1952

Adsorption of aliphatic alcohols and acids from binary aqueous solution by non-porous carbons

Roy Phillip Craig
Iowa State College

Recommended Citation

Craig, Roy Phillip, "Adsorption of aliphatic alcohols and acids from binary aqueous solution by non-porous carbons " (1952). *Retrospective Theses and Dissertations*. 13408.
https://lib.dr.iastate.edu/rtd/13408

ADSORPTION OF ALIPHATIC ALCOHOLS AND ACIDS FROM BINARY AQUEOUS SOLUTION BY NON-POROUS CARBONS

BY

Roy Phillip Craig

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

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College
1952

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

ACKNOWLEDGMENTS

The author wishes to thank Mr. F. A. Miller for furnishing activity data for the alcohols, and allowing their presentation here before publication. He also wishes to thank Mr. W. V. Fackler for furnishing surface-area measurements, and Mr. R. D. Hansen for his interest in this work and interesting discussions concerning solution adsorption problems.

It would be difficult to express adequately the author's appreciation to Dr. R. S. Hansen, whose greatness has been demonstrated in numerous respects during the course of this work.

TABLE OF CONTENTS

I. INTRODUCTION

Adsorption from solution, which has been of important practical interest for centuries, has taken a position of increased importance to chemists in recent years. While older applications of adsorption from solution, such as the art of textile dying and decolorization with charcoal, are based purely upon empirical knowledge, theoretical understanding of the adsorption process has become even more strongly desired since the beginning of wide-spread application of chromatography and co-precipitation of trace elements. This understanding is also needed for such phenomena as heterogeneous chemical reactions and crystal growth.

Problems with which one is concerned in this regard relate to the factors which determine or influence the tendency of the solute or solvent to concentrate at the surface of a solid adsorbent. One needs to understand the types of forces which exist at the solid-solution interface, as well as the distance from the surface over which these forces are effective. In spite of voluminous literature published on adsorption (6,002 references have been compiled in the single volume Bibliography of Solid Adsorbents by V. R. Deitz, several pages of which consist of titles of articles concerned specifically with adsorption from solution), present understanding of this process is very unsatisfactory.

Until 1938, nearly all adsorption measurements were explained in terms of one or the other of the two famous adsorption equations, the Freundlich equation and the Langmuir equation. These equations are discussed in detail in any textbook which discusses adsorption, and both are of limited applicability. Since 1938, the adsorption equation of Brunauer, Emmett, and Teller (1), commonly referred to as the BET equation, has come into favor in this field. Originally developed for gas adsorption, and shown by R. S. Hansen (2) to be equally adaptable to adsorption from solutions, this equation allows multi-layer adsorption of the sorbate and can often be fit by experimental data over a fairly wide concentration range; the equation is, however, based upon assumptions which are physically untenable.

The development of a satisfactory general theory of adsorption from solution awaits the availability of experimental data taken under such conditions that the observed effects can be attributed definitely to particular parameters involved. While the present work will not be sufficient for the basis of a general theory, it is hoped that this work will be of value in showing systematic trends in adsorption characteristics upon systematic variation of a single parameter, namely, variation of the chain length of the sorbate molecules, the type of functional group contained in the molecule, or the nature of the carbon surface. In this way, it is hoped that these data, considered in correlation with other experimental work of this type, will indicate the direction which should be followed for the most fruitful development of a general theory of adsorption from solution.

A very large part of the data which have previously been reported in the literature concerning adsorption from solution has been uninterpretable because of incomplete knowledge of the physical nature of the adsorbents used. Since porous adsorbents, such as charcoal, were used in much of this work, the adsorption effected by forces existent at the solid-solution interface was obscured by the concurrent process of capillary condensation in the pores of the adsorbent, due purely to the physical structure of that adsorbent. Since such pores are of various sizes and the surface within these pores constitutes the greater part of the total surface area of the adsorbent, separation of these two effects in measured adsorption data cannot be accomplished satisfactorily. Complications of adsorption data arising from capillary condensation can be eliminated, however, by the use of adsorbents which contain no capillaries, so that all observed adsorption must be due solely to interactions at the solid-solution interface. It is from this consideration that the present study was undertaken with carbon adsorbents which were known to be nonporous in nature.

Even when the physical structure of the adsorbent particles is known, there remains an uncertainty as to the true chemical composition of the outer layer of the adsorbent, since the composition of carbon surfaces is known to vary according to the treatments which the adsorbent has undergone. This layer, rather than a layer of carbon atoms, constitutes the surface which determines the adsorption properties, and knowledge of its nature is of prime importance in understanding the adsorption process. Current studies of the surface complexes on carbon blacks by Anderson and Emmett (3), which include one of the blacks used in the work described below, may help to resolve this difficulty.

A good review of previous contributions in the field of adsorption of non-electrolytes from solution has recently been published by Kipling (4). Other good discussions can be found in the volume Adsorption and Chromatography by H. G. Cassidy (5). These reviews, however, cannot be exhaustive in their coverage of previous work, and some of the more significant contributions will be mentioned here briefly to familiarize the reader with the types of problems encountered in such work and the lines along which workers in this field have endeavored to explain theri results in the most illuminating manner.

In the opinion of this writer the articles by Ostwald and deIzaguirre (6) and Heymann and Boye (7) are outstanding among the earlier works in this field. Ostwald and de Izaguirre showed clearly, as had been suggested earlier by

Williams (8), that both components of a binary liquid mixture of non-electrolytes are adsorbed by solid adsorbents, and pointed out that isotherms resulting from the measurement of changes in concentration of the solute in the solution upon exposure to the adsorbent, which is the usual method of determining the amount of solute adsorbed, are actually composite isotherms resulting from both the adsorption of solute and the adsorption of solvent.

Separation of such a composite isotherm into its two components is a major problem still to be solved, for the two isotherms cannot be directly determined independently. Williams (8) attempted to correct for the adsorption of solvent by carrying out blank experiments in which his charcoal adsorbent was exposed to the saturated vapor of pure solvent until its weight no longer increased. Assuming that the same weight of solvent was adsorbed in all experiments with this particular solvent at the same temperature, he used these data in conjunction with the results of usual adsorption experiments to calculate the amount of solute adsorption. The assumption on which he based his work was not valid, however, for the adsorption of each component is influenced by the presence of the other.

Ostwald and de Izaguirre attempted to separate the isotherms by assuming that each would follow an equation similar to the Freundlich equation. By using a graphical method to evaluate the constants in these two equations, they arrived at individual equations which, when combined, would produce the observed composite isotherm. A similar approach was used by Bartell and Sloan (9), who developed the individual equations to fit their curves by successive approximations. Curves so developed are rather meaningless, however, since by including enough constants to evaluate in the individual equations assumed, any curve could be fit in numerous such ways.

Other attempts to separate the adsorption of solvent and solute include that of Bachmann (10), who immersed his adsorbent in the solution, analyzed the solution in the usual manner, and withdrew the adsorbent, blotted all liquid which was not firmly held off quickly with a blotter, and weighed the adsorbent with the solution it held. From these data, the amount of solute and solvent held by the adsorbent could be calculated separately. As crude as the blotting method was, it was followed by several other investigators in similar work.

A method suggested by J. W. McBain, as reported by Bakr and King (11), involved equilibration of the adsorbent with the solution through the vapor phase, rather than with the pure solvent as Williams had done. From the increase in weight of the carbon and analysis of the residual liquid, the absolute amount of each component adsorbed could be directly determined. The weight of substance held by the adsorbent is much more accurately determined by this procedure than by the method of Bachmann, but one would need to verify experimentally whether or not the adsorbent caused the same change in solution concentration when equilibrated through the vapor phase as when immersed in the solution. Although this procedure would be awkward and time-consuming for the determination of entire isotherms, this now seems the best approach toward resolution of the composite isotherm. Even though the chemical potentials of both components would be identical in the various phases of such a system, the interfacial tension between solution and solid would be quite different from that between vapor and solid, and the effect of this interfacial tension on adsorption is uncertain in the absence of experimental data. Since the adsorption would be such as to minimize the free energy of the entire system, and the summation of interfacial energies may be minimized by a different composition at the solid surface under the two situations here involved, the adsorption from the vapor phase would not necessarily be identical with that from the liquid solution.

Accurate determination of the amount of solute and solvent adsorbed would allow computation of the distance from the solid surface over which so-called adsorption forces are effective. While such calculations are not possible from composite isotherms, under certain conditions the composite isotherms suffice to prove that the forces extend more than a single diameter of the sorbate molecule. Although most adsorption work has been interpreted under the assumption that all adsorbed molecules lie within a distance of one molecular thickness from the solid surface, Brunauer, Emmet, and Teller (1) established the fact of the existence of multimolecular adsorption from gases, and R. S. Hansen (2) demonstrated that such multilayer adsorption also occurs in solution. While multilayer adsorption from solution has been established only for liquids which are not totally miscible, there is indication that multilayer adsorption occurs in miscible systems as well. An argument has been presented by Fu, Hansen, and Bartell (12), based upon activity coefficients which they calculated for adsorbed layers of n-butyric acid on graphite in aqueous solution, which indicates that adsorption may be multimolecular in this case. Their argument is based upon a sharp change observed in a plot of the logarithm of the activity coefficient of the surface layer versus the logarithm of the surface molality.

In cases where multilayer adsorption can be demonstrated, under conditions where no instability toward phase separation exists, the assumption of adsorption forces extending from the surface beyond the first molecular layer is a necessary consequence. Since forces acting at this distance would be small, such forces decreasing exponentially with distance, multilayer adsorption, considered as a phase condensation at the surface, would be expected only when the energy difference between the molecule in solution and the molecule in the condensed phase is small; that is, when the solution is approaching saturation concentration or the solute activity in solution is nearly the same as its activity in the adsorbed phase. In other words, the amount of sorbate adsorbed is a function of the work required to remove the sorbate from solution. Condensation of this type may be effected partly by lateral forces exerted by adsorbing molecules upon each other so that small surface forces suffice to cause such condensation.

In considering forces arising from the solid surface, several approaches have been followed. These are somewhat supplememtary, but are, in general, merely different ways of looking at the same observed phenomena. Adsorption can be considered as the simple reduction of interfacial tension in minimizing the total free energy of the system. It can also be considered as the result of definite attractive forces arising from the outer layers of adsorbent molecules. Included in the latter approach is the well-known Polanyi potential theory (13) of adsorption, in which Polanyi assumed volume increments surrounding the solid surfaces enclosed by surfaces of equal potential such that, for solutions of slightly soluble liquids,

$$Eg = -RT \log \frac{C}{C_o} + E_1 \, V_g/V_1,$$

in which

Eg = the adsorption potential of the solute.
E_1 = the adsorption potential of the solvent.
C = concentration of solute.
C_o = saturation concentration of solute.

V_g= molecular volume of the solute.
V_1= molecular volume of the solvent.

E_g and E_1 are evaluated from adsorption measurements on pure solute and pure solvent vapors. It is seen that the first term on the right side of this equation is the energy required to take a mole of solute from concentration C to either saturation concentration or pure liquid solute. The second term does not occur in gas adsorption, and is included here because Polanyi realized that the solvent also had a positive adsorption potential and solute could be adsorbed only by removing solvent from the space it occupied. The second term, then, accounts for the competitive effect of solvent and solute molecules for the adsorbent surface.

Although Polanyi himself found much fault with his potential theory, this approach has considerable merit, and further fruitful developments may be expected from it. Surfaces of equal potential would not be at a uniform distance from the physical surface for most adsorbents, for certain sites on the adsorbent surfaces are more active than others, as shown by poisoning effects of minute quantities of specific foreign substances on catalysts and by the often observed fact that the first fraction of sorbate adsorbed releases a larger heat of adsorption than later fractions. The adsorption potential surrounding these active sites would be greater than that near other points on the surface, so the volume elements enclosed by the surface of highest equal potential would consist of small elements in the immediate vicinity of the most active sites.

The factor C/C_o, often referred to as the reduced concentration, which appears in the term of the Polanyi equation representing the work required to remove the solute from solution, has considerable significance in determining the adsorption of partially miscible liquids. The reduced concentration can be used as an approximation to the absolute rational activity of the solute in such systems, and insofar as the amount of adsorption is a function of the solute activity, the reduced concentration is a far more significant quantity than absolute concentration to consider in analyzing adsorption data for these systems. The importance of this factor will be emphasized in the experimental work herein described.

A high percentage of early investigations of adsorption from solution were restricted to such narrow concentration ranges of very dilute solutions that such effects as concomitant adsorption of solvent never became apparent. In a few instances in which the investigation was carried over nearly the entire concentration range for miscible systems, it was noted that the complete isotherm was sigmoid in shape, showing positive adsorption of one component at low concentration, then crossing the adsorption axis and indicating negative adsorption of that component in the high concentration range. This type of isotherm was included in Ostwald and de Izaguirre's analysis of composite isotherms (6), and is one of the two types of isotherms from binary liquid solutions discussed by Heymann and Boye (7), the other type showing positive adsorption of one component over the entire concentration range. Bartell and Sheffler (14) observed a regular progression in adsorption through a series of alcohols dissolved in benzene from positive adsorption of methanol on silica adsorbent over the entire concentration range to isotherms more and more sigmoid in shape as the alcohol chain length increased. They also observed a corresponding progression with a carbon adsorbent, although in this case the benzene was preferentially adsorbed over most of the concentration range. The concentrations at which the isotherms cross the concentration axis were observed to vary in a non-uniform manner with the different alcohols. In an earlier paper (9), Bartell and Sloan stated that, for the non-aqueous binary systems with which they worked, the component with the highest adhesion tension against carbon is adsorbed to the greater extent, but the other component is preferentially adsorbed when present at very low concentrations, causing the adsorption curves to be sigmoid in shape. The explanation of the shapes of such complete isotherms rests in a knowledge of the relative adhesion tensions, adsorption affinities, or adsorption potentials of the two components, and a realization that one component must compete with the other for space near the adsorbent surface. This latter consideration was over-looked by Elton in a recent publication (15) in which he presents an argument that, when binary liquid solutions are investigated over the entire concentration range, the composite isotherm must always show some sigmoid character.

Within the last decade much work has been carried out by Russian investigators using series of immiscible alcohols and acids in aqueous solutions as sorbate to determine the differences and trends observed, as is intended in part for the experimental work described in this thesis. The Russian work now published has nearly all been performed with charcoals as adsorbent, however, and the effect of capillary condensation far over-shadowed any other effects. Kiselev and Shcherbakova (16) reported that in the adsorption of alcohols and acids ranging from four to seven carbon atoms in chain length, adsorption at low concentrations increased with increased molecular weight, apparently being controlled by contending forces acting on the adsorbate; at higher concentrations, however, a constant maximum adsorption was obtained for each solute of such magnitude that the volume adsorbed was constant for all solutes. Dzhigit and co-workers (17) found similar constant limiting volumes for the alcohols butanol through heptanol on six different charcoals, again indicating that the micropores of the charcoals are equally accessible to the different alcohols and are densely filled by the alcohol molecules at the limiting adsorption. Similar results were reported for the acids (18).

