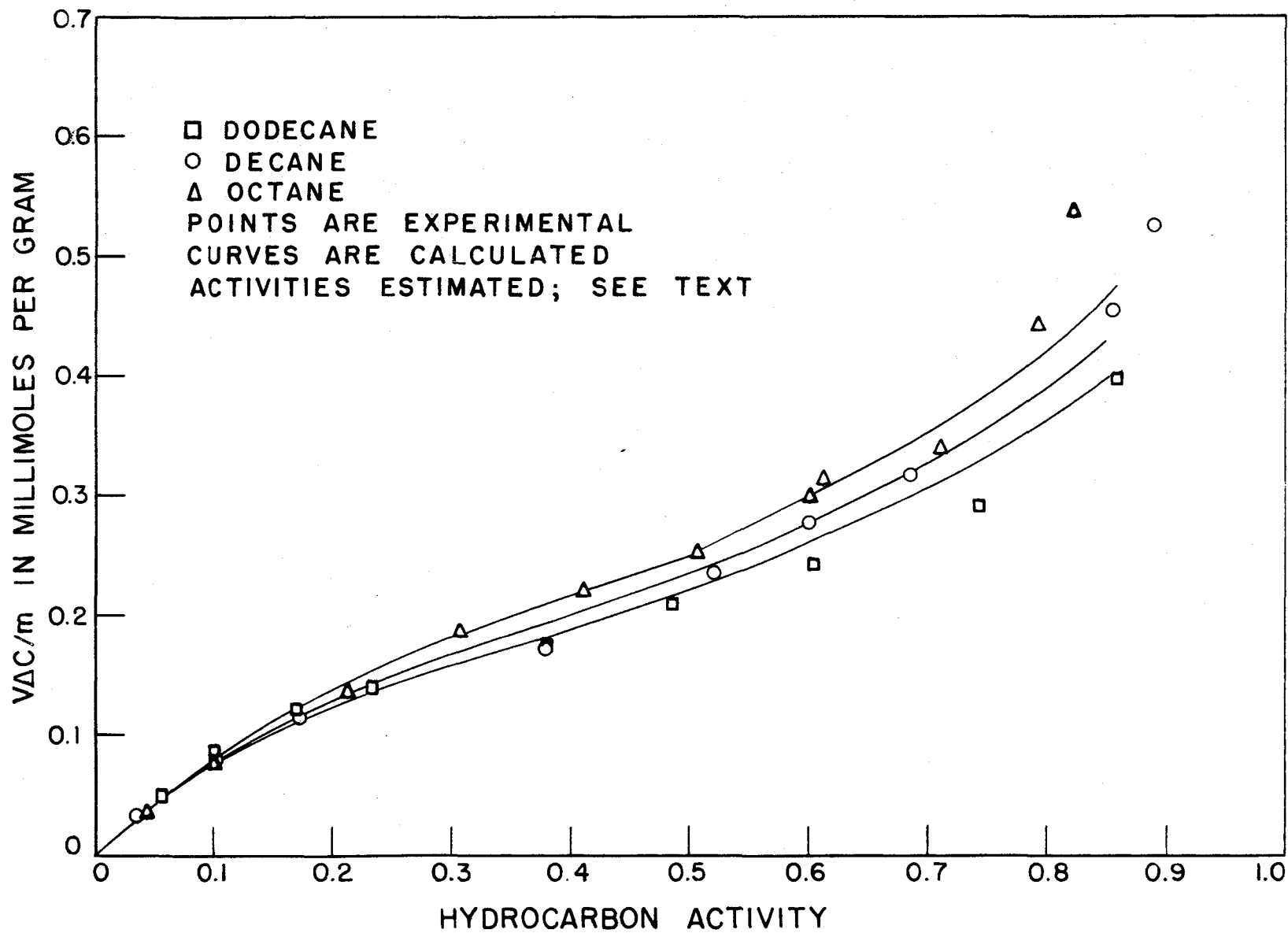
To test the spherical model outlined above, the isotherm for decane-methanol as a function of activity was analyzed to obtain the constants  $\alpha$ ,  $\beta$ ,  $K$  and  $\phi_0$ . The following expressions were used for these constants:

$$\begin{aligned}\alpha &= 0.145 v_H^{-2/3} \\ K &= 3.87 \times 10^{-4} (v_H - v_A) \\ \phi_0 &= 0.0725 v_H^{1/3} .\end{aligned}$$

The values of  $\beta$  were calculated from Equation 2 where the activity was equal to 0.4. Since the polarizabilities are very closely approximated by the molar volumes, the difference in molar volumes was used to obtain the variation of  $K$ . The three isotherms obtained by this method are shown in Figure 7 together with the experimental results. It can be seen that the agreement is at least qualitative, indicating that the spherical model might be close to the correct picture.

The treatment proposed here seems to be capable of fitting the experimental isotherms with a fair degree of success. It is not the purpose of the author, however, to present this agreement of calculations with experiment as evidence of proof of the suggested model. It is merely intended that the model presented here be offered as a possible explanation for the behavior of the isotherms of partly miscible binary systems. It is believed, however,

Figure 7. Comparison of Experimental Results with Isotherms Calculated on the Basis of Spherically Adsorbed Molecules for the Adsorption of Normal Hydrocarbons on Spheron-6.



that the model presented here is based on assumptions that are physically tenable; and it is hoped that this treatment will shed some light upon the mechanism of adsorption from solution.

#### D. The Form of the Isotherms of the Miscible Binary Systems

The shapes of the isotherms for the miscible binary solutions are fundamentally different from the shapes of the isotherms for the partly miscible systems. Whereas the isotherms for the partly miscible systems rise asymptotically as the reduced concentration approaches unity, the isotherms for the miscible systems must necessarily approach zero as the concentration approaches that of pure solute. This difference in shape is a necessary consequence of the method of measuring adsorption. Since the adsorption is measured as a surface excess, it is impossible for the surface excess of solute to attain a large value when the solution is very nearly pure solute.

As was mentioned previously, it is not the solute only that is adsorbed, but also the solvent. This leads to two possible types of isotherms for miscible binary systems. After the isotherm indicating the surface excess of one component passes through a maximum, it can approach zero asymptotically, or it can cross the concentration axis at

some point and pass through a minimum before reaching zero. The presence of such a minimum is frequently referred to as negative adsorption. It is evident that this latter type isotherm, showing both a maximum and a minimum, will occur when both components are adsorbed with forces comparable in magnitude. Isotherms of both types are noted in observing Figures 8 to 10. For all systems the isotherms on Graphon are of the first type, showing preferential adsorption of hydrocarbon throughout the entire concentration range. All isotherms on Spheron-6 and DAG-1 are of the second type, the isotherms containing both maxima and minima. The conclusion can be drawn that ethanol is much less strongly adsorbed on Graphon than the hydrocarbons, while on Spheron-6 and DAG-1 ethanol is adsorbed with forces comparable to those adsorbing the hydrocarbons.

As mentioned in the introduction, Doss and Rao (25) have suggested that a sigmoid-shaped isotherm is due to a preferred composition of the adsorbed layer. They identified the inversion points on their isotherms with simple compounds having the same compositions of the inversion points. While the findings of Bartell and Lloyd (25) would seem to invalidate the argument of Doss, it might be interesting to examine the present results. The concentrations at which the isotherms cut the concentration axes are listed in Table 11.

Figure 8. Adsorption of Hydrocarbons from Ethanol  
Solution on Spheron-6.