At the risk of giving insufficient credit for a large amount of excellent experimental work, it may be said that the original contributions claimed by the Russian workers in this field are generally identical with ideas or approaches which can be found in earlier American and European journals. Kiselev (19) claimed the discovery of capillary condensations of partially-miscible liquids in adsorbent pores as late as 1947. His recognition of the fact that the measured surface excess is not identical with the total amount of adsorbed component at the surface of the adsorbent, and method (19) of correcting the measured excesses for the amount of material which would have been present in the adsorption volume even if no adsorption had occurred, is identical with the method used in 1931 by Wynne-Jones (21). The method of Wynne-Jones and Kiselev gives the total amount present in the surface layer as

$$U = \Gamma + kC$$

where Γ is the measured surface excess, C is the sorbate concentration in solution, and k the thickness of the adsorbed layer. No independent method of determining k is given, and the treatments of both authors reduce to the assumption of a monomolecular thickness for this value.

The above statements are not meant to belittle the work of Russian scientists in this field, for much significant and interesting work is now being performed in their laboratories. It is indeed unfortunate that the results of this work are not more readily available to other workers in this field.

II. OBJECTIVES

While the long-range objective of the investigations herein described is to assist in the development of a satisfactory general theory of adsorption from solution, the immediate objectives were considerably less broad in scope. The research undertaken involved the determination of adsorption isotherms for the normal aliphatic alcohols and the fatty acids of chain lengths from two to seven carbon atoms, inclusive, from aqueous solution, these isotherms being determined over the entire concentration ranges as nearly as possible, using three different non-porous carbon adsorbents with each system. The compilation of data from these investigations was to be used in the pursuit of the following immediate objectives:

To determine, in the absence of the capillary condensation which has confused a large part of previous experimental data of this type, the adsorption which can be attributed directly to interactions at the solid-solution interface, rather than to any structural features of the adsorbent.

To show that the amount of adsorption is dependent not only upon forces existent at the solid surface but also on the work required to remove a molecule of the sorbate from solution, that is, on the activity of the sorbate in solution, and to determine to what extent this adsorption is a function of the activity of the adsorbed component.

To determine the effect of chain length on adsorption of members of a particular homologous series, and to examine this effect to see if a particular orientation of the adsorbed molecules can be inferred therefrom.

To compare the adsorptions of normal acids and normal alcohols and to determine the effect of variation of the functional group of the adsorbed molecule.

To examine the complete isotherms of the miscible systems for sigmoid character and, if the curves should cross the adsorption axis, to determine whether such behavior may be attributed to the establishment of a preferred molecular structure, involving both solute and solvent, at the solid surface, or whether it may be attributed to the existence of certain areas on the surface which possess quite different adsorptive properties from the remainder of the solid surface.

To compare the adsorptions on the different solid adsorbents and determine the effect of graphitization in changing the adsorptive properties of carbon blacks.

To determine whether the adsorption is multimolecular in nature.

To examine all data comparatively to see if a treatment can be developed by which these data can be made to indicate the thickness of the adsorbed layers, the magnitude of forces existing beyond the first molecular layer, or the nature of the adsorption potential as a function of distance from solid surface.

And, finally, to estimate the rate at which the adsorption takes place.

III. MATERIALS AND APPARATUS

A. Adsorbents

In order to eliminate uncertainties in interpretation of subsequent adsorption data which might arise from capillary condensation, non-porous carbon blacks were chosen for this work. Three such blacks were selected, their surfaces having been shown to be non-porous by the agreement of surface areas determined by low-temperature nitrogen adsorption with areas determined microscopically. The particular adsorbents used were selected also because other investigators have carried out adsorption measurements with them and, consequently, there is a greater chance that the results of this work can be correlated profitably with the work of other investigators.

When received for this work, a sample of each adsorbent had been leached with hydrochloric acid, and the filtered acid shown to be free of iron. This had been done by Mr. W. V. Fackler, who had also treated each bulk adsorbent by heating it to 1000° C. in vacuum for 24 hours, and storing it in a Mason jar. At least one year elapsed between this treatment and use of the adsorbents in this work, with occasional exposures of the adsorbents to the atmosphere as small samples were removed from the jars. To check if these exposures altered the adsorptive properties, adsorption measurements were made with aqueous n-butanol solutions on samples of the adsorbent which received no further treatment and samples heated in vacuum to about 200° C. and cooled, still under vacuum, immediately before exposure to the solutions. The amount of butanol adsorbed was identical in the two cases, and the adsorbents were subsequently used directly from the storage jars for most of the work herein described; however, under certain conditions, alterations of the adsorbent surfaces from atmospheric exposure did have significant effect upon subsequent adsorption measurements. These effects will be described in detail below, after examination of experimental results. A description of the original adsorbents follows:

1. Spheron-6

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

2. DAG-1

   A deflocculated Acheson graphite, with a surface area of 102.4 square meters per gram.

3. Graphon

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

The surface aresa of these adsorbents were determined by W. V. Fackler, Jr. and S. D. Christian, using the low-temperature nitrogen adsorption method of Brunauer, Emmett, and Teller (1).

During measurements of adsorption of fatty acids from extremely dilute aqueous solutions, after most of the other experimental work with these adsorbents had been completed, it was noted that the adsorption isotherms for Graphon actually did not extrapolate to zero adsorption as the concentration of acid approached zero, but, at extreme dilution, indicated negative adsorption of the acid. This anomaly occurred only with Graphon, and was traced to the leaching of some material with a refractive index higher than that of water from the Graphon surface. Two tenths of a gram of Graphon shaken for 24 hours with five milliliters of water increased the refractive index of the water about 6×10^{-6} units. A similar test with pure propanol showed no change in refractive index of the propanol. It is apparent, therefore, that either the material which leached into the water is not removed from the surface by the propanol, perhaps because of insolubility in alcohols, or else the material has a refractive index similar to that of propanol, so that its presence in propanol in small amounts is not detected interferometrically. Kinetic measurements which had been made with dilute valeric acid showed this leaching of material from the Graphon surface into aqueous solutions to be a much slower process than the process of adsorption of the valeric acid, as will be seen from data presented below with discussion of the rate of adsorption. All measurements of adsorption from aqueous solutions on Graphon were corrected to account for the effect of the material leached from the Graphon surface.

B. Solution Components

1. Water

All water was redistilled from alkaline permanganate solutions.

2. Alcohols

Ethanol, commercial grade absolute, was purified by the method of Lund and Bjerrum (22). The final product was constant boiling within 0.02 degrees, boiling at 78.08° C. under a pressure of 745.4 mm. of Hg, or 78.63° C. corrected to 760 mm.

Propanol-1, chemically pure, obtained from Columbia Organic Chemicals Company, Columbia, South Carolina, was redistilled. A constant-boiling middle fraction, three-fifths of the total liquid, was retained for use. The boiling point was 97.4° C. at 753.3 mm. Hg or 97.6° C. corrected to 760 mm.

Butanol-1, commercial grade, contained a small amount of water-insoluble material, probably dibutyl ether, after distillation. This alcohol was purified by a tedious process of extracting into water, heating to separate the butanol phase, drying chemically, and distilling. The final product boiled at 117.54° C. at 741.0 mm. Hg. Corrected to 760 mm. Hg, the boiling range was 118.29 ± .01° C.

Pentanol-1, Eastman Kodak white label grade, was purified by distillation. The central fraction, boiling at 137.68° C. under 739.4 mm. Hg pressure, was retained.

Hexanol-1, Eastman practical grade, was redistilled twice, the second time over Mg. metal, in an effort to reduce the boiling range. The final boiling point varied from 156.48 to 156.60 at 738.0 mm. Hg. A second batch of hexanol-1 was purified for measurements of the adsorption of water from the hexanol phase; for this, Matheson practical grade material was distilled, and the central fraction, boiling from 156.5° C. to 156.7° C. at 735.1 mm. Hg, was retained for use.

Heptanol-1, Eastman white label, was distilled. The thermometer readings each carried uncertainties of ± 0.05° due to rapid fluctuations over this range. The central fraction which was retained was collected between readings of 175.50° C. at 734.0 mm. Hg and 175.75 at 741.0 mm. Hg. Thus the boiling point, corrected to 760 mm. Hg, was constant within reading errors at 176.57 ± .05° C.

3. Aliphatic Acids

All aliphatic acids used in this work were purified by redistillation. The starting materials and final products were as follows:

Acetic acid, commercial grade. The central fraction, retained for use, boiled from 117.0° C. at 738 mm. Hg to 117.4° C. at 739.5 mm. Hg.

Propionic acid, Eastman white label. The central fraction boiled from 140.60° C. at 738.4 mm. Hg to 140.70° C. at 739.0 mm. Hg.

n-Butyric acid, Eastman white label. The central fraction, retained for use, boiled from 162.7° C. at 735.6 mm. Hg. to 162.9° C. at 734.6 mm. Hg.

n-Valeric acid, Eastman white label. The central fraction boiled from 183.7° C. at 717 mm. Hg to 185.48° C. at 743.6 mm. Hg. Converted to the same pressures this represents a boiling range of 0.3° C.

n-Caproic acid, Eastman practical grade. A fraction boiling from 202° to 204° C. at 745 mm. Hg was retained for use.

n-Heptylic acid, Eastman white label. The boiling point of the central fraction, which was retained for use, varied from 221.74 ± .05° C. at 732.7 mm. Hg to 222.04 ± .05° C. at 734.0 mm. Hg.

Distillations of alcohols and fatty acids were performed using a thirty-plate Oldershaw distilling column, and a reflux ratio of 10:1 for all except heptanol-1, caproic acid, and heptylic acid, in which cases a ratio of 20:1 was used.

C. Equipment

1. Distilling column

A thirty-plate, vacuum-jacketed, D-1 Oldershaw distilling column, with liquid-dividing still head, was used for purification of the organic liquids. The performance of this column has been studied and reported in detail by Colins and Lantz (23).

2. Adsorption cells

Adsorption cells were made from 19/38 standard-taper joints, with annular wells around the middle of the taper to provide for mercury seals. The capacity of these cells was about 15 milliliters.

3. Shaking device

Shaking of filled adsorption cells was done by a mechanical shaker in an air-thermostated box, the shaker motor being mounted outside the box to allow maintainance of a more uniform temperature within the box. The air-thermostated box was maintained at a temperature of 25.0 ± 0.1° C.

4. Interferometer

A Hilger Rayleigh-type interference refractometer was used for this work, with both one-centimeter and four-centimeter liquid cells made of fuzed quartz. The interferometer was surrounded by an air-thermostated box, the temperature of which was controlled by a Precision Scientific Company "Merc-to-Merc" thermoregulator to 25.0° ± .1° C. The cells were covered with special covers carved from Teflon, with provisions made for forming a mercury seal around the tops of the cells.

IV. METHOD OF PROCEDURE

A. Preparation of Solutions

Standard solutions were prepared at 25° C. All molar concentrations used in this work refer to moles per liter at 25° C.

The number of standard solutions of varying concentrations required in order to construct an interferometer calibration curve for a single system varied greatly with different systems. While six or eight solutions were sufficient for some systems of low miscibility, those which are miscible in all proportions required several times this number of standard solutions for calibration purposes. Since only small refractive index differences can be measured on the interferometer, solutions of miscible liquids were prepared in pairs with concentrations sufficiently close to permit interferometric measurement of their difference, and the pairs prepared at such concentrations as to cover the entire concentration range.

Standard solutions used for calibration of the interferometer were also used in the subsequent adsorption experiments, since more than a number of solutions sufficient for the entire isotherm were generally thus already available.

Each individual standard solution was prepared by both weight and volume for the aqueous systems of ethanol, propanol, acetic acid, propionic acid, butyric acid, and valeric acid, and for the organic-predominating systems of water in butanol, pentanol, hexanol, valeric acid, and caproic acid. The other aqueous solutions were prepared by dilution of a nearly-saturated standard solution; those of butanol, hexanol, and heptanol having been prepared by both weight and volume, and those of caproic acid and heptylic acid prepared by volume only. Since the solubilities of heptanol and heptanoic acid in water are extremely low, the original standard solution in each of these cases was prepared by weighing, on a sensitive balance, the amount of alcohol or acid removed from a small hypodermic syringe, from which the liquid had been transferred easily without loss into a tared one-liter volumetric flask for dilution to volume. Weighing of small differences between large weights was thus avoided, and accuracy increased.

B. Calibration of the Interferometer

The sensitivity of the interferometric method of analysis depends not only upon the system under investigation, but also upon the concentrations of the components. The relative sensitivities for different systems and different concentrations are indicated in a later section. Standard solutions for use in interferometer calibrations, prepared as indicated in the preceding paragraph and stored in glass-stoppered volumetric flasks, were transferred into the interferometer cells with a hypodermic syringe to prevent any slight changes in concentration due to evaporation during transfer. The mercury-sealed Teflon cell covers, which have been described above, had a needle-sized hole over each cell cup, through which the cup could be filled from the hypodermic syringe. This hole was plugged with a tiny Teflon plug after the cell was filled, and then sealed with a drop of mercury. One-centimeter cells were used in all calibrations, in order that solutions of maximum difference in concentration could be compared and a complete calibration curve could be constructed from a reasonable number of standard solutions. Pairs of standard solutions were compared in the interferometer, and the ratios of the interferometer readings in scale divisions to the concentration differences of the compared solutions were plotted against the average concentrations of these solutions. These plots were used as the calibration curves, from which interferometer measurements could be converted directly into concentration differences at any known concentration.

C. General Procedure for Adsorption Measurements

The usual procedure followed in making adsorption measurements was to weigh a group of adsorbent samples into adsorption cells, pipette a definite volume of each of a series of adsorbate solutions of known concentrations into the cells, seal the cells with a mercury seal, and place them in the mechanical shaker. After about twenty-four hours of shaking at constant temperature (25.0 ± 0.1°C.), the adsorbent was centrifuged from the solution, and the supernatant liquid drawn from the cell with a capillary syringe, from which it was either transferred directly into an interferometer cell for comparison with another sample of the same solution initially pipetted into the adsorption cell, or stored in a 5 ml. or 10 ml. glass-stoppered flask until such an interferometric comparison could be made. In a few instances, when the final adsorbate concentration was extremely low, greater accuracy in analysis could be achieved by comparing this final solution with pure water rather than with the initial solution, and this was done in such cases.

Since the interferometer reading gave, by use of the calibration curve for the system under investigation, the difference in concentration between the original solution and the same solution after exposure to the adsorbent, the amount of either component adsorbed, as surface excess of that component, was thus determined directly. If the slope of the calibration curve at the concentration concerned was great enough to give significantly different values at the initial and the final solution concentrations, a second approximation was made on this curve after the change in concentration was roughly determined, so the calibration value corresponding to the true mean concentration of the solutions being compared was used in the final calculation of the amount of adsorption.