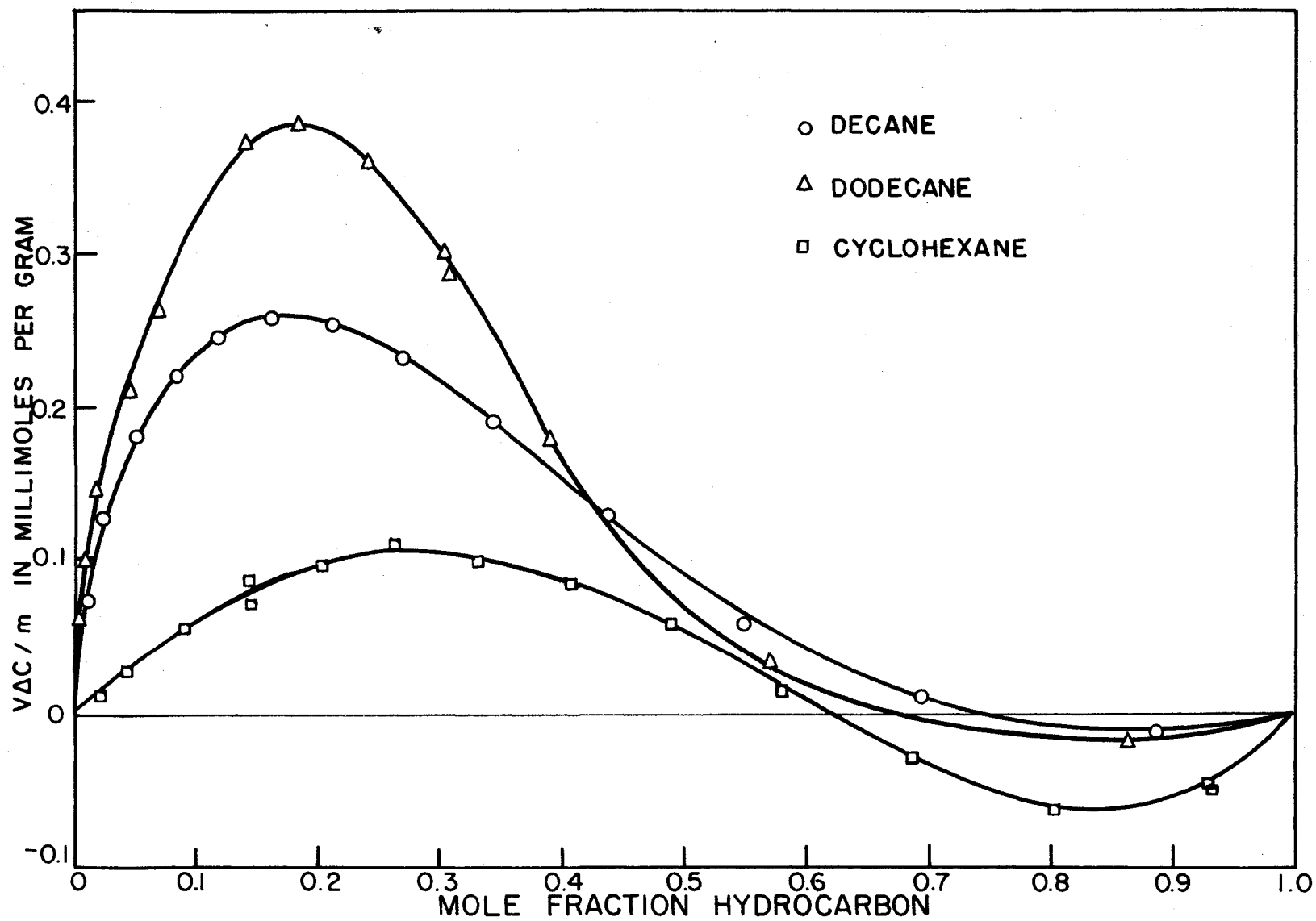




Figure 9. Adsorption of Hydrocarbons from Ethanol Solution on Graphon.

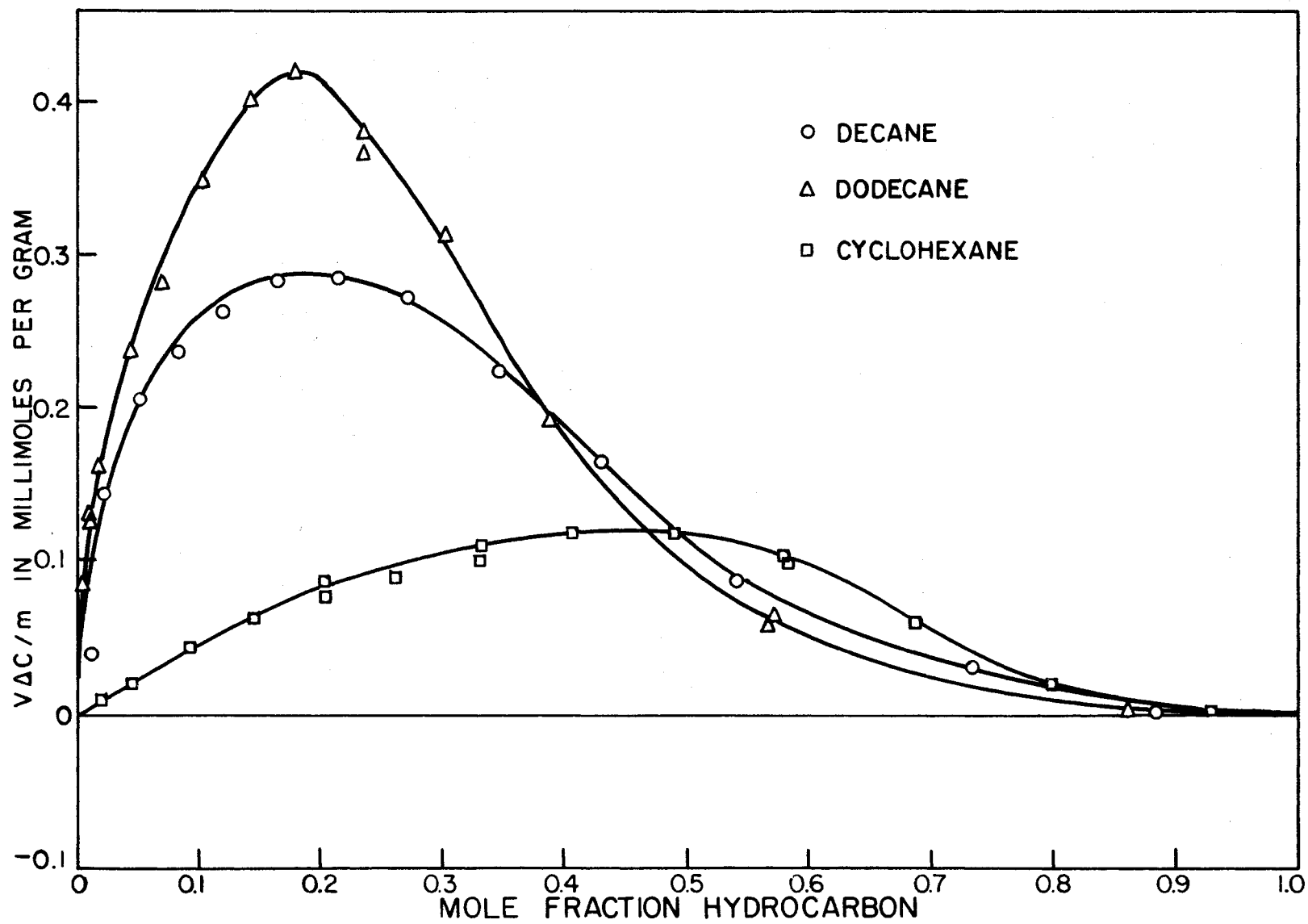


Figure 10. Adsorption of Hydrocarbons from Ethanol  
Solution on DAG-1.