The time interval of twenty-four hours for shaking the solution with adsorbent was selected arbitrarily after a preliminary test with aqueous butanol solution showed the same amount of butanol adsorption after seven hours of contact as after nineteen hours of contact with the adsorbent. It was assumed from this test that equilibrium between adsorbent and adsorbate was established in less than seven hours, and a twenty-four hour shaking period would be adequate to insure the establishment of such equilibrium. A more complete study of the rate of attainment of adsorption equilibrium in these systems was made later. The results are shown in detail below. This study showed that a period of twenty-four hours was more than sufficient for equilibrium attainment.

The amount of adsorbent used in each sample was generally 0.200 or 0.400 gram. In a few cases, in which this amount of adsorbent would deplete the solution of adsorbate almost completely, lesser amounts of adsorbent were used, the minimum being 0.050 gram. Either 5.00 ml. or 10.00 ml. of solution was used, 10.00 ml. generally being used with 0.400 gram adsorbent samples. Determinations were made in groups of about twelve, since twelve adsorption cells could conveniently be placed in the shaker at one time.

The results of these measurements, the adsorption isotherms, were plotted as $V\Delta C/m$ versus the activity of the solution; where V is the volume of solution used, m the mass of adsorbent, and ΔC the measured change in concentration of the solution upon exposure to the adsorbent. Abscissa values were expressed in millimoles per gram of adsorbent, and may be divided by the specific surface area of the adsorbent to obtain the $\Gamma_2^{(V)}$ surface excesses of Guggenheim and Adam (24). For slightly-miscible systems, reduced concentrations were used as ordinates in lieu of activity values; reduced concentrations being the actual concentration of solute divided by its concentration in a saturated solution.

A modification of the usual adsorption procedure was employed with aqueous solutions of n-heptanol and heptylic acid. The solubility of these substances in water is so low that use of the usual ratio of adsorbent to solution volume would remove nearly all the solute even from nearly saturated solutions, and it would be impossible in this manner to get measurements at equilibrium concentrations approaching saturation concentration. One is, therefore, faced with the choice of using either very small amounts of adsorbent or large quantities of solution. The first alternative would be entirely unsatisfactory because of possibilities of inhomogeneity of the adsorbent; the latter would give satisfactory accuracy, but would require the preparation of greater quantities of standard solutions of varying concentrations, as well as the use of a different type of adsorption cell and other procedure modifications, since the larger quantities of liquid could not be centrifuged in the equipment that was available.

A third approach to this problem would be to add fresh portions of nearly-saturated solution to adsorbent samples which already held a known amount of adsorbate from previous equilibrations. This third approach was used in this work, each portion of equilibrated solution being withdrawn, after thorough centrifugation, and its concentration determined interferometrically. The amount of solution withdrawn each time was nearly as large as the original portion introduced, and was determined to the nearest 0.01 ml. by weighing the liquid removed. Knowing the volumes and concentrations of the portions introduced and removed, the amount of sorbate retained by the adsorbent at each step in the procedure could readily be calculated. Such calculations are straightforward, and will not be discussed here. By this technique, it was possible to build up the amount of sorbate on the adsorbent samples to such a degree that the final equilibrium concentrations approached the saturation concentrations close enough to show the character of the isotherms over the complete solubility range. An advantage of this technique is that numerous points of the isotherm can be obtained from a single standard solution and a single sample of adsorbent.

Since any error in this procedure is carried through all subsequent points, the results were checked by using several different adsorbent samples and solutions of such initial concentrations that equilibrium concentrations with different adsorbent samples overlapped each other. No more than five points were taken with any particular sample of adsorbent.

Another modification in the usual procedure, used when it appeared necessary, consisted of evacuation of the adsorbent samples immediately before exposure to the solutions. The adsorption tubes, containing the adsorbent samples, were pumped down to a pressure of less than one micron of mercury, and heated in a sand bath at 115° C. to 210° C. for four hours. Each tube was held at a temperature of at least 180° C. for a minimum of one-half hour during this period. Dry air was admitted to the tubes, and the desired solutions pipetted into them immediately. The special conditions under which this evacuation was found necessary will be considered later in a discussion of the effects of such treatment on adsorption measurements.

V. EXPERIMENTAL RESULTS

A. Adsorption of Normal Alcohols and Aliphatic Acids from Aqueous Solutions

Results of measurements of adsorption of the normal alcohols and fatty acids from aqueous solutions are collected and presented in Tables 1A through 12C. The data for the alcohols are given in Tables 1 to 6; those for the acids in Tables 7 to 12. The letters included with table numbers indicate the different adsorbents used with each binary system, Tables 1A, 1B, and 1C, for instance, giving the data for the water-ethanol system on Spheron-6, Graphon, and DAG-1 respectively.

In these tables, C is the concentration of organic component in moles per liter of solution at 25° C., C_0 is the concentration of a saturated solution at 25° C., A is the absolute rational activity of the organic component, and V is the volume in milliliters of solution which was equilibrated with m grams of adsorbent. $V\Delta C/m$ values are, therefore, surface excesses of organic component per gram of adsorbent, these surface excesses being of the $\Gamma_2^{(V)}$ convention type of Guggenheim and Adam (24).

Analytical uncertainties indicated in these tables are based upon one scale division of the interferometer scale in cases where one-centimeter cells were used, since this is the range of variation in successive interferometer readings on the same solutions. This amount of uncertainity in the interferometer reading produced widely varying uncertainties in surface excesses, as is readily seen in the Tables. The magnitudes of the uncertainties were, of course, determined by the shapes of the calibration curves for the different systems.

Activity values shown in Tables 1A to 2C were taken from unpublished data of F. A. Miller, and were obtained by Miller's technique of condensing and analyzing the vapors which were in equilibrium with binary solutions of known composition.

No satisfactory activity data are yet available in the literature for aqueous solutions of the miscible acids. The values given in Tables 7 to 9C are considered the best available at this time. These values arise from cryoscopic data of either Giacalone, Accascina, and Carnesi (25) or Jones and Bury (26), and are strictly applicable only at the melting points of the solutions. While the activity values for acetic acid and propionic acid, as shown in Tables 7 and 8, respectively, were taken directly from the results published by Giacalone and his co-workers, the activity coefficients published by these workers for butyric acid lead to activity values which are thermodynamically impossible, since some values at relatively high concentration were lower than activity values at a lower concentration. The freezing point depressions measured by Giacalone for butyric acid solutions of very low concentration, however, agree quite well with those measured by Jones and Bury (26) at corresponding concentrations. On the basis of this agreement, the lowest concentration results from Giacalone's work were used in comparison with Jones and Bury's molal activity coefficients to establish the factor for converting all the molal activities of Jones and Bury into rational activities, since the data of these workers appear, on the whole, considerably more reliable than those of Giacalone. The activity values for butyric acid solutions given in Tables 9A, 9B, and 9C were obtained in this manner.

Table 1A

Adsorption of Ethanol from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.168	.0031	.0103	0.067 ± .020[a]
0.382	.0071	.0232	0.117 ± .008
0.718	.0133	.0434	0.166 ± .008
1.681	.0324	.107	0.295 ± .008
3.376	.0693	.216	0.397 ± .007
5.089	.1123	.316	0.342 ± .007
6.784	.1618	.397	0.280 ± .005
8.476	.2218	.460	0.203 ± .012
10.17	.2963	.510	0.123 ± .018
11.98	.398	.560	-0.043 ± .032
13.65	.523	.626	-0.2 ± .15
15.885	.781	.793	-0.070 ± .041[b]
16.484	.884	.885	-0.011 ± .022[b]
16.786	.944	.944	-0.035 ± .015[b]
16.896	.969	.969	-0.005 ± .012[b]

[*] Activity data is that of F. A. Miller of this Laboratory, as yet unpublished.

[a] Uncertainty indicated is the uncertainty in analysis.

[b] Adsorbent sample evacuated at 150-200°C for four hours immediately before use. Non-evacuated samples gave positive $\frac{V\Delta C}{m}$ values at concentrations greater than 15.4 moles per liter $\left(\frac{V\Delta C}{m} = .05 \pm .013 \text{ at } 16.06 \text{ moles/l.}\right)$.

Table 1B

Adsorption of Ethanol from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.169	.0031	.0103	0.048 ± .021[a]
0.384	.0071	.0232	0.081 ± .010
0.716	.0133	.0434	0.183 ± .010
1.681	.0324	.107	0.299 ± .010
3.378	.0694	.216	0.345 ± .010
3.848	.0805	.243	0.394 ± .016
6.777	.1612	.396	0.39; 0.42 ± .012
7.847	.1976	.437	0.324 ± .027
8.471	.2217	.460	0.290 ± .015
10.17	.2963	.510	0.301 ± .020
10.697	.322	.523	0.238 ± .048
11.97	.398	.560	0.265 ± .038
15.882	.780	.792	0.059 ± .041
16.484	.884	.885	-0.013 ± .022
16.784	.944	.944	0.030 ± .015

*Activity data is that of F. A. Miller.

[a] Uncertainty indicated is the uncertainty in analysis.

Table 1C

Adsorption of Ethanol from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	A[*]	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.168	.0031	.0103	0.051 ± .020[a]
0.384	.0071	.0232	0.072 ± .010
0.717	.0133	.0434	0.170 ± .008
1.681	.0324	.107	0.291 ± .008
3.378	.0694	.216	0.369 ± .006
5.086	.1122	.316	0.398 ± .005
6.778	.1612	.396	0.38; 0.40 ± .010
8.469	.2217	.460	0.338 ± .013
10.17	.2963	.510	0.236 ± .018
11.97	.398	.560	0.156 ± .030
13.65	.523	.626	0.00 ± .100
15.37	.706	.738	-0.021 ± .023
16.484	.884	.885	0.00 ± .022
16.785	.944	.944	-0.018 ± .015

[*] Activity data is that of F. A. Miller.

[a] Uncertainty indicated is the uncertainty in analysis.

Table 2A

Adsorption of Propanol-1 from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.191	.0038	.038	0.192 ± .006[a]
0.385	.0077	.077	0.327 ± .006
0.780	.0162	.162	0.419 ± .006
1.971	.0415	.392	0.520 ± .005
3.960	.0910	.548	0.484 ± .006
6.639	.187	.608	0.299 ± .008
9.481	.358	.641	-0.075 ± .008
9.922	.400	.654	-0.083 ± .014[b]
10.86	.496	.690	-0.08 ± .02
			-0.154 ± .02[b]
11.34	.561	.719	-0.188 ± .018
11.88	.646	.758	-0.18 ± .022[b]
12.01	.668	.770	-0.150 ± .024
12.63	.796	.854	-0.131 ± .06[b]
12.65	.800	.857	-0.190 ± .04
12.99	.891	.921	-0.125 ± .03[b]

*Activity data of F. A. Miller of this Laboratory, as yet unpublished.

[a] Uncertainty indicated is the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use.

Table 2B

Adsorption of Propanol-1 from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.130	.0026	.026	0.136 ± .006[a]
0.189	.0038	.038	0.249 ± .006
0.383	.0077	.077	0.368 ± .006
0.780	.0162	.162	0.419 ± .006
1.974	.0415	.392	0.439 ± .006
3.962	.0910	.548	0.443 ± .006
6.640	.187	.608	0.278 ± .008
9.472	.358	.641	0.142 ± .01
10.84	.494	.690	0.065 ± .01[b]
12.62	.794	.852	-0.010 ± .03[b]
12.98	.888	.920	0.044 ± .06[b]

*Activity data of F. A. Miller.

[a] Uncertainty indicated is the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use.

Table 2C

Adsorption of Propanol-1 from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.192	.0038	.038	0.169 ± .006[a]
0.389	.0078	.078	0.289 ± .006
0.782	.0162	.162	0.359 ± .006
1.974	.0415	.392	0.446 ± .006
3.961	.0910	.548	0.473 ± .006
6.640	.187	.608	0.279 ± .008
9.474	.359	.641	0.096 ± .010
10.85	.495	.690	0.046 ± .010[b]
11.87	.644	.757	0.010 ± .011[b]
12.62	.794	.852	0.013 ± .03[b]
12.98	.888	.920	0.06 ± .06[b]

*Activity data of F. A. Miller.

[a] Uncertainty indicated is the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use.

Table 3A

Adsorption of Butanol-1 from Aqueous Solution on Spheron-6

C(moles/1.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0212	0.00040	0.0215	0.096
.0428	.00081	.0435	.177
.0889	.0017	.0903	.278
.1845	.0035	.187	.388
.381	.0072	.387	.477
.578	.0109	.587	.554
.775	.0146	.787	.635
.871	.0164	.884	.723
.926	.0174	.940	.908

*Analytical uncertainty in $V\Delta C/m$ is 0.004 millimoles per gram over the entire concentration range.

Table 3B

Adsorption of Butanol-1 from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/Co	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0215	0.00040	.0218	0.088
.0408	.00077	.0414	.228
.0867	.0016	.0880	.334
.1850	.0035	.188	.377
.3828	.0072	.388	.429
.5815	.0109	.590	.464
.780	.0146	.793	.482
.879	.0165	.892	.534
.934	.0175	.948	.717

*Analytical uncertainty in $V\Delta C/m$ is 0.004 over the entire concentration range.

Table 3C

Adsorption of Butanol-1 from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0214	0.00040	0.0217	0.089
.0429	.00081	.0436	.174
.0881	.0017	.0894	.268
.186	.0035	.189	.337
.383	.0072	.389	.391
.582	.0109	.590	.462
.779	.0146	.791	.534
.875	.0164	.888	.638
.930	.0175	.944	.821

*Analytical uncertainty in $V\Delta C/m$ is 0.004 millimiles per gram over the entire concentration range.

Table 4A

Adsorption of Pentanol-1 from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00244	0.0000446	0.0091	0.049
.00688	.000126	.0255	.115
.0151	.000276	.056	.198
.0238	.000435	.088	.262
.0441	.000806	.164	.335
.0651	.00119	.242	.387
.0866	.00158	.322	.428
.1078	.00197	.400	.456
.1301	.00238	.483	.494
.1520	.00278	.564	.523
.1735	.00317	.644	.563
.1946	.00356	.723	.634
.2041	.00373	.758	.644
.2365	.00432	.878	.69
.2494	.00456	.926	.73
.2545	.00465	.945	.940

---

*Analytical uncertainty in $V\Delta C/m$ is 0.0028 over the entire concentration range.

Table 4B

Adsorption of Pentanol-1 from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00269	0.0000492	0.010	0.043
.00603	.000110	.022	.137
.01293	.000236	.048	.252
.02239	.000409	.083	.297
.04401	.000805	.163	.338
.06644	.00121	.246	.353
.0885	.00162	.328	.380
.1102	.00201	.409	.398
.1333	.00244	.495	.413
.1559	.00285	.579	.427
.1776	.00325	.659	.461
.1993	.00364	.741	.492
.2090	.00382	.776	.523
.2408	.00440	.894	.58
.2495	.00456	.928	.71
.2540	.00464	.945	.941

*Analytical uncertainty in $V\Delta C/m$ is 0.0028 over the entire concentration range.