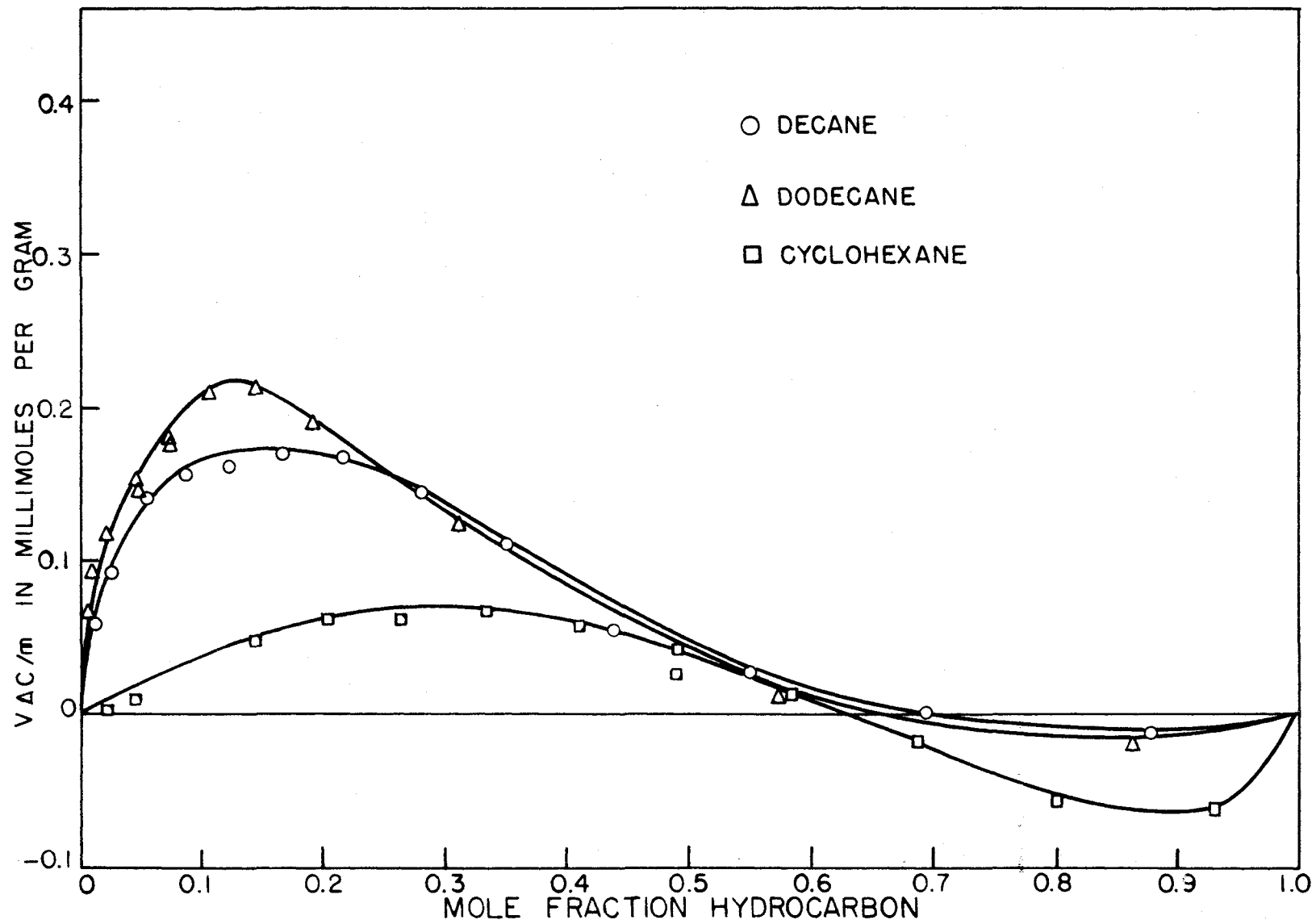


Table 11

## Inversion Points for Isotherms of the Miscible Systems

Adsorbent	Mole Fraction Decane	Mole Fraction Dodecane	Mole Fraction Cyclohexane
Spheron-6	0.740	0.671	0.617
DAG-1	0.734	0.652	0.641

The composition of these inversion points do not correspond to compounds of a simple nature. If a compound such as decane-ethanol were responsible for the inversion on an isotherm, then for the system dodecane-ethanol the inversion point would have to be at the same mole fraction, presuming that the same type compound would be hypothesized. On the contrary, it is observed on both Spheron-6 and DAG-1 that the inversion points for the system dodecane-ethanol are at smaller mole fractions than for the system decane-ethanol. Thus, the isotherms on Spheron-6 and DAG-1 seem to indicate that the shape of the isotherms are dependent on phenomena other than the existence of a preferred molecular structure in the adsorbed layer.

The shapes of the isotherms may be due to the forms of the Polanyi potentials for the two components. If the alcohol were adsorbed by a portion of the surface that was covered by surface complexes of the type found by Anderson and Emmett (2), then the adsorption potential for alcohol would be due to a two-dimensional attracting layer. Integration of this interaction energy over this two-dimensional layer would lead to a potential of the form  $k/Z^4$ . The effective potential, or the difference between the potentials of the two components, would then be of the form  $k_1/Z^3 - k_2/Z^4$ . This type of potential function will lead to an inversion in the isotherm of the type observed, and the point at which this inversion occurs is dependent on the relative magnitude of  $k_1$  and  $k_2$ .

The maxima and minima in the isotherms for miscible binary systems have also been identified on the basis of complex formation (27). To explain the minima in the isotherms of dodecane-ethanol and decane-ethanol on Spheron-6, it would be necessary to postulate the existence of the complexes 7 dodecane • ethanol and 7 decane • ethanol. Complexes of this nature would appear to be quite unlikely. It seems more likely that the maxima are determined solely by the relative magnitudes of the adsorption potentials of the two components.

While activity data are not available for the solutions of decane and dodecane in ethanol, a fair approximation to the activity curves for these hydrocarbons can be made. The activity curves for hexane (37) and heptane (38) in ethanol solutions rise steeply as the mole fraction of hydrocarbon increases. The activity of heptane is 0.9 at mole fraction 0.37. Since deviations from ideality increase with chain length, the activity curves for decane and dodecane can be estimated with reasonable accuracy, for at mole fraction 0.37 the activities of decane and dodecane are constrained to be less than 1 but greater than 0.9. The Margules equation,  $\ln \gamma_1 = BX_2^2$ , was used to establish the activity curves at low hydrocarbon mole fractions;  $\gamma_1$  is the activity coefficient of hydrocarbon, B is a constant, and  $X_2$  is the ethanol mole fraction. The constant B was found to vary linearly with hydrocarbon chain length in the partly miscible hydrocarbon-methanol solutions. It was therefore assumed that the constant B would vary in a linear manner with chain length in the hydrocarbon-ethanol solutions. Values of B were determined for the systems hexane-ethanol and heptane-ethanol using the activity data; the values of B for the systems decane-ethanol and dodecane-ethanol were obtained by extrapolation. The activity curves at higher hydrocarbon concentrations were estimated, subject to the condition that the deviation from ideality is greater the

longer the chain length. Using the estimated activity curve, the isotherm for the system dodecane-ethanol is shown in Figure 11, where the amount adsorbed is plotted against the dodecane activity. In Figure 12 is shown the isotherm for cyclohexane-ethanol, also plotted as a function of the activity. At low solute activities the isotherms resemble closely the isotherms of the partly miscible systems. As the solute activity increases the isotherms begin to rise steeply in the manner characteristic of the isotherms of the partly miscible systems, which are known to demonstrate multilayer adsorption. Thus, although the maxima in the isotherms do not exceed a close-packed monolayer, from the sharp increase in adsorption shown by these isotherms it seems that the systems are demonstrating multilayer adsorption. As mentioned previously, due to the nature of the measurements, the surface excess of hydrocarbon cannot increase as the hydrocarbon mole fraction approaches unity. The isotherms for the system decane-ethanol plotted as functions of the activity are not shown because the rise, though present, is not nearly as pronounced as with the two systems shown.



Figure 11. Adsorption of Dodecane from Ethanol  
Solution.