Table 4C

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00232	0.0000424	0.0086	0.052
.00659	.000120	.0245	.122
.0148	.000271	.055	.206
.0241	.000410	.089	.255
.0454	.000830	.169	.302
.0671	.00123	.249	.336
.0900	.00165	.334	.342
.1102	.00201	.409	.398
.1327	.00243	.493	.428
.1547	.00283	.574	.459
.1755	.00321	.652	.512
.1962	.00359	.729	.570
.2063	.00377	.766	.591
.2389	.00437	.887	.63
.2491	.00455	.925	.74
.2561	.00468	.951	.779

*Analytical uncertainty in $V\Delta C/m$ is 0.0028 over the entire concentration range.

Table 5A

Adsorption of Hexanol-1 from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00030	0.0000054	0.005	0.048
.00153	.0000278	.026	.128
.00326	.0000592	.056	.194
.00567	.000103	.097	.245
.00978	.000177	.167	.307
.01496	.000271	.255	.344
.01826	.000331	.312	.371
.02135	.000387	.364	.405
.02183	.000396	.373	.393
.02501	.000454	.427	.421
.02657	.000482	.454	.440
.03647	.000662	.622	.532
.04466	.000810	.763	.654
.04987	.000905	.851	.787
.05421	.000984	.926	1.41

*Analytical uncertainty is 0.0023 millimoles per gram.

Table 5B

Adsorption of Hexanol-1 from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00079	0.0000143	0.013	0.071
.00237	.0000430	.040	.213
.00530	.0000962	.090	.286
.00940	.000171	.160	.303
.01556	.000282	.265	.325
.02167	.000393	.370	.353
.02960	.000537	.505	.397
.03548	.000644	.606	.433
.04006	.000723	.684	.442
.04740	.000860	.809	.517
.05060	.000918	.864	.714
.05471	.000993	.934	1.22

*Analytical uncertainty is 0.0023 millimoles per gram.

Table 5C

Adsorption of Hexanol-1 from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.001165	0.0000211	0.020	0.137
.00308	.0000559	.052	.199
.00557	.00101	.095	.247
.01046	.000190	.179	.290
.01565	.000284	.268	.327
.01929	.000350	.330	.346
.02283	.000414	.390	.363
.02615	.000474	.446	.393
.02809	.000510	.479	.402
.03860	.000700	.659	.478
.04579	.000831	.782	.597
.05021	.000911	.857	.753
.05495	.000997	.938	1.12

---

*Analytical uncertainty is 0.0023 millimoles per gram.

Table 6A

Adsorption of Heptanol-1 from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0000593	0.0000011	0.004	0.016
.0001502	.0000027	.010	.031
.0002134	.0000039	.014	.082
.0007708	.0000140	.052	.173
.001854	.0000336	.125	.251
.002715	.0000491	.183[a]	.280
.006020	.000109	.407[b]	.396
.006273	.000114	.424[c]	.399
.007095	.000128	.479[a]	.418
.009062	.000164	.612[d]	.520
.009892	.000179	.668[b]	.583
.009980	.000181	.674[a]	.622
.01002	.000181	.676[c]	.599
.01120	.000203	.756[b]	.713
.01136	.000206	.767[a]	.745
.01168	.000211	.789[d]	.751
.01192	.000216	.805[b]	.812
.01200	.000217	.811[a]	.837
.01257	.000228	.849[d]	.913
.01300	.000235	.878[d]	1.04
.01317	.000238	.889[d]	1.20

*Analytical uncertainty is 0.004 millimoles per gram.

[a,b,c,d] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of heptanol-1.

Table 6B

Adsorption of Heptanol-1 from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.000111	0.0000020	0.008	0.0147
.000189	.0000034	.013	.0304
.000242	.0000044	.016	.134
.000293	.0000053	.020	.081
.000346	.0000063	.023	.184
.000634	.0000115	.043	.229
.002691	.0000487	$.182^a$	.281
.006509	.000118	$.440^b$	.371
.006908	.000125	$.467^c$	.368
.008003	.000145	$.540^a$	.414
.009366	.000170	$.633^d$	.512
.01010	.000183	$.682^b$	.544
.01034	.000187	$.698^c$	.554
.01055	.000191	$.713^a$	.575
.01126	.000204	$.760^b$	.675
.01157	.000209	$.781^d$	.793
.01181	.000214	$.798^b$	.780
.01248	.000226	$.843^d$	.988
.01312	.000237	$.886^d$	1.121
.01317	.000238	$.889^d$	1.252

*Analytical uncertainty in $V\Delta C/m$ is 0.004 millimoles per gram.

[a,b,c,d] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of heptanol-1

Table 6C

Adsorption of Heptanol-1 from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0001028	0.0000019	0.007	0.084
.0005415	.0000098	.037	.179
.001040	.0000188	.070	.219
.002905	.0000526	.196[a]	.276
.006217	.000113	.420[b]	.386
.006727	.000123	.454[c]	.377
.007596	.000137	.513[a]	.408
.009493	.000172	.641[d]	.477
.01010	.000183	.682[b]	.559
.01024	.000185	.691[c]	.557
.01035	.000187	.699[a]	.483
.01141	.000207	.771[b]	.679
.01183	.000214	.799[d]	.695
.01211	.000219	.818[b]	.768
.01295	.000234	.875[d]	.816
.01391	.000252	.939[d]	1.76

*Analytical uncertainty in $V\Delta C/m$ is 0.004 millimoles per gram.

[a,b,c,d] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of heptanol-1.

Table 7

Adsorption of Acetic Acid from Aqueous Solution

C(moles/l.)	Mole Fraction	A[*]	$V\Delta C/m$ (millimoles/g.)			Analyt. Uncert.
			Spheron-6	Graphon	DAG-1	
0.1737	0.0032	0.0105	0.12	0.09	0.11	± .01
0.3491	.0065	.0213	.18	.14	.14	.01
0.6825	.0127	.0415	.21	.19	.18	.015
1.721	.0333	.0959	.28	.23	.24	.015
3.456	.0712	.177	.275	.27	.30	.015
4.324	.0923	.222	----	.26	---	.015
5.175	.1146	.261	.265	.255	.27	.015
6.929	.166	.339	.21	.195	.20	.02
6.929	.166	.339	----	----	.305[a]	.02
8.666	.227	.409	.085	.17	.195	.02
8.666	.227	.409	----	.11[a]	----	.04
10.420	.307	.500	.015	.17	.13	.02
10.420	.307	.500	----	.12[a]	.185[a]	.025
11.253	.346	.557	----	.11	-----	.025
12.122	.395	.632	-.02	.10	.15	.03
12.122	.395	.632	----	---	.17[a]	.03
13.893	.520	.770	-.15	.00	.06	.05
15.630	.701	.911	-.06	---	---	.08
16.272	.785	.942	-.04	.09	.08	.03
16.272	.785	.942	----	---	.055[a]	.03
16.846	.884	.972	.00	.05	.07	.02
17.123	.938	.985	.02	.05	.065	.01
17.123	.938	.985	---	.01[a]	----	.01
17.245	.968	.987	.01	.025	.05	.01

[*] These activity values were taken from the data of A. Giacalone, F. Accascina, and G. Carnesi, *Gazz. chim. ital. 72*, 109 (1942).

[a] In cases where two values are given, the original was not reproduced, and no valid grounds were evident for discarding either value. When the original value was reproduced within .005 millimoles, only the one value is given.

Table 8

Adsorption of Propionic Acid from Aqueous Solution

C(moles/l.)	Mole Fraction	A*	$V\Delta C/m$ (millimoles/g.)			Analyt. Uncert.
			Spheron-6	Graphon	DAG-1	
0.1226	0.0023	0.0189	0.170	0.137	0.142	± .009
0.2612	.0049	.0372	.221	.197	.197	.009
0.5185	.0097	.0712	.272	.274	.241	.009
0.7877	.0149	.107	.284	.314	.286	.009
1.317	.0256	.168	.376	.339	.352	.009
2.639	.0550	.305	.404	.392	.448	.009
3.985	.0907	.413	.344	.388	.403	.010
5.318	.132	.479	.25	.333	.297	.011
6.664	.185	.508	.154	.262	.276	.012
7.997	.252	.535	.087	.147	.205	.013
9.330	.339	.562	-.016	.078	.123	.015
10.676	.461	.596	-.194	-.06[b]	.06[b]	.021
11.329	.540	.618	-.269[a]	-.05[c]	.06[c]	.031
12.902	.853	.853	-.097[a]	.039	.00	.018
13.115	.921	.921	-.05[a]	.031	.034	.011
13.235	.960	.960	-.015[a]	.016	.02	.008

*Activity values were obtained from the data of A. Giacalone, F. Accascina, and G. Carnesi, *Gazz. chim. ital.* *72*, 109 (1942).

[a] Adsorbent evacuated immediately before use.

[b] Reproducibility at this concentration was only within 0.04 millimoles. These values are the mean values.

[c] Reproducibility was especially poor at this concentration. Values were obtained which varied on either side of the values listed by 0.07 and 0.04 millimoles per gram for graphon and DAG-1, respectively.

Table 9A

Adsorption of n-Butyric Acid from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.0973	0.0019	0.0568	0.23 ± .013[a]
0.216	.0042	.126	.30 ± .014
0.681	.0132	.397	.47 ± .014
2.259	.0481	.843	.86 ± .015
4.519	.119	.880	.54 ± .016
6.724	.232	.891	.12 ± .017
8.313	.376	.905	-0.12 ± .02[b]
8.832	.443	.911	- .15 ± .02[b]
9.870	.637	.930	- .22 ± .04[b]
10.075	.694	.935	- .21 ± .09[b]
10.648	.906	.957	- .10 ± .04[b]
10.713	.950	.962	- .07 ± .016[b]
10.734	.953	.965	- .05 ± .025[b]

[*] Activity values were obtained from the data of E. R. Jones and C. R. Bury, Phil. Mag. 4, 841 (1927), using the low concentration data of A. Giacalone, F. Accascina, and G. Carnesi, Gazz, chim. ital. 72, 109 (1942) to establish the factor for conversion to absolute rational activities.

[a] Indicated uncertainty is due to the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use. Results with samples used without this evacuation were in qualitative agreement with these, but points were more scattered.

Table 9B

Adsorption of n-Butyric Acid from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	A[*]	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.0973	0.0019	0.0568	0.23 ± .013[a]
0.216	.0042	.126	.30 ± .014
0.443	.0086	.275	.37 ± .014
0.897	.0175	.511	.50 ± .014
1.816	.0375	.806	.71 ± .015
4.075	.102	.878	.66 ± .016
6.281	.204	.888	.29 ± .017
8.313	.376	.905	.04 ± .02[b]
9.275	.512	.918	.00 ± .03[b]
9.880	.640	.930	- .08 ± .05[b]
10.075	.721	.938	- .03 ± .06[b]
10.648	.906	.956	.06 ± 042[b]
10.734	.953	.965	.02 ± .025[b]

[*] Activity values were obtained from the data of E. R. Jones and C. R. Bury, *Phil. Mag.* 4, 841 (1927), using the low concentration data of A. Giacalone, F. Accascina, and G. Carnesi, *Gazz. chim. ital.* *72*, 109 (1942) to establish the factor for conversion to absolute rational activities.

[a] Uncertainty indicated is due to the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use. Samples used without this evacuation gave results in qualitative agreement with these, but more scattered.

Table 9C

Adsorption of n-Butyric Acid from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	A*	$\frac{V\Delta C}{m}$ (millimoles/g.)
0.0973	0.0019	0.0568	0.23 ± .013[a]
0.216	.0042	.126	.27 ± .014
0.691	.0133	.400	.40 ± .014
2.259	.0481	.843	.66 ± .015
4.529	.120	.880	.41 ± .016
6.724	.232	.891	.23 ± .017
8.313	.376	.905	.05 ± .02[b]
9.264	.510	.917	-.04 ± .03[b]
9.880	.640	.930	-.04 ± .04[b]
10.075	.721	.938	.03 ± .06[b]
10.648	.906	.956	.02 ± .04[b]
10.724	.952	.963	-.04 ± .028[b]

* Activity values were obtained from the data of E. R. Jones and C. R. Bury, *Phil. Mag.* 4, 841 (1927), using the low concentration data of A. Giacalone, F. Accascina, and G. Carnesi, *Gazz. chim. ital.* 72, 109 (1942) to establish the factor for conversion to absolute rational activities.

[a] Indicated uncertainty is due to the uncertainty in analysis.

[b] Adsorbent evacuated immediately before use. Results from samples used without this evacuation were in qualitative agreement with these, but points were more scattered.

Table 10A

Adsorption of n-Valeric Acid from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.00057	.0000105	0.0015	0.043
.00116	.0000214	.0031	.056
.00188	.0000347	.0051	.068
.00298	.0000550	.0080	.080
.00511	.0000943	.0137	.101
.00679	.000125	.0183	.118
.0123	.000227	.0331	.151
.0150	.000277	.0403	.164
.0221	.000408	.0593	.205
.0346	.000639	.0930	.260
.0353	.000652	.095	.265
.0767	.00142	.206	.369
.1203	.00222	.323	.424
.1614	.00297	.434	.503 ± .015
.2022	.00373	.544	.566
.2053	.00379	.552	.570
.2461	.00454	.662	.658
.2873	.00531	.772	.751
.3319	.00614	.892	.959
.3496	.00649	.940	1.033
.3584	.00665	.963	1.192

---

*Analytical uncertainty is 0.005 millimoles per gram over the entire concentration range.

Table 10B

Adsorption of n-Valeric Acid from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0115	.000212	0.031	0.172
.0346	.000639	.093	.270
.0785	.00145	.211	.332
.1217	.00225	.327	.400
.1633	.00301	.439	.457
.2042	.00377	.549	.523
.2470	.00456	.664	.639
.2883	.00532	.775	.727
.3374	.00623	.907	.825
.3512	.00648	.944	.962
.3586	.00662	.964	1.153

*Analytical uncertainty is 0.005 millimoles per gram.

Table 10C

Adsorption of n-Valeric Acid from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.0119	.000220	0.032	0.160
.0358	.000661	.096	.252
.0785	.00145	.211	.326
.1217	.00225	.327	.390
.1630	.00301	.438	.463
.2050	.00378	.551	.498
.2077	.00383	.558	.509
.2503	.00462	.673	.552
.2914	.00538	.783	.648
.3389	.00626	.911	.785
.3519	.00650	.946	.919
.3597	.00664	.967	1.059

*Analytical uncertainty is 0.005 millimoles per gram.