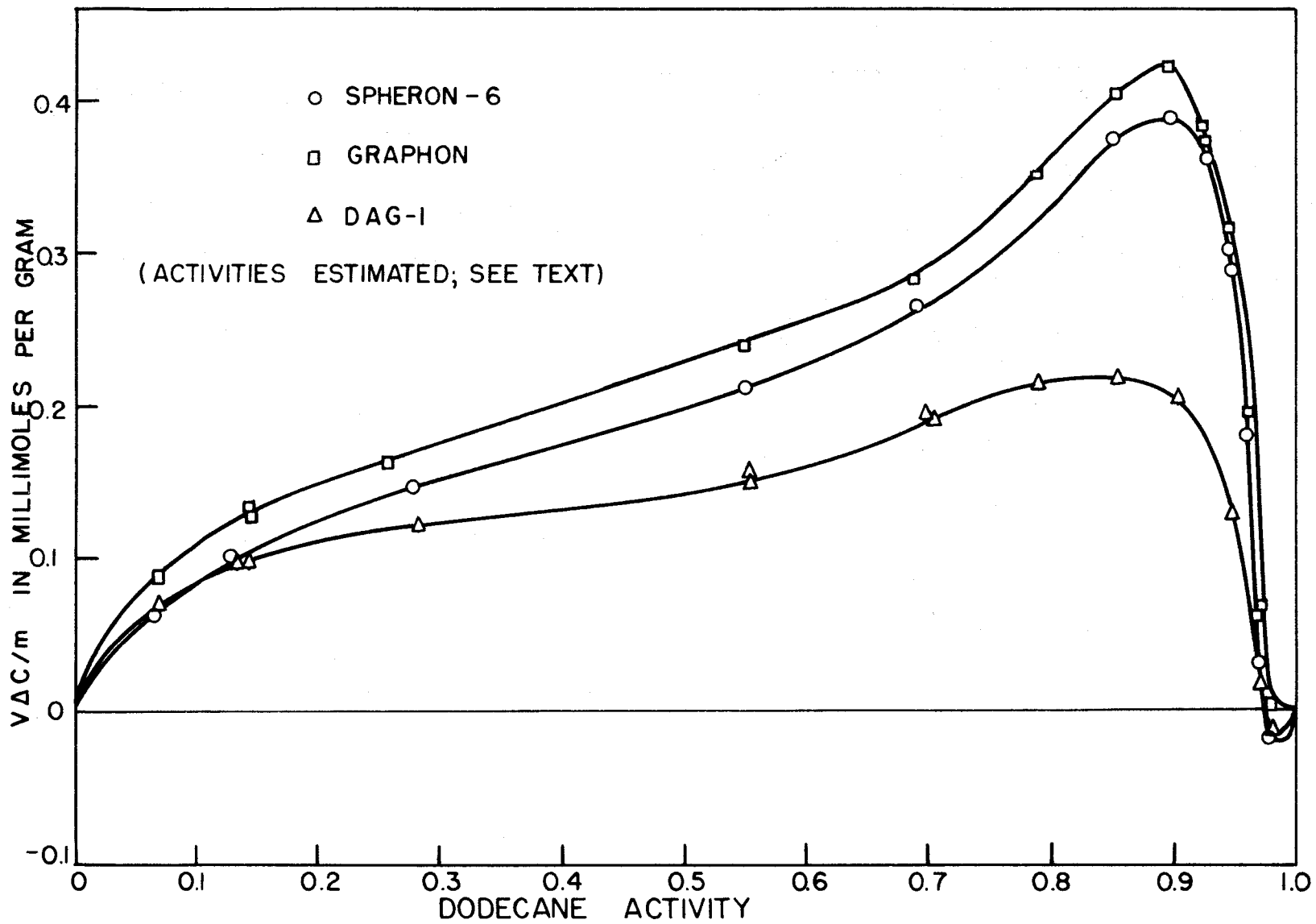
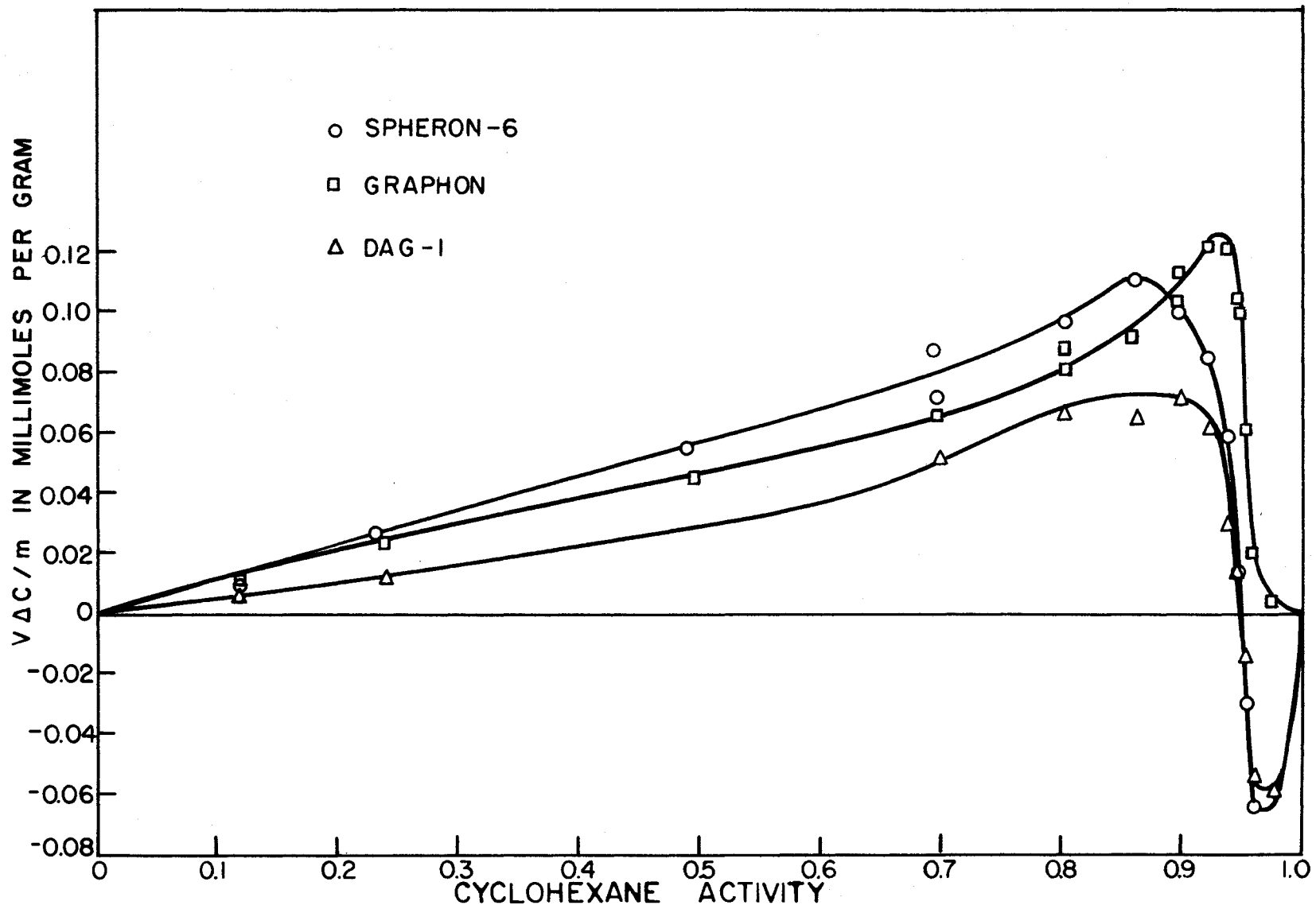


Figure 12. Adsorption of Cyclohexane from Ethanol Solution.



### E. Comparison of Adsorptive Properties of Different Carbon Adsorbents

A comparison of the adsorption isotherms determined on different adsorbents can give information concerning the nature of the surface of these adsorbents. In order to compare the adsorbents used in the present studies, the isotherms were plotted as  $\sqrt{2}^{(v)}$  versus the reduced concentration for the partly miscible systems and as  $\sqrt{2}^{(v)}$  versus solute mole fraction for the miscible systems. These plots are shown in Figures 13 to 19 where  $\sqrt{2}^{(v)}$  is the surface excess of hydrocarbon in millimoles per square centimeter of surface area. These plots, therefore, indicate the amounts adsorbed on a unit surface area basis.

Examination of Figures 13 to 16 shows that for the partly miscible systems the adsorption of hydrocarbon was greater on Graphon than the adsorption on either Spheron-6 or DAG-1. Since Graphon shows no preferential adsorption of ethanol from the miscible binary systems, the strong adsorption of hydrocarbon on Graphon could be due to the weak competition offered by methanol for the Graphon surface. Comparison of the Spheron and DAG isotherms shows that the adsorption of hydrocarbon from the partly miscible systems is in general greater on Spheron-6 than on DAG-1. The exceptions to this, while not great, follow a definite trend.

Figure 13. Adsorption of Octane from Methanol Solution.

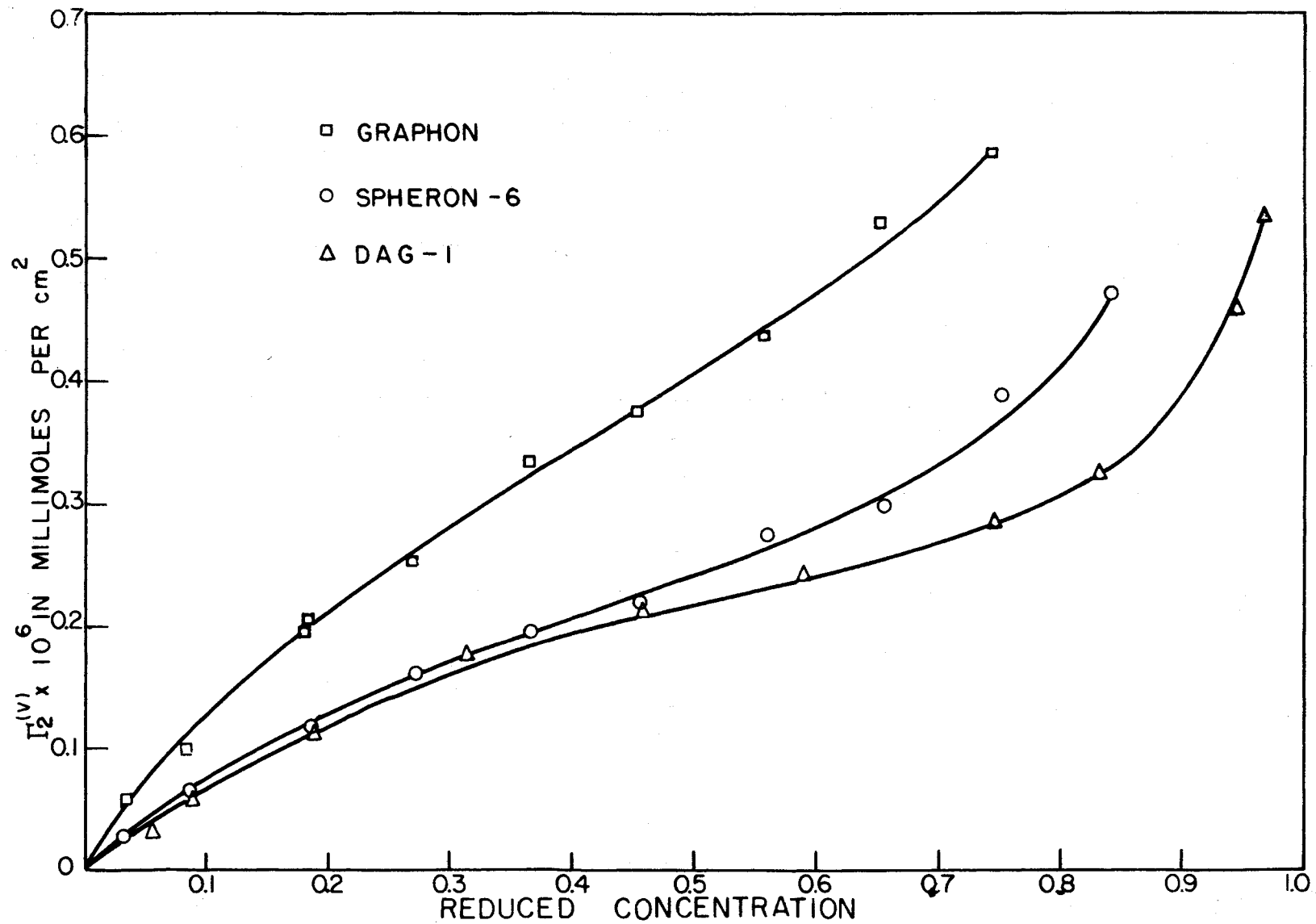


Figure 14. Adsorption of Decane from Methanol  
Solution.



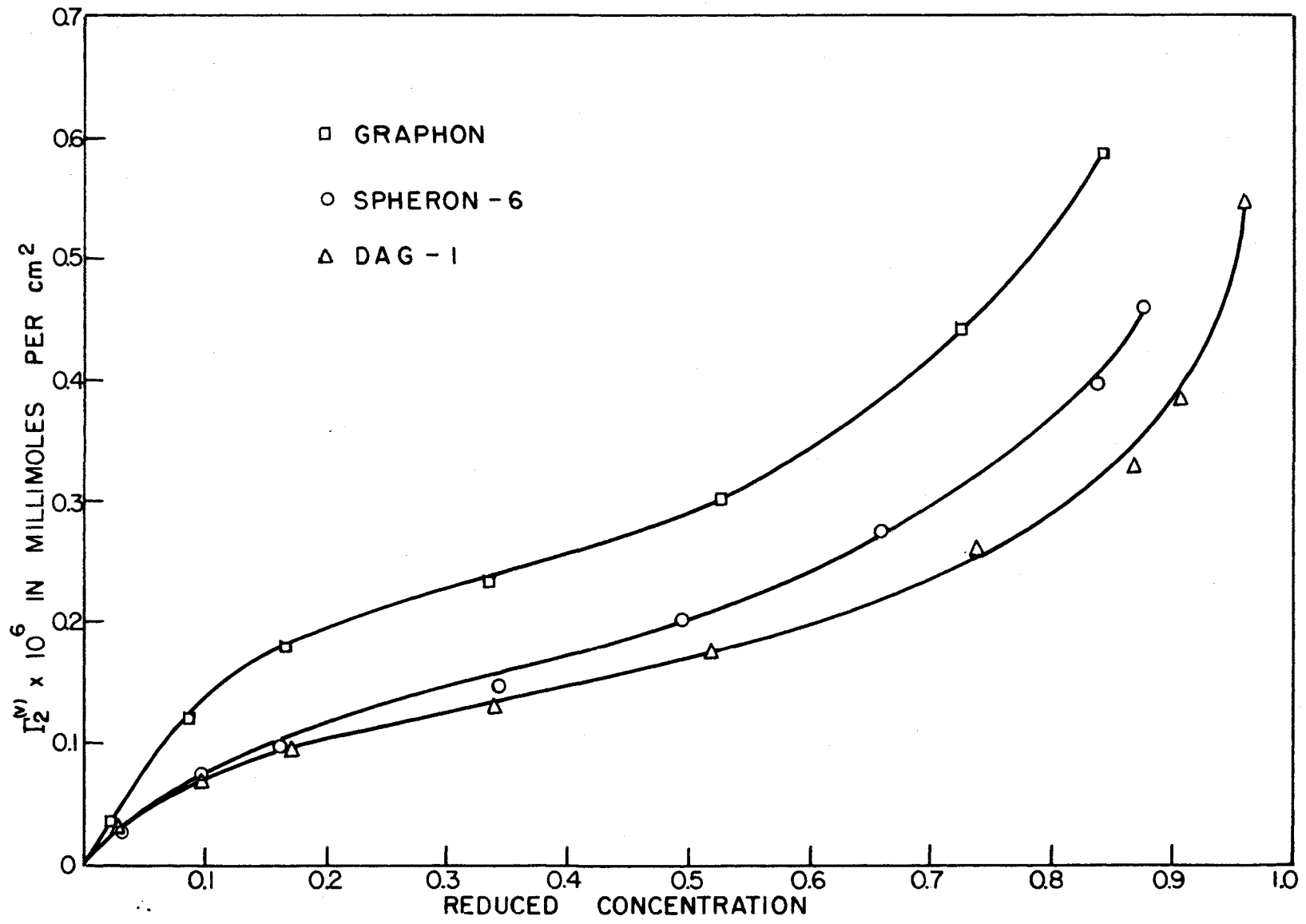


Figure 15. Adsorption of Dodecane from Methanol  
Solution.