Table 11

Adsorption of n-Caproic Acid from Aqueous Solution

C(moles/l.)	Mole Fraction	C/C_o	$V\Delta C/m$ (millimoles/g.)*		
			Spheron-6	Graphon	DAG-1
0.00267	0.000049	0.031	0.170		
.0304	.000554	.348	.422		
.0454	.000827	.519	.522		
.0598	.00109	.684	.689		
.0658	.00120	.753	.721		
.0716	.00130	.819	.788		
.0788	.00144	.902	.855		
0.00228	.000042	0.026		0.180	
.0158	.000288	.180		.314	
.0302	.000550	.345		.428	
.0465	.000847	.532		.505	
.0592	.00108	.677		.651	
.0729	.00133	.834		.71	
.0786	.00143	.899		.84	
0.00245	.000045	0.028			0.176
.0165	.000301	.188			.297
.0317	.000578	.363			.390
.0473	.000862	.541			.475
.0635	.00116	.727			.596
.0737	.00134	.843			.686
.0799	.00146	.914			.752
.0831	.00151	.951			.850

*Analytical uncertainty is 0.003 millimoles per gram over the entire concentration range.

Table 12A

Adsorption of n-Heptylic Acid from Aqueous Solution on Spheron-6

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)[*]
0.000060	.0000011	.003	0.044 ± .0015
.000294	.0000053	.014	.107 ± .0015
.00168	.0000304	.078	.187 ± .0015
.00345	.0000625	.160	.257 ± .0015
.00570	.000103	.265	.316 ± .0015
.00944	.000171	.439	.444 ± .003[a]
.01152	.000209	.535	.500 ± .003[b]
.01423	.000258	.661	.642 ± .003[a]
.01494	.000271	.694	.658 ± .006[c]
.01618	.000293	.752	.742 ± .003[a]
.01640	.000297	.762	.737 ± .003[b]
.01681	.000304	.781	.814 ± .003[a]
.01832	.000332	.851	.889 ± .003[b]
.01920	.000348	.892	1.002 ± .003[b]
.01925	.000349	.894	.858 ± .006[c]
.01996	.000361	.928	1.008 ± .006[c]
.02001	.000362	.930	1.159 ± .006[c]
.02019	.000366	.938	1.290 ± .006[c]

[*] Uncertainty indicated is due to the uncertainty in analysis.

[a,b,c] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of n-heptylic acid.

Table 12B

Adsorption of n-Heptylic Acid from Aqueous Solution on Graphon

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
0.000060	.0000011	0.003	0.021 ± .0015
.00046	.0000083	.021	.103 ± .0015
.00047	.0000085	.022	.034 ± .0015
.00115	.0000208	.053	.201 ± .0015
.00301	.0000545	.140	.269 ± .0015
.00576	.000104	.267	.314 ± .0015
.00942	.000171	.438	.445 ± .003
.01133	.000205	.531	.510 ± .003[a]
.01526	.000276	.712	.627 ± .006[b]
.01692	.000306	.786	.718 ± .003[a]
.01889	.000342	.878	.840 ± .003[a]
.01929	.000349	.896	.833 ± .006[b]
.01957	.000354	.909	.933 ± .003[a]
.01989	.000360	.924	.992 ± .006[b]
.02044	.000370	.950	1.096 ± .006[b]
.02048	.000371	.951	1.200 ± .006[b]

*Uncertainty indicated is due to the uncertainty in analysis.

[a,b] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of n-heptylic acid.

Table 12C

Adsorption of n-Heptylic Acid from Aqueous Solution on DAG-1

C(moles/l.)	Mole Fraction	C/C_o	$\frac{V\Delta C}{m}$ (millimoles/g.)*
.00003	.0000005	0.001	0.045 ± .0015
.00030	.0000054	.014	.107 ± .0015
.00141	.0000255	.066	.194 ± .0015
.00363	.0000657	.169	.253 ± .0015
.00609	.000110	.283	.306 ± .0015
.01006	.000182	.467	.413 ± .003
.01217	.000220	.566	.467 ± .003[a]
.01706	.000309	.793	.610 ± .003[a]
.01816	.000329	.844	.673 ± .012[b]
.01885	.000341	.876	.740 ± .003[a]
.01985	.000359	.922	.814 ± .003[a]
.02046	.000371	.951	.854 ± .012[b]
.02077	.000376	.965	1.000 ± .012[b]
.02094	.000379	.973	1.114 ± .012[b]

*Uncertainty indicated is due to the uncertainty in analysis.

[a,b] The same adsorbent sample was used for all values marked with the same letter. Each such series of values was obtained by removing equilibrated liquid and adding fresh solution to the adsorbent, which thus already held a known excess of n-heptylic acid.

B. Adsorption of Water from Organic-Rich Phases of Immiscible Alcohols and Acids

Results of measurements of adsorption from organic-rich phases of immiscible systems are shown in Tables 13, 14, 15, and 16. Symbols used in these tables have the same meanings as those in previous tables. No estimates of errors due to analytical uncertainties are given in these tables because difficulties encountered in the interferometric analysis of organic liquids were such as to make close estimates of such errors impossible. Furthermore, change in water concentration in these systems produces only about one-tenth the difference in refractive index of the solution produced by a similar change in concentration of the alcohol or acid in the aqueous phase; therefore, even had no special experimental difficulties been encountered with these systems, the interferometric method of analysis would have been much less sensitive for these systems than for most of the aqueous systems recorded in previous tables, and the errors in surface excesses resulting from analytical uncertainties would have been greater by a factor of about ten. The relative sensitivities of various systems toward interferometric analysis are indicated below in a general discussion of interferometric analytical results, along with a description of the difficulties encountered with organic liquids.

Table 13

Adsorption of Water from n-Butanol Solutions on Spheron-6*

Spheron-6, not evacuated		Spheron-6, evacuated	
C/C_0[a]	$\frac{V\Delta C}{m}$[b]	C/C_0	$\frac{V\Delta C}{m}$
0.109	0.23	0.0554	0.174
.215	.90	.1085	0.477
.431	.94	.213	1.20
.650	.86	.430	1.32
.967	.75	.649	1.10
.996	.82	.866	1.012

[a] C_0 = 9.566 moles water per liter.

[b] $\frac{V\Delta C}{m}$ given in millimoles water per gram adsorbent.

*No change in concentration of solution is observed for this system with either Graphon or DAG-1 as adsorbent.

Table 14

Adsorption of Water from n-Pentanol Solutions
Non-evacuated Adsorbents

Spheron-6*	
C/C_0[a]	$\frac{V\Delta C}{m}$[b]
0.112	0.42
.225	.67
.337	.60 to .82
.447	.89
.673	.80
.786	.67 to 1.06
.900	.85
.993	.77
.998	.78

---

[a] C_0 = 4.933 moles H_2O per liter.

[b] Given in millimoles water per gram adsorbent.

*Within experimental error, there was no concentration change with either Graphon or DAG-1 as adsorbent. Both of were checked at the following reduced concentrations: 0.11, 0.23, 0.45, 0.68, and 0.91.

Table 15

Adsorption of Water from n-Hexanol Solutions

Spheron-Six,not evacuated*		Spheron-Six, evacuated	
C/C_0[a]	$\frac{V\Delta C}{m}$[b]	C/C_0	$\frac{V\Delta C}{m}$
0.163	0.15	0.078	0.37
.315	.75	.16	0.54
.642	.72, .82	.30	1.08
.979	.30, .90	.62	1.24
		.97	1.26
		.982	1.51
		.991	1.61
		.997	0.87

[a] C_0 = 3.373 moles H_2O per liter.

[b] Given in millimoles water per gram of adsorbent.

*Within experimental error, there was no change in concentration with either Graphon or DAG-1 as adsorbent. These were checked at reduced concentrations of 0.32, 0.64, 0.98, and 0.99 and, with evacuated DAG-1, at 0.16, 0.32, and 0.98.

Table 16

Adsorption of Water from n-Valeric Acid and n-Caproic Acid Solutions on Spheron-6*

n-Valeric Acid		n-Caproic Acid	
C/C_0[a]	$V\Delta C/m$[b]	C/C_0[a]	$V\Delta C/m$[b]
0.25	3.0	0.087	0.70
.39	1.6	.367	1.15
.52	2.6	.562	1.13
.66	2.0	.737	1.13
.79	2.0	.99	0.8 to 2.2
.92	0.9		

[a] C_0 = 8.332 moles water per liter of n-valeric acid solution, and 2.95 moles water per liter of n-caproic acid solution.

[b] Given in units of millimoles water per gram adsorbent.

*Adsorption on Graphon and DAG-1 was checked for solutions in n-valeric acid at reduced concentrations of 0.27, 0.53, and 0.79. In no case was the measured adsorption greater than 0.4 millimoles water per gram of adsorbent. Similar checks showed no observable adsorption of water from n-caproic acid by either Graphon or DAG-1.

C. Rate of Attainment of Adsorption Equilibrium

Table 17 shows the results of a study of the effect of variation in the time of contact of a valeric acid solution with each of the three adsorbents. These data were obtained by shaking 5.00 ml. samples of 0.225 molar valeric acid solution with 0.200 gram samples of adsorbent at 25° C. for the time indicated, centrifuging, and comparing interferometrically with the original solution in the usual manner.

Table 17

Rate of Adsorption of Valeric Acid

Time of Contact	ΔR-1 cm. Interferometer Readings		
	Graphon	Spheron-6	DAG-1
1 hour	102.4	(110.6)	96.4
2 hours	101.5	(110.1)	96.9
4 hours	100.7	(109.7)	97.7
8 hours	97.1	(110.0)	(95.2)
16 hours	96.1	109.9	95.5
32 hours	95.7	(110.2)	(96.5)
64 hours	98.1	109.0	98.7
9 days	96.2	107.2	98.4

Interferometer readings shown in this table are for one-centimeter cells. The numbers shown in parentheses are one-fourth the readings observed with four-centimeter cells.

It is seen that none of the adsorbents showed significant increase in adsorption with time after one hour. Since the adsorption on Spheron-6 was constant after one hour of exposure, addition tests were made with this adsorbent at shorter time intervals. The results of these tests are shown in Table 18.

Table 18

Rate of Adsorption of Valeric Acid on Spheron-6

Contact Time	ΔR-4 cm.
2 min.	205.2
5 min.	204.0
11 min.	205.1
20 min.	206.0
41 min.	204.2
120 min.	202.5
Blank (2 min.)	0.

In these tests, 0.0450 molar valeric acid solution was used, and the interferometer readings shown are for four-centimeter cells. The shortest time samples were shaken by hand at room temperature, which was 25.1 to 25.3° C. For times greater than five minutes, the samples were shaken in the mechanical shaker at 25° C. The blank test included in Table 18 was run in the same manner as the other tests, except that no adsorbent was present in the adsorption tube.

It is seen from Table 18 that adsorption equilibrium was established in less than two minutes. Because of the nature of these tests, especially in requiring separation of the adsorbent from the solution by centrifugation, it would be impractical to attempt measurements at less than two minutes of contact.

The values shown in Table 17 for Graphon were especially puzzling, since one would expect an increase in adsorption with time if any change at all occurred. The decrease shown by Graphon, however, was significantly greater than expected experimental error. To eliminate possible errors arising from variation in adsorbent samples, another series of tests was made with Graphon using a single large sample of adsorbent. In these tests, 100 ml. of 0.0450 molar valeric acid solution were added to 4.000 grams of Graphon in a 125 ml. glass-stoppered Erlenmeyer flask. Two to five ml. samples of solution were removed at the intervals indicated, after allowing the adsorbent to settle from the solution, and analyzed interferometrically. The flask was shaken mechanically at 25° C. The results are shown in Table 19.

A slight decrease in interferometer reading with time is again apparent from the data in this table. As mentioned above in the description of the various adsorbents, this anomalous behavior of Graphon was later traced to the leaching of some material of high refractive index from the Graphon surface. The changes in interferometer readings produced upon shaking Graphon with pure water were of such magnitude that if applied as a correction to the Graphon values of Tables 17 and 19, these values would indicate a constant adsorption of valeric acid after the shortest time measured.

Table 19

Rate of Adsorption of Valeric Acid on Graphon Using a Single Adsorbent Sample

Contact Time	ΔR-1 cm.
1 Hour	52.4
2 Hours	51.8
4 Hours	51.1
8 Hours	49.1
24 Hours	49.7
48 Hours	49.8
96 Hours	49.9

The values in these tables indicate that, while the adsorption of the organic component is a rapid process requiring less than two minutes for the attainment of adsorption equilibrium, approximately eight hours are required for completion of the anomalous leaching process from Graphon.

D. Solubilities

Solubilities measured during the course of this work are listed in Tables 20 and 21.

Table 20

Solubility of Water in Organic Liquids

Solvent	Temp.°C.	Moles Water/Liter	Wt % Water	Mole Fraction
Butanol-1	25.	9.566	20.337	.513
Pentanol-1	25.3	4.933	10.74	.371
Hexanol-1	25.4	3.373	7.362	.311
Valeric Acid	25.	7.804	14.88	.495
Caproic Acid	25.	2.95	5.72	.282

The value for butanol shown in Table 20 agrees well with that of Butler, Thomson, and Maclennan (27), which is 29.36 weight per cent water, or mole fraction 0.5124, at 25° C. Values recently published by Donahue and Bartell (28) for the alcohols are consistently lower than the observed values shown in Table 20, being 9.15, 4.75, and 3.07 moles of water per liter, or .500, .357, and 288 mole fraction, respectively, in butanol, pentanol, and hexanol. No values for the solubility of water in the acids have yet appeared in the literature. The observed saturation concentration of water in pentanol was precisely reproducible at 25.3° C., the solubility being 4.933 ± .002 moles of water per liter of solution.

No value is given in Table 21 for the solubility of butanol in water, since in this work the value of 0.9850 moles per liter, determined by R. S. Hansen (2), was used without re-determination.

Table 21

Solubility of Alcohols and Acids in Water

Solute	Temp.°C.	Molarity	Weight %	Solute Mole Fraction
Pentanol-1	25.0	0.2693	2.39[a]	0.00498
Hexanol-1	25.0	0.05857	0.601[b]	.00107
Heptanol-1	25.3	0.01481	0.1726[c]	.0002680
Valeric Acid	25.3	0.3707	3.798	.006915
Caproic Acid	25.3	0.0874	1.0184[d]	.001593
Heptylic Acid	25.3	0.02152	0.2810	.0003899

[a] Reported as 2.19 by Ginnings and Baum, J. Am. Chem. Soc. 59, 1111 (1937), 2.208 by Butler, Thomson, and Maclennan, J. Chem. Soc. 674 (1933), 2.54 ± .02 by R. S. Hansen, Thesis, Univ. of Michigan (1948).

[b] Reported as 0.624 by Butler, Thomson, and Maclennan, J. Chem. Soc. 674 (1933).

[c] Reported as 0.1807 at 25° by Butler, Thomson, and Maclennan, J. Chem. Soc. 674 (1933).

[d] Reported as 1.018 ± .006 by R. S. Hansen, Thesis, Univ. of Michigan (1948).