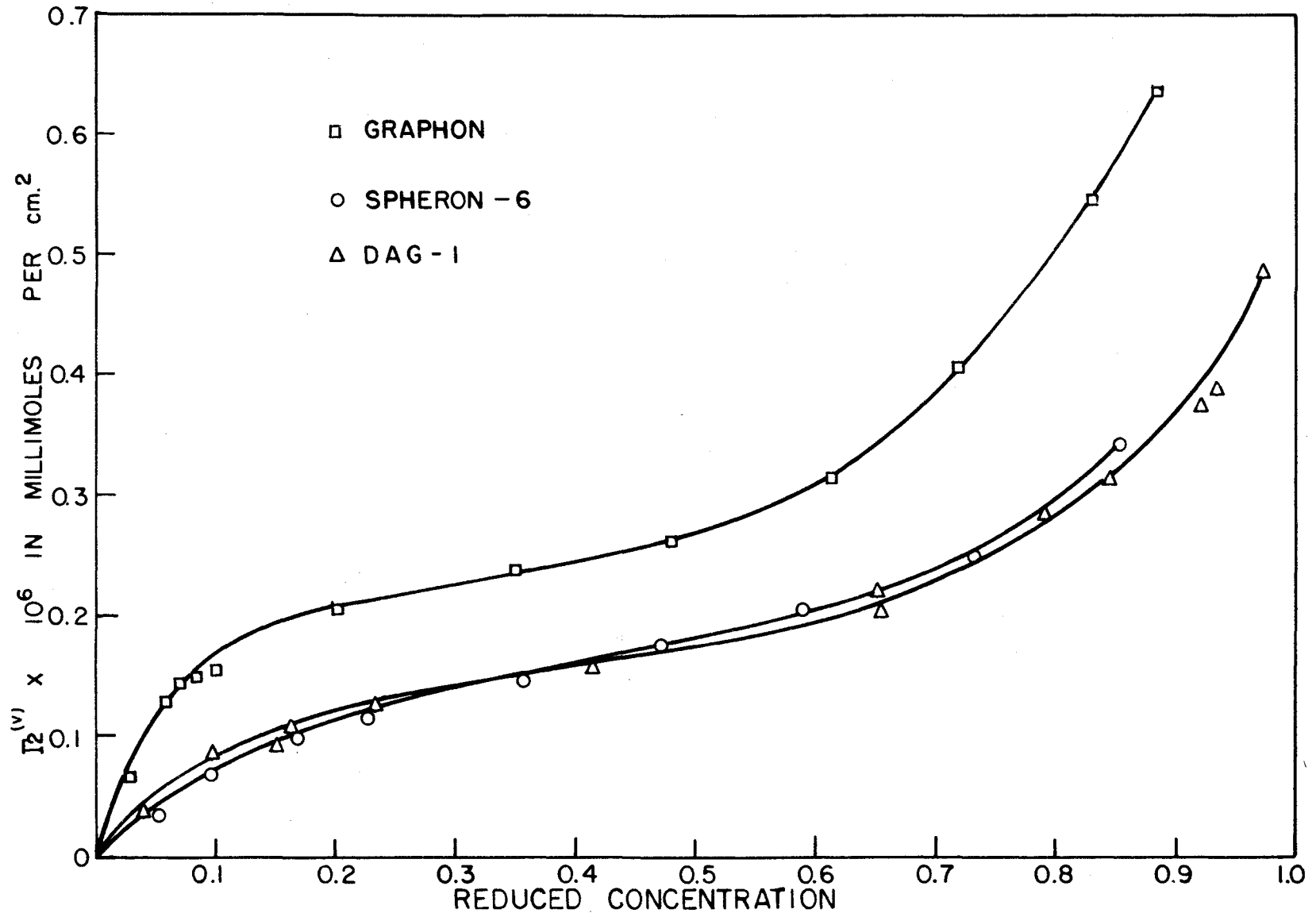
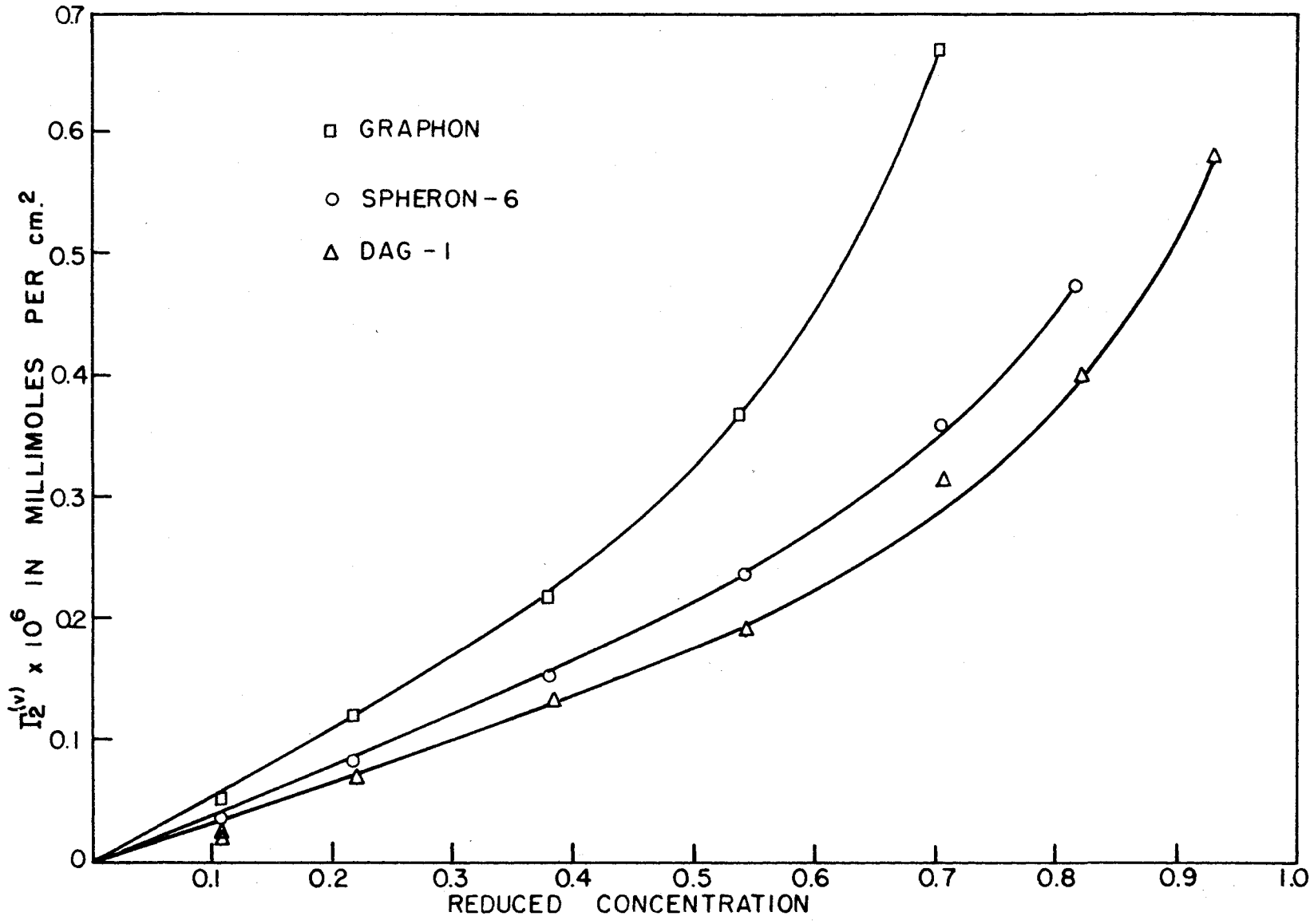


Figure 16. Adsorption of Cyclohexane from Methanol  
Solution.



**Figure 17. Adsorption of Decane from Ethanol Solution.**

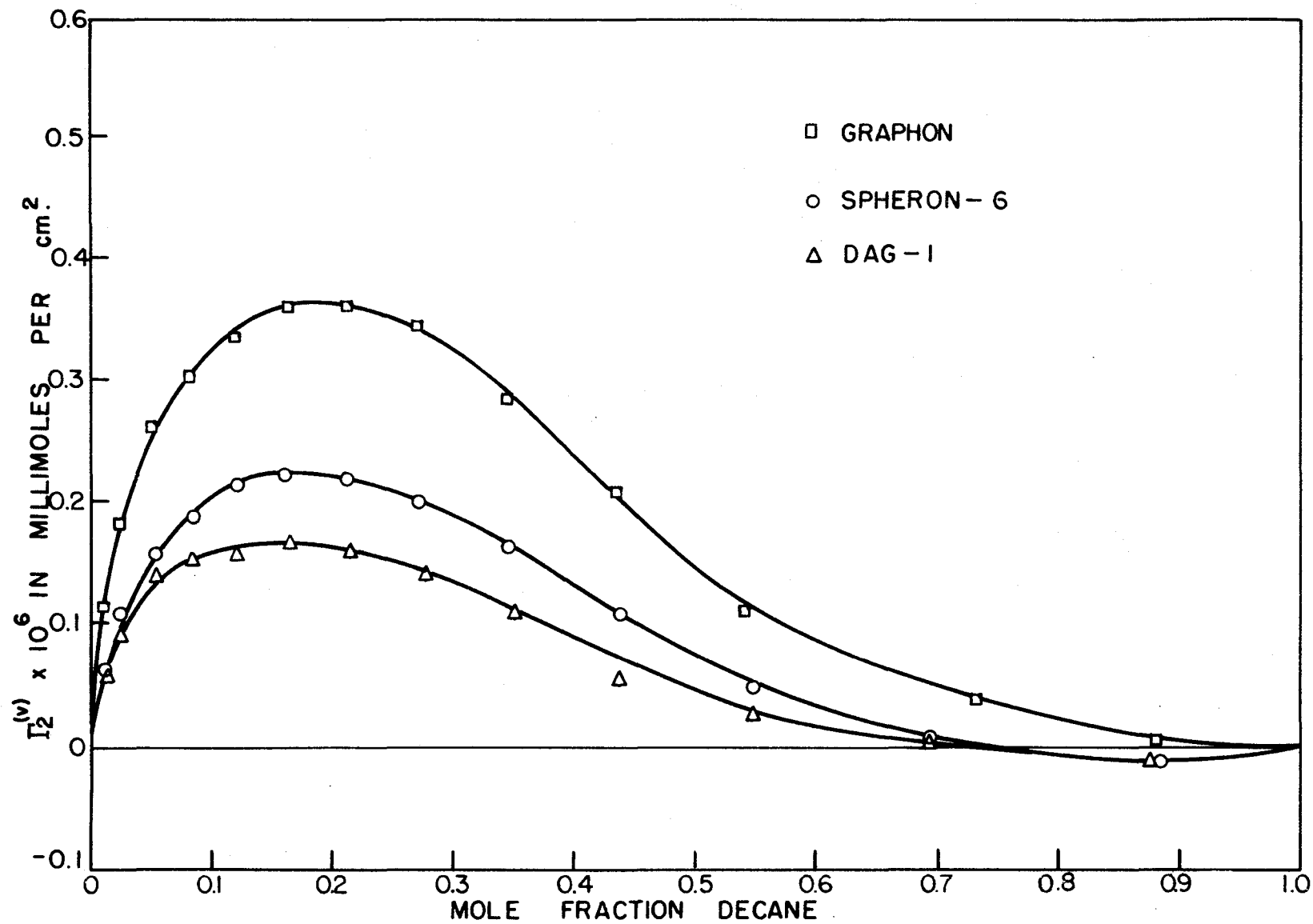


Figure 18. Adsorption of Dodecane from Ethanol  
Solution.



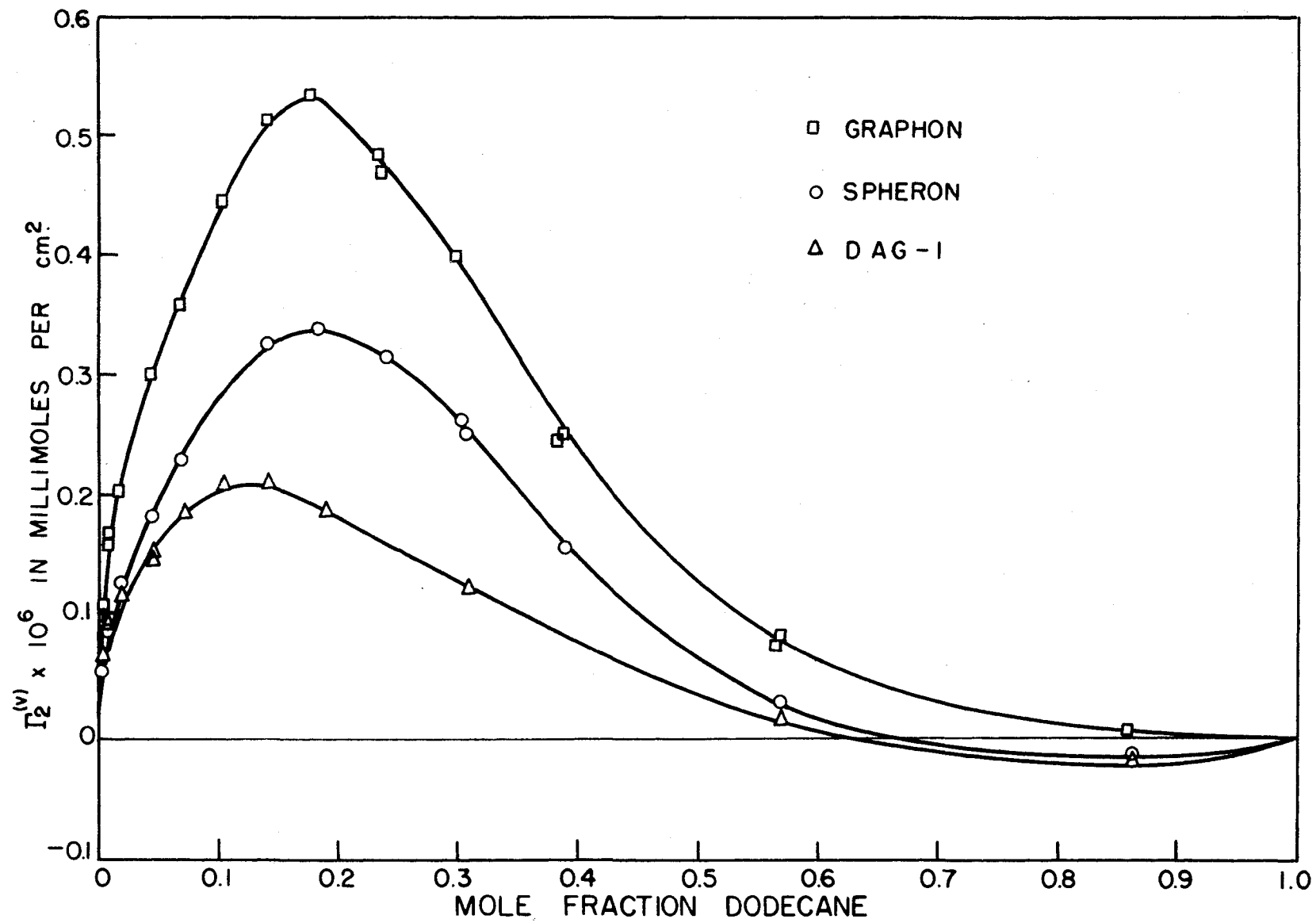
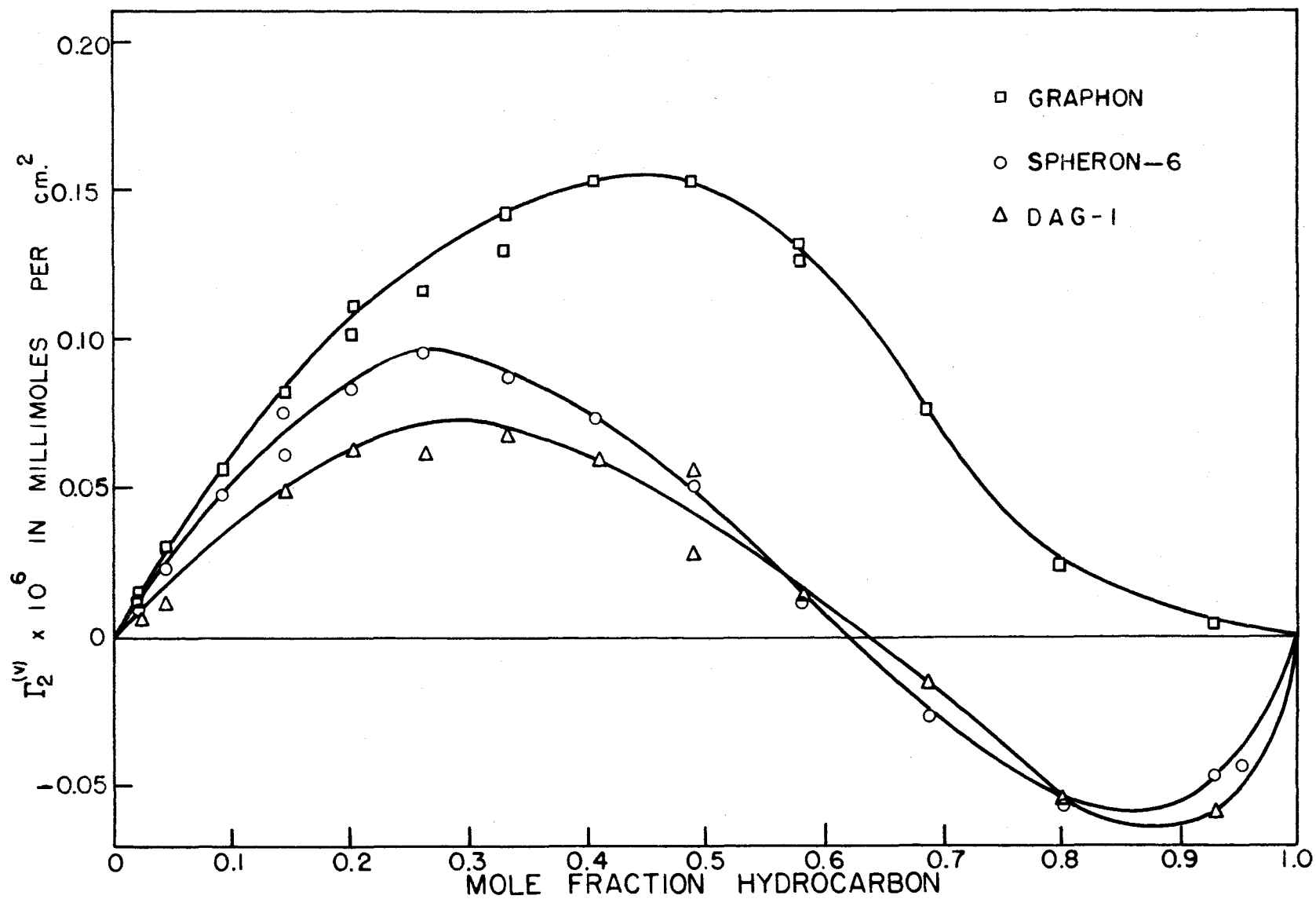