The value shown for pentanol is considered the best of several determinations, which gave values ranging from 2.33 to 2.48 weight per cent pentanol. This lack of reproducibility was probably due in large part to inaccurate control of temperature. The variation in values reported by different authors, as indicated in the footnote of Table 21, is considerably greater even than the variation herein observed, and may be tracable to lack of purity of the alcohols tested. The value for the solubility of caproic acid is seen to be in very good agreement with that determined by R. S. Hansen. For valeric acid, the observed solubility was checked by numerous re-determinations because of disagreement with the value previously published in the literature, and since corrected. The several determinations of valeric acid solubility gave results in excellent agreement with each other, variations being in the fourth significant figure.

VI. DISCUSSION

A. Evaluation of Experimental Data

1. Interferometric analysis

An important source of error often encountered in interferometric work is the shift in the central colorless band as the concentration differences increase, due to differences in optical dispersion. In checks made during this work, there was no apparent band shift with solutions of butanol and hexanoic acid when the interferometer scale readings were less than 660 and 500, respectively. These checks were made by summing interferometer readings taken between consecutive solutions of a series with small concentration differences and comparing this value with a direct reading between the end members of the series. The maximum reading on the scale was approximately 1300, and readings greater than 500 were encountered only during the determination of calibration curves. It is not believed that band shifts caused any error in this work. If a band shift should have occurred at readings above 500, the maximum error from this source would be five per cent, since one band measured from 25 to 28 units on the interferometer scale.

Since complete calibration curves are not included in this dissertation, some approximate sensitivities of different systems toward interferometric analysis are listed below to give an indication of the relative accuracy possible in such analyses with different systems and with different concentrations of the same system. The sensitivities are given in divisions of the interferometer scale per millimole change in concentration.

Hexanol: 21.
Pentanol: 18.
Butanol: 13 to 16.

Water in Butanol: 0.9 to 1.5
Water in Hexanol: ca 2.1
Water in Caproic Acid: 0.6 to 1.6

Propanol: 9, 10, 8, 6, 2, 0 to -3.
Ethanol: 5, 6, 4, 3, 1, 0, -1, -5.
Methanol: 1, 1.5, 0.5, 0, -1, -3, -6.

Where not otherwise stated, the systems refer to the aqueous phases. The series of numbers given for the miscible alcohols indicate the sensitivities at increasing alcohol concentrations, from left to right, from low concentration to nearly pure alcohol. The numbers for each alcohol were taken at approximately equal concentration intervals, and show that in each case there is a concentration at which the interferometric method cannot be used to measure small changes in concentration. Methanol, which was not used in adsorption work, is included in this list to show the extremely low analytical sensitivity of methanol solutions over nearly the entire concentration range. The precision of reading the interferometer readings was about one scale division.

Reproducibility of interferometer readings upon refilling the dried cells with the same solutions was quite satisfactory for aqueous systems. Several such checks were made, including three points on the propanol calibration curve, and the readings were within one scale division of each other. When the solutions consisted predominately of the organic component, however, reproducibility was erratic and reflected the general difficulties encountered with organic liquids. Paramount among these difficulties was the non-reproducibility of zero readings, that is, readings made with the same solutions in both sides of the interferometer cell. The most perplexing aspect of this difficulty was the fact that the average of many zero readings for each pure organic liquid was invariably several scale divisions higher than the zero reading for water. The two sides of each cell were practically identical in length, the water zero reading being only two scale divisions higher than the reading with empty cells; therefore, the zero readings for all the alcohols and acids should not have varied more than a fraction of a scale division from that of water. The observed averages, with one-centimeter cells, were five divisions above the water zero reading for pure hexanol and about three divisions above for ethanol, acetic acid, propionic acid, and butyric acid. With four-centimeter cells, the average was about fourteen units and ten units above the water zero for acetic acid and ethanol, respectively. The readings themselves varied as much as seven units for one liquid in four-centimeter cells. The cells were dried carefully before use, and the reasons for this lack of reproducibility and apparent highness of zero readings could not be ascertained. In making analyses with the organic systems, the determined averages were used as the zero points, and for miscible systems zero readings varying linearly from that of water to that of the organic liquid were used for intermediate concentrations. Zero readings made directly with intermediate concentrations showed fair agreement with these values. Actual readings between solutions of slightly different concentrations in the organic-rich phases were, amazingly enough, generally reproducible within about two scale divisions or less; thus, while the absolute magnitudes of indicated adsorption values may be considerably in error because of uncertainties in the proper zero-point, the relative values for points on the same isotherm retain significance.

Another major difficulty was encountered in analyzing propanol solutions in the region of very high propanol concentration. These solutions tended to creep under and around the mercury seals, and reproducibility of isotherm points in this region was very poor. Various attempts to eliminate these difficulties proved unsuccessful, and points recorded were finally obtained by making numerous determinations at a particular concentration and using the resulting average value. Less volatile organic liquids did not show this creeping tendency.

It should perhaps be emphasized that difficulties of this nature were not encountered in solutions which were predominately aqueous in composition, as were most of the solutions used in the major part of this work. Water zero readings were reproducible to a fraction of a scale division, and, as mentioned previously, other readings were generally reproducible to within one division.

2. Temperature control

Both the mechanical shaker and the interferometer were air-thermostated at 25.0° C. However, while the air surrounding the shaker was maintained at this temperature, several checks of the temperature within an adsorption cell immediately after the shaker was stopped showed this temperature to be 25.4° to 25.6° C. This difference in temperature probably arises from friction of the liquid and adsorbent shaking against the walls of the adsorption cell. The temperature at which the adsorption took place was, therefore, about 25.5° C. rather than 25.0° C. A device for shaking in a water thermostat would give much better temperature control than was obtained with the air bath. This may be immaterial, however, for the amazingly rapid equilibration of adsorbent and solution which has been shown above would indicate that the temperature of centrifugation would be the controlling temperature.

3. Surface areas

The surface area measurements used in this work were computed, as indicated previously, from the equations of

Brunauer, Emmett, and Teller. The values are precise to within about two per cent. The Anderson modification (29) of the BET equation for surface areas would give values about ten per cent higher than those from the simple BET equation, and higher areas may indeed be more accurate. Since the same areas were used in all calculations, however, the comparisons made in this work would hold in either case.

4. General

In work of this type it would be highly desirable to make all determinations in duplicate. This was not done in this work because of the large volume of experimental work required and the great amount of time required for the various determinations. A few selected points were re-determined, and, except for organic-rich solutions as mentioned above, found to agree within analytical uncertainty. The values of neighboring points on an isotherm and of corresponding points on isotherms of different adsorbents serve to substantiate each individual value, and would show the existence of any gross error in a particular point. In cases where error was indicated from such comparisons, the points concerned were redetermined.

Since it is generally assumed that only non-dissociated molecules are adsorbed (4), the effect of dissociation of the fatty acids upon the concentration of undissociated molecules should be examined. It is readily seen, however, that this effect is entirely insignificant in this work, for in the most dilute solution used, one of aqueous valeric acid, the acid only five per cent dissociated. At higher concentrations, the per cent dissociation is negligible.

Blank determinations, carried through the procedure without having adsorbent in the adsorption cell, were made with eight solutions of propanol and hexanol. These showed no significant change in concentration when the solution was less than 95 per cent saturated or the propanol solution predominately aqueous. A slight loss of hexanol from solution was indicated at concentrations higher than 95 per cent saturation.

Because the above considerations and the wide variations in analytical sensitivity cause such great differences in the accuracy of different points on the various isotherms, no general estimate of the per cent accuracy of the experimental data can be made; analytical uncertainties are indicated, however, in the basic data (Tables 1 to 12).

B. Use of Reduced Concentrations

The reduced concentrations of immiscible alcohols and acids are used in this work as approximations to the absolute activities. Since the activity of organic component in its saturated solution is not that of the pure component, but rather is that of a solution of that component saturated with water, this approximation is closer to the actual activity when water is practically insoluble in the organic liquid. While actual activity data for most of these alcohols and acids are not available, the activity of butanol in its saturated solution, calculated from the data of Butler, Thomson, and Maclennan (27) is 0.701, and those for the other alcohols and the acids could be estimated reasonably well from the water solubilities in these substances. These values would all be closer to unity than that of butanol, since these liquids dissolve considerably less water than does butanol, as is seen from the solubility data given above.

While it is possible in this way to get a closer approximation to the actual activity than is given by the reduced concentrations, the reduced concentration may still be the more significant quantity. This would be true if the sorbate condensed on the adsorbent surface as a separate liquid phase consisting of the alcohol or acid saturated with water, rather than of the pure organic liquid. In this case the energy required to cause the separation of phases would be the difference between the free energy of the solute in the solution and its free energy in a saturated solution, which is controlled by the activity of the saturated solution rather than that of the pure liquid. If the adsorbed phase consisted of pure organic liquid, however, the absolute rational activity would determine the energy required to bring about this phase change. Use of actual activity values in place of reduced concentrations would not alter the isotherms greatly, but would show the asymptotic rise in adsorption as saturation concentration is approached to occur at a slightly lower activity.

For easier comparison of the adsorption of different members of a homologous series, the data of Tables 1 to 12 have been plotted with all members of the series on a single graph for a particular adsorbent. These plots are shown in Figures 1 to 12, the abscissa being the activity of the organic component for miscible liquids and the reduced concentration for those not miscible with water in all proportions. In Figures 1 to 6, the adsorption at low concentrations is plotted both against the activity and against the molar concentrations of the organic component.

C. The Basis for Traube's Rule

While studying the decrease in the surface tension of water caused by the presence of varying concentrations of the different members of homologous series of acids, alcohols, and esters, Traube (30) noticed a surprising regularity, as the length of the carbon chain increased, in the increasing effectiveness of members of the series in lowering the surface tension. This regularity was stated as the now famous Traube's rule. Since reports of inversions or transformations of Traube's rule frequently occur in current literature, as discussed below, and since the rational basis for this rule is apparent from examination of Figures 1 to 6