Figure 19. Adsorption of Cyclohexane from Ethanol Solution.



At low reduced concentrations, the adsorption of dodecane is greater on DAG-1, and at low reduced concentrations the adsorption of decane on Spheron-6 and DAG-1 is practically the same. Thus bearing in mind the relative solubilities of the hydrocarbons in methanol, it appears that at low molar concentrations of hydrocarbon the adsorption is greater on DAG-1 than on Spheron-6, but at higher concentrations the reverse is true. Inspection of Figures 13 to 15 also brings out the fact that the ratio of the adsorption on Spheron-6 to that on DAG-1 at a fixed reduced concentration is greater for the system octane-methanol than for the system dodecane-methanol. This variation in the relative adsorptive properties of Spheron-6 and DAG-1 can be explained on the basis of the decrease of the adsorption potentials as the distance from the surface increases. All of the previous observations are reasonable if the adsorption potential between the surface and the solute decreases more rapidly for DAG-1 than for Spheron-6. Thus, at low concentrations the adsorbed molecules are close to the surface, and the adsorption on DAG-1 is slightly greater than the adsorption on Spheron-6. However, at higher concentrations some of the adsorbed molecules are more distant from the surface, and the rapid fall-off of the adsorption potential of DAG-1 leads to lower adsorption on DAG-1 than on Spheron-6.

This difference in the rate of fall-off of the adsorption potentials might be due to several factors. Differences in the crystal structures of the two adsorbents could conceivably lead to different forms for the adsorption potentials. Or, as mentioned previously, if the energy of interaction between two polarizable molecules is integrated over a semi-infinite solid, an adsorption potential of the form  $k_1/Z^3$  is obtained, where Z is the distance from the surface to the molecule. If this same interaction energy is the result of a two-dimensional layer, integration over this two-dimensional layer leads to an adsorption potential of the form  $k_2/Z^4$ . If the adsorption potential for a given adsorbent was a combination of these two potentials, that is, of the form  $k_1/Z^3 + k_2/Z^4$ , and if the potential for another adsorbent was of the form  $k_3/Z^3 + k_4/Z^4$ , it is evident that the rate of fall-off of these two potentials would depend upon the relative magnitudes of the four k's. Potentials of the types described here would explain the difference in the fall-off rates of the adsorption potentials for Spheron-6 and DAG-1.

Examination of the miscible isotherms shown in Figures 17 to 19 shows that the adsorption on Graphon is again greater than the adsorption on either Spheron-6 or DAG-1 at all concentrations. Graphon also shows no preferential adsorption of ethanol. As was previously mentioned, the

fact that preferential adsorption of ethanol is not found with Graphon indicates that the interaction forces between the Graphon surface and ethanol are much weaker than the forces between the Graphon surface and the hydrocarbons. In studies on Spheron-6, Anderson and Emmett (2) found that the surface of Spheron-6 contained certain oxygen complexes. They also found that removal of these oxygen complexes affected the adsorptive properties, the adsorption of water vapor being considerably smaller. A reasonable explanation for the weak adsorption of ethanol on Graphon compared to that on Spheron-6 can be made on the assumption that ethanol is adsorbed on those parts of the surfaces covered by the oxygen complexes. The oxygen complexes known to exist on Spheron-6 are probably partially or completely removed during the high-temperature graphitization process by which Spheron-6 is converted to Graphon. Consistency with this explanation would require that the surface of DAG-1 be partially covered with oxygen complexes of a similar nature. It thus appears that comparison of isotherms obtained with different adsorbents can lead to qualitative information concerning both the adsorption potentials and the chemical nature of the surfaces.

## VII. SUMMARY

The adsorption of cyclohexane, decane, and dodecane from methanol and ethanol solutions, and of octane from methanol solution by the carbon black Spheron-6, the graphitized carbon black Graphon, and the artificial graphite DAG-1 was investigated at 25°C. Solubilities of the hydrocarbon in methanol were determined.

All hydrocarbon-methanol systems were of limited miscibility, and with each adsorbent the isotherms for the adsorption of hydrocarbon were of sigmoid shape, the adsorption of hydrocarbon becoming very large as the concentration of hydrocarbon approached saturation.

At hydrocarbon concentrations sufficiently near saturation, the adsorption of all hydrocarbons from methanol solutions by the adsorbents Spheron-6 and Graphon was demonstrably multimolecular, the amount of hydrocarbon adsorbed exceeding that which could be accommodated in the known surface area of the adsorbents even if minimum molecular cross-sections were assumed. While this criterion did not serve to prove multimolecular adsorption in the case of DAG-1, the similarity of isotherms on this adsorbent to those on adsorbents with which adsorption is demonstrably multimolecular indicates that the adsorption of slightly soluble hydrocarbons from methanol solutions from

DAG-1 is also multimolecular.

In contrast to the adsorption of slightly soluble aliphatic alcohols and aliphatic acids from aqueous solutions by these same adsorbents, the adsorptions of different hydrocarbon homologues from methanol solutions at the same absolute hydrocarbon activity are not the same but vary systematically along the homologous series, the lower homologues being more extensively adsorbed at higher activities.

The theory of adsorption from solution developed by Hansen and Fackler is specialized to slightly soluble systems and an analytical adsorption isotherm derived. The theory herein presented uses a Langmuir mechanism to describe adsorption in the first molecular layer and a van der Waals force law to describe adsorption in higher molecular layers. The adsorption equation derived was found to represent hydrocarbon-methanol experimental data satisfactorily, and the constants showed a physically reasonable variation along the homologous series.

The adsorbent Graphon was found to adsorb all hydrocarbons positively from ethanol solutions over the entire concentration range. The adsorbents Spheron-6 and DAG-1 led to isotherms which inverted at high hydrocarbon concentrations in ethanol, the ethanol being positively adsorbed at very high hydrocarbon concentrations.



It is shown that the adsorption of hydrocarbons from ethanol cannot be interpreted reasonably in terms of the complex theory of Rao, or in terms of a preferred surface structure, but can be interpreted reasonably in terms of surface oxide complexes and differences in fall-off laws for van der Waals forces from infinite films and semi-infinite slabs.

Arguments based on the comparison of isotherms for adsorption of hydrocarbons from methanol and ethanol solutions are presented to show that adsorption of hydrocarbons from ethanol by the adsorbents studied is also multimolecular.

Comparison of the adsorption of hydrocarbons from methanol solution on the different adsorbents showed that the adsorption on Graphon was the greatest at all concentrations. The difference in the adsorption on Spheron-6 and the adsorption on DAG-1 from methanol solution is explained in terms of differences in fall-off laws of the adsorption potentials for these two adsorbents.

The preferential adsorption of ethanol from hydrocarbon-ethanol solutions on the adsorbents Spheron-6 and DAG-1 is explained on the basis of surface complexes which possess specific affinity for alcohol molecules. The absence of preferential adsorption of ethanol on Graphon is the result of the removal of these surface complexes during the graphitization treatment.

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