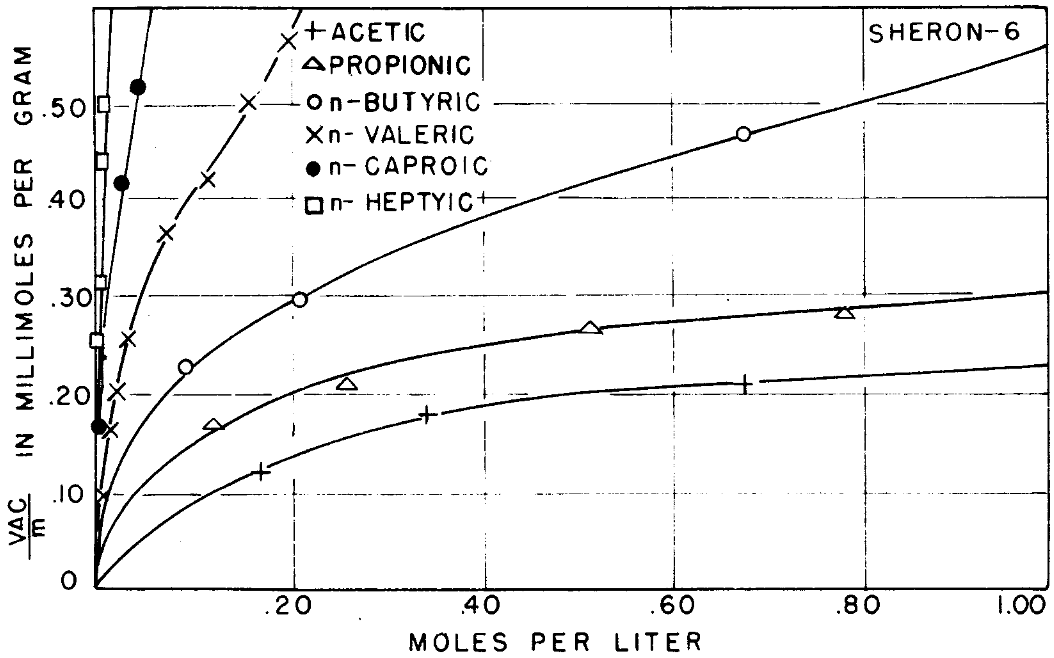

Fig. 1A ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON SPHERON-6

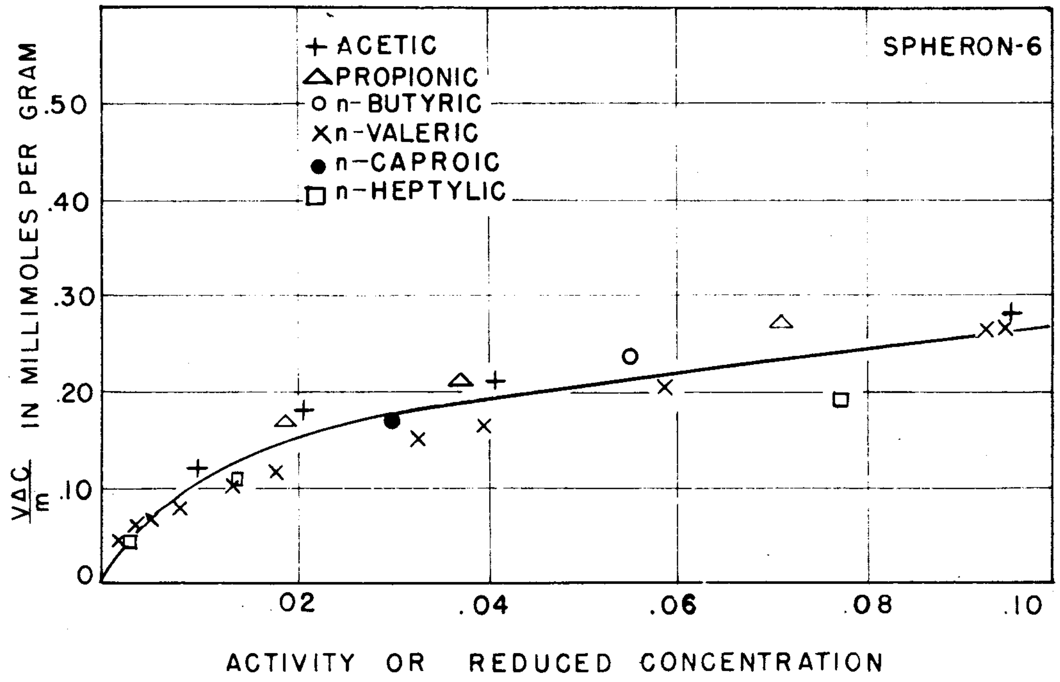

Fig. 1B Adsorption of Fatty Acids on Spheron-6

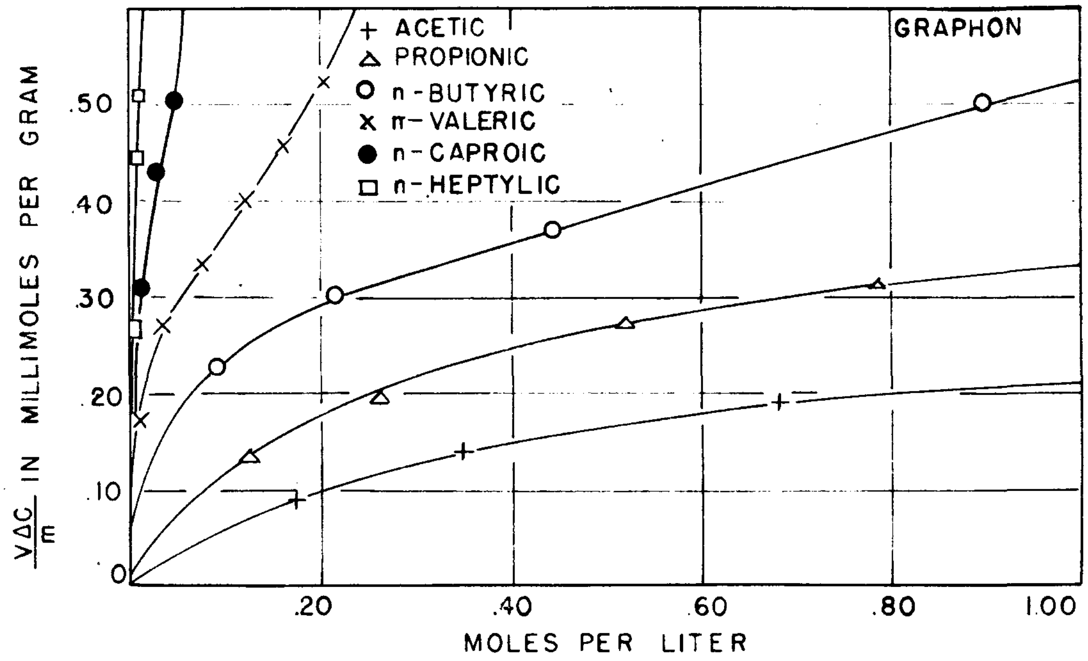

Fig. 2A ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON GRAPHON

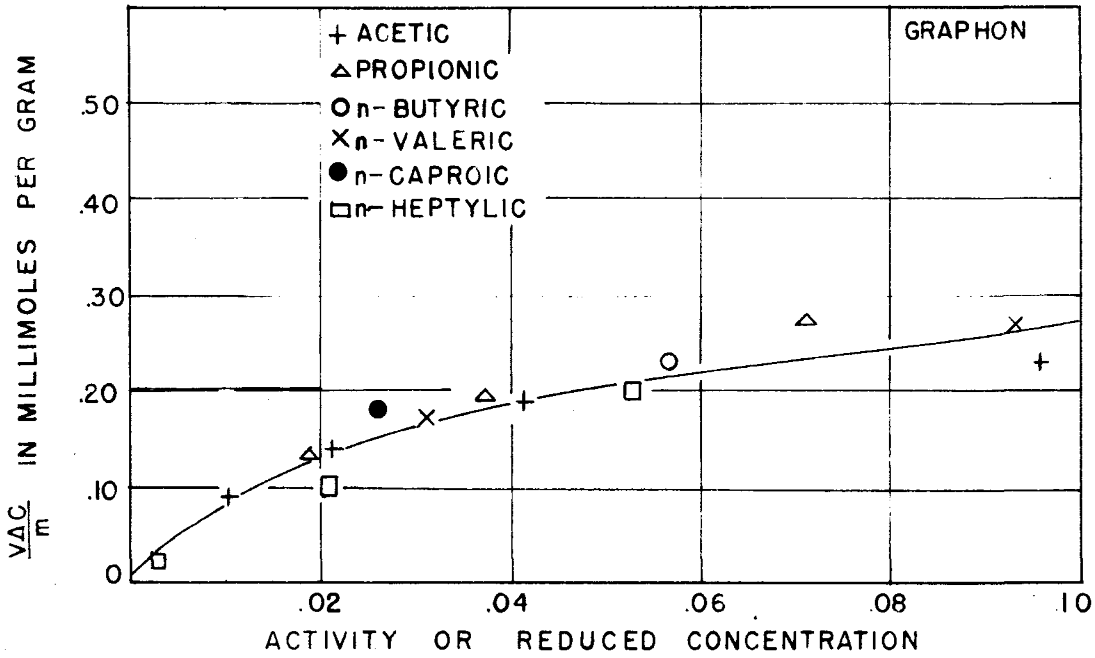

Fig. 2B Adsorption of Fatty Acids on Graphon

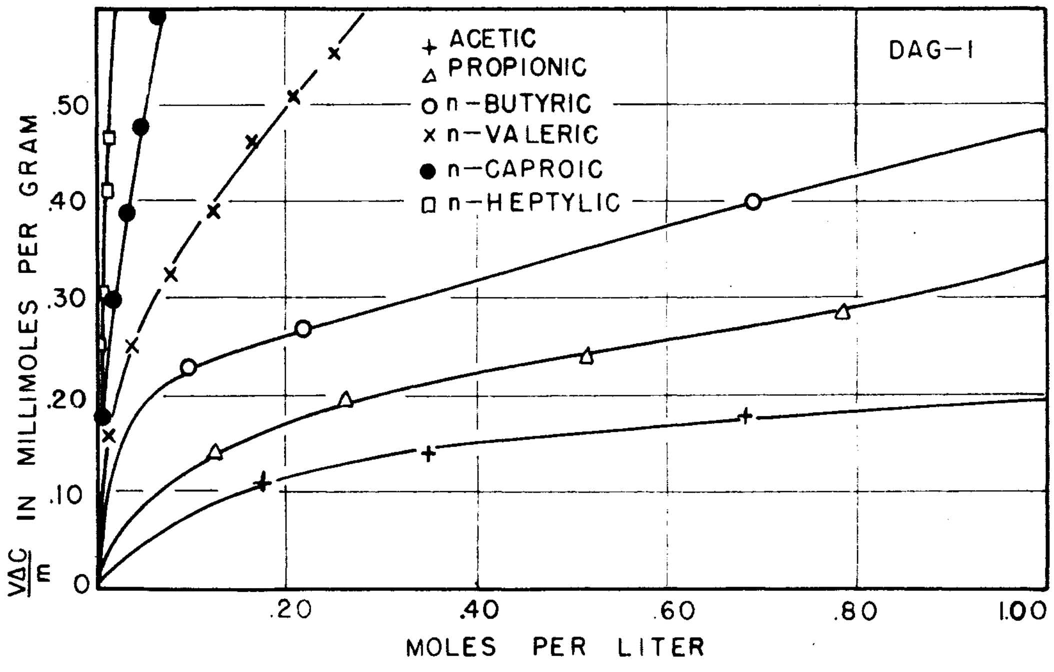

Fig. 3A ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON DAG — I

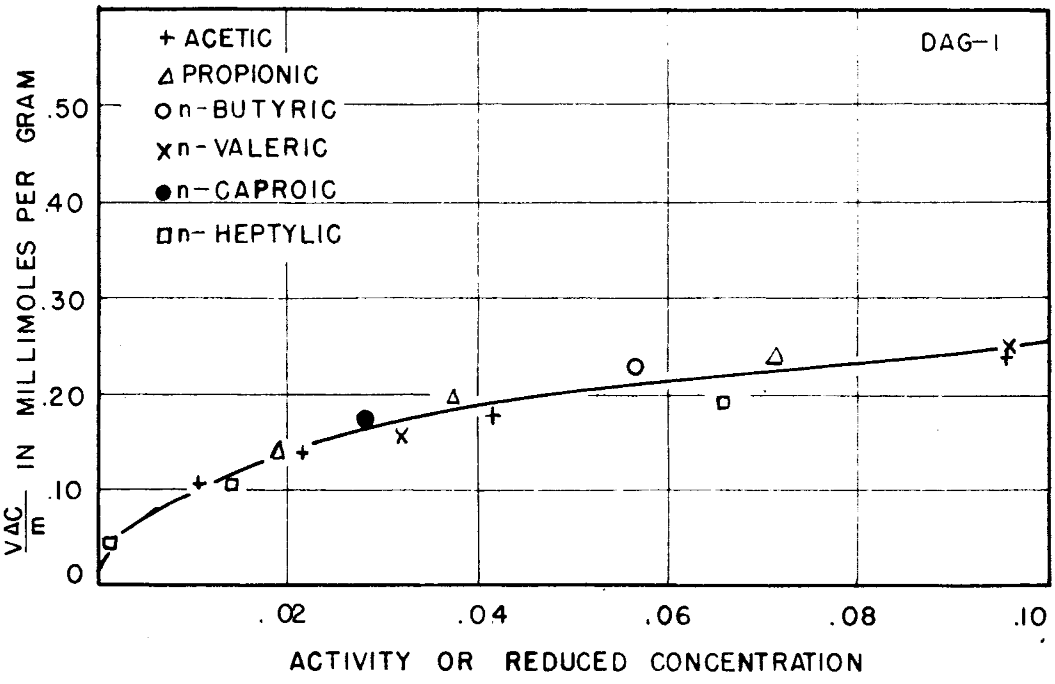

Fig. 3B Adsorption of Fatty Acids on DAG-1

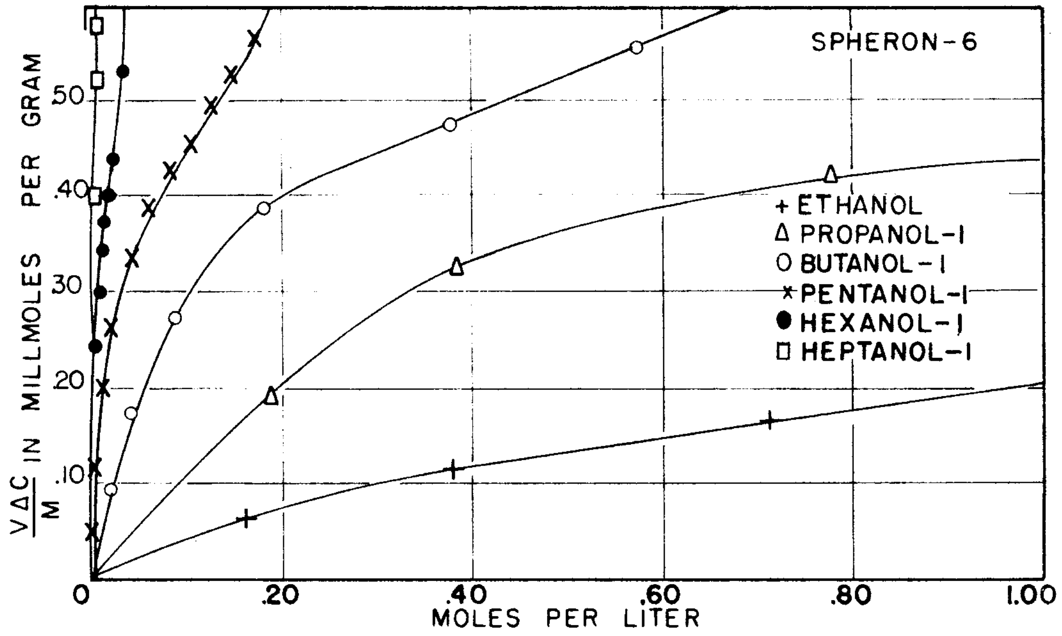

Fig. 4A ADSORPTION OF NORMAL ALCOHOLS FROM AQUEOUS SOLUTION ON SPHERON—6

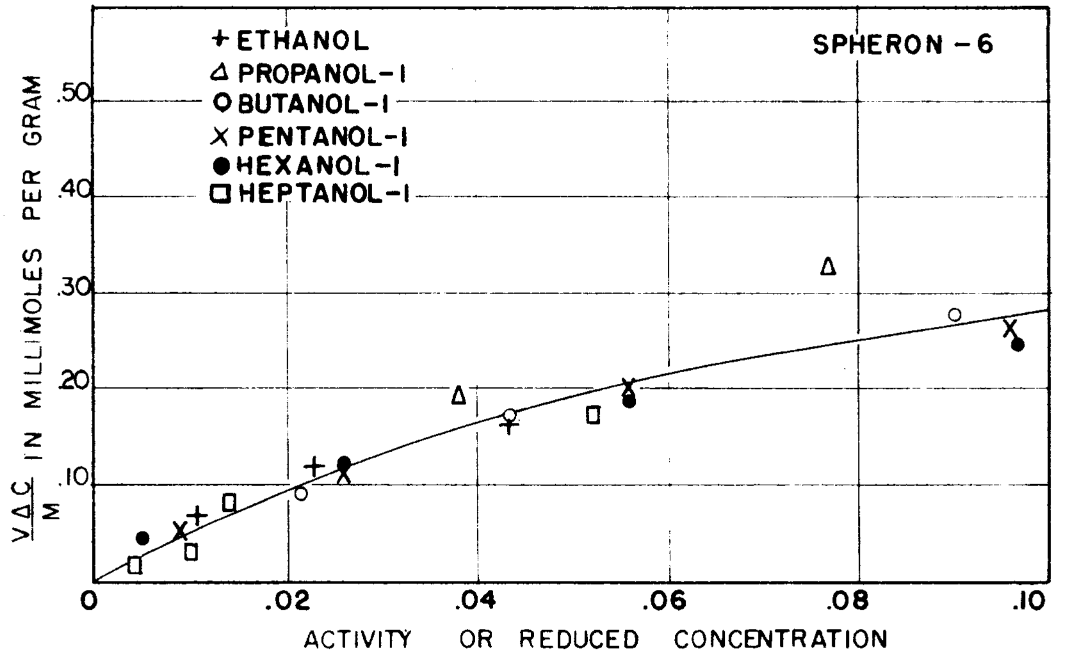

Fig. 4B Adsorption of Normal Alcohols on Spheron-6

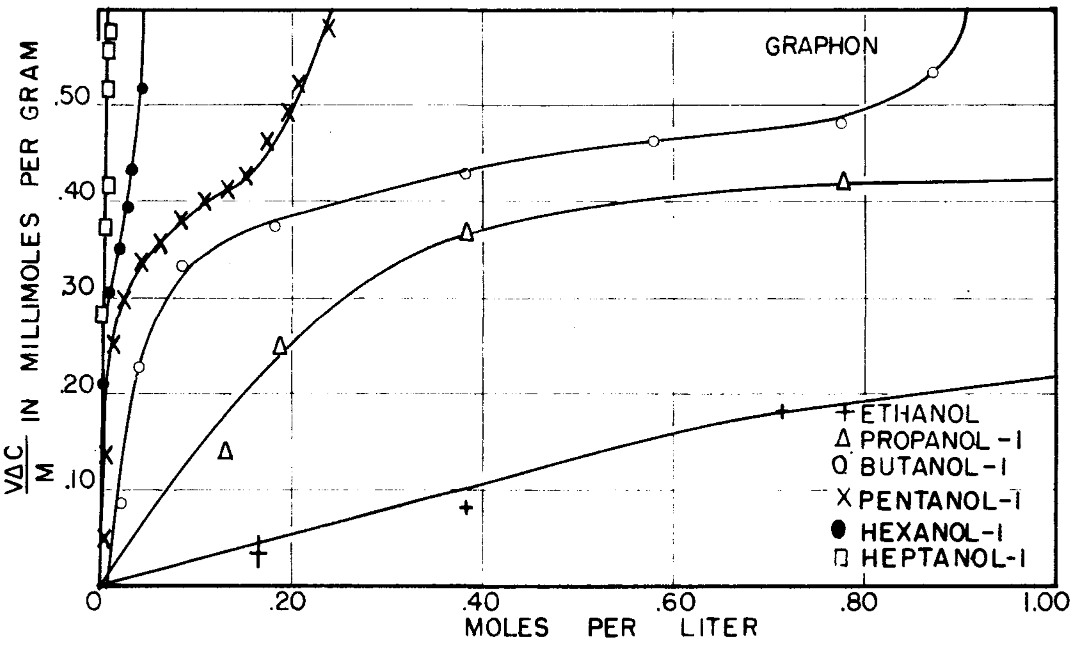

Fig. 5A ADSORPTION OF NORMAL ALCOHOLS FROM AQUEOUS SOLUTION ON GRAPON

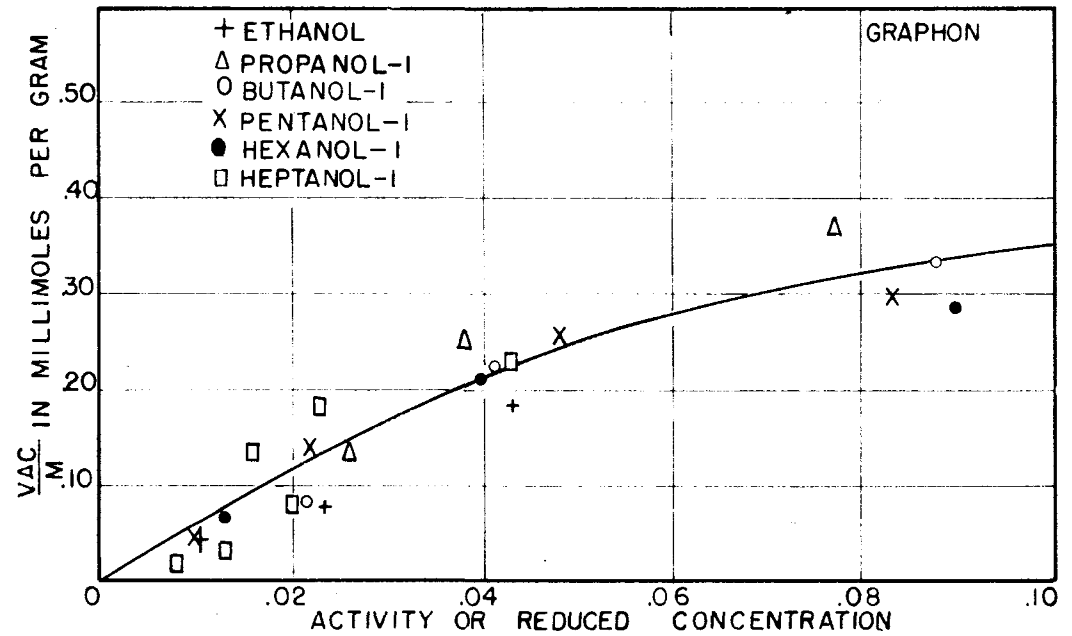

Fig. 5B Adsorption of Normal Alcohols on Graphon

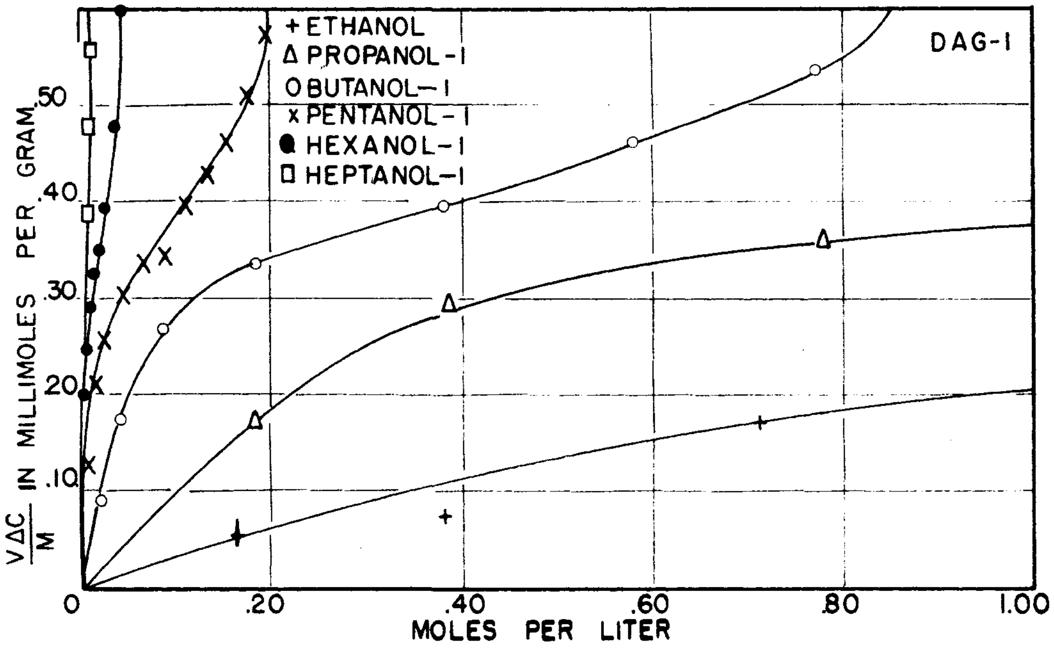

Fig. 6A ADSORPTION OF NORMAL ALCOHOLS FROM AQUEOUS SOLUTION ON DAG — 1

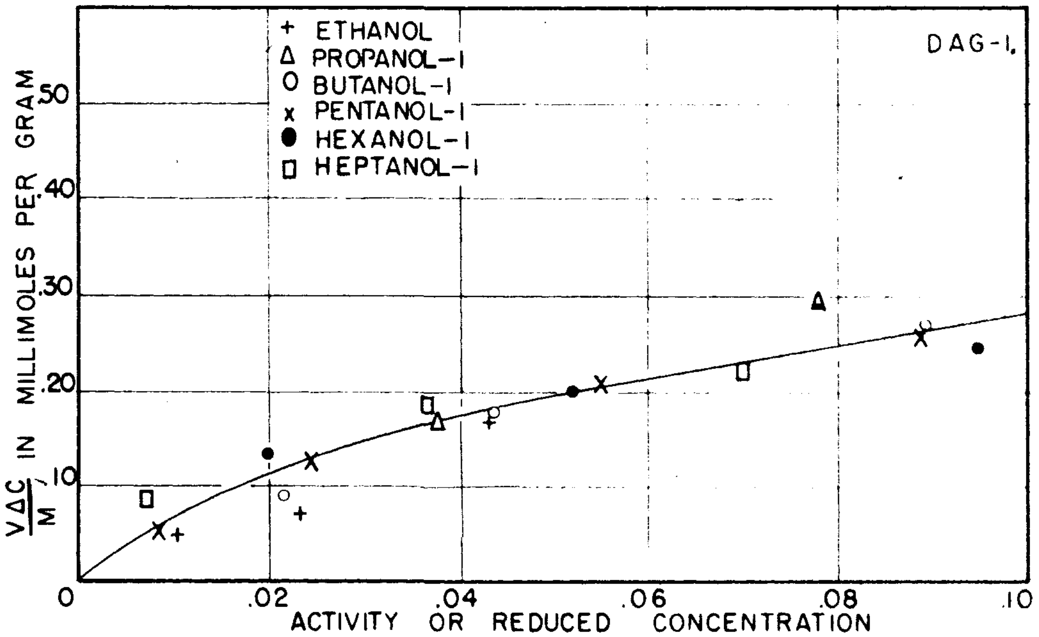

Fig. 6B Adsorption of Normal Alcohols on DAG-1

in conjunction with activity and solubility values for the acids and alcohols, Traube's rule will be discussed in some detail.

Among Traube's original observations (30) was the observation that for very dilute solutions the decrease in surface tension, F, is proportional to the concentration; that is, F/C is constant. Traube's rule, based on the further observation that the ratio F/C for dilute solutions increases three-fold for each CH_2 group added to the hydrocarbon chain in the molecule, was stated, in one of its forms, as follows: "The pressure exerted on the surface of a solution by dissolved molecules of homologous series of capillary active substances increases by the addition of a CH_2 group in the ratio $1:3:3^2:3^3$." Traube found this regularity most surprising, and did not conjecture over its meaning. A statement of Traube's rule more commonly encountered today is that the concentrations at which equal lowering of surface tension is observed decrease three-fold for each additional CH_2 group in a given series.

Langmuir (31) gave an explanation of Traube's observations based on a theory of the structure of the surface layer, making use of the kinetic equilibrium between molecules in the surface and those in the interior of the solution. Following the Langmuir treatment, we note that the rate of passage of molecules into the surface depends only on the concentration of the solute, while the rate of passage from the surface back into solution depends on the number of molecules in the surface and also strongly on the difference in potential energy of the molecule in the two states, the potential energy of the molecule being lower in the surface than in bulk solution. Expressing the decrease in potential energy when a mole of solute passes from the interior to the surface layer as λ, kinetic equilibrium between the surface and the solution requires that

$$q/C = K \exp(\lambda/RT), \tag{1}$$

where q is the amount of solute adsorbed at concentration C, and K is a constant.

From Traube's observation that F/C is constant for dilute solutions and the Gibb's equation

$q = -\frac{C}{RT}\frac{d\gamma}{dC}$, in which γ represents the surface tension, and since F/C is identical with $-\frac{d\gamma}{dC}$, we see that

$$q = F/RT. \tag{2}$$

The similarity of this equation with the ideal gas equation suggests a correspondence of F, the decrease in surface tension, with a PV term, or, in two dimensions, a πA term, where π is a two-dimensional surface pressure and A is the surface area. For treatments in which such a surface pressure is considered, the reader is referred to the work of Brown (32).

Combining equations (1) and (2),

$$F/C = k \exp(\lambda/RT),$$

and applying this equation to any two members of a homologous series,

$$(F/C) / (F/C)' = \exp [(\lambda - \lambda')/RT].$$

Traube's rule, resulting from his experimental data, allows the evaluation of $(\lambda - \lambda')$, which is the difference in the decreases in potential energy when a mole of each solute separately is moved from bulk solution to the surface layer. This difference is 651 calories per mole for neighboring members of a series.

Using assumptions similar to those above for dilute solutions, Langmuir arrived at a value of 710 calories per mole for this difference in potential energy. He thus came to the following conclusions from the experimental data. 1) Each CH_2 added to the hydrocarbon chain of a fatty acid increases the potential energy in very dilute solutions by the constant amount of 710 calories per mole. 2) This must mean that each CH_2 added occupies a similar position, in regard to the structure of the surface layer, as the CH_2 groups already present. 3) Since the range of the forces involved is small compared with the size of the molecule, it must, therefore, follow that each CH_2 group in these dilute solutions forms a part of the surface. 4) At higher concentrations, the hydrocarbon chains no longer lie flat on the surface, but gradually pass over into a vertical close-packed structure.

In forming these conclusions, Langmuir assumed that the increase in λ upon addition of a CH_2 group was due to a decrease in potential at the surface layer; that is, each CH_2 group, in entering into the surface layer, loses a definite, and equal, amount of energy which thus, in a manner of speaking, "pulls" the molecules to the surface. From such a viewpoint, the amount of adsorption would be determined by the surface structure, and also the standard molar free energy of adsorption would be proportional to the chain length in a homologous series. Results of the present investigations allow an explanation of the observed effects from a different standpoint, and, indeed, indicate that Langmuir's model of surface structure for dilute solutions is incorrect, although his model for concentrated solutions still serves adequately to explain phenomena observed in that region.

Examination of Figures 1 to 6, showing the surface excesses of acids and alcohols on carbon surfaces in equilibrium with solutions of low concentration, reveals not only the striking difference in the isotherms when plotted against solution concentration and against solution activity, but, most important, reveals that for a given adsorbent and homologous series, the surface excess depends only on the absolute activity of the solute in the activity range between zero and one-tenth. Average deviations of the isotherms of the different members of a homologous series from a mean isotherm were only five to ten per cent, varying somewhat with different adsorbents. This dependence on activity alone indicates that over this concentration range the standard molar free energy of adsorption is the same for all members of a homologous series, and suggests that the adsorption forces of the solid act on the same functional group for each member of the homologous series.

The constant difference of 651 or 710 calories per mole in potential energy for each CH_2 group added to the chain is due, then, to an increase in chemical potential of the molecule in the bulk solution, rather than to a surface effect as pictured by Langmuir. It is not surprising that this increase should be nearly linear with chain length, for, in dilute solutions, the same area of additional water-hydrocarbon interface is created for each CH_2 group added. In the language of a previous paragraph, the observed relative effect is due to an increased tendency of water molecules to "kick" the acid or alcohol molecules from the interior of the solution (the activity of the solute increasing in a regular manner with increasing chain length), rather than to an increased effect of the surface itself.

Applying this viewpoint to surface tension depressions, since it seems logical that if surface excesses at solution-solid interfaces are governed by the activities of the solute, excesses at solution-air interfaces should also be so governed, we see that the condition necessary to bring about the three-fold decreases observed by Traube is simply that, in very dilute solutions, the activity coefficients of neighboring members of a series be at a ratio of 3:1. The observed limiting activity coefficients at extreme dilution shown by the data of Giacalone (25) are 3, 9, and 30 for acetic, propionic, and butyric acid, respectively. The initial slopes of activity curves of F. A. Miller (33) are at a ratio of 1:2.3:8.5 for methanol, ethanol, and propanol-1, respectively. This condition is, therefore, very nearly fulfilled, and Traube's rule for dilute solutions has its basis entirely in the activities of the solutes in solution.

Although Traube's data for homologous series did not extend to the members which are sparingly soluble in water, the progression would be expected to continue in much the same manner as through the soluble members, since the activity coefficients increase by the approximate ratios 1:4:17:67 for butanol-1, pentanol-1, hexanol-1, and heptanol-1, respectively, and 1:4:17 for valeric acid, caproic acid, and heptylic acid, respectively. These approximate activity coefficients are taken as the reciprocals of the solubilities of these substances in water, since the absolute activities of slightly-soluble substances are very nearly equal to their reduced concentrations.

Traube made the further observations that as the concentrations of the solutions increased F ceased to be proportional to C, but increased more slowly than C, and that the concentration at which this occurred was lower the longer the chain. These observations are also readily explained from activity considerations, along with considerations of surface capacity. This effect merely follows from the shapes of activity versus concentration plots, F being proportional to C only as long as the activity is approximately proportional to C and there is sufficient free surface available so that the entrance of additional solute molecules is not restricted by those already at the surface. The maximum molar concentration below which the activity is nearly proportional to C is lower the longer the carbon chain.

Numerous cases of the reversal of Traube's rule and exceptions to Traube's rule have been reported (7) (17) (34), especially in cases of adsorption on activated charcoal. The explanation of most such cases is found in Iliin's statement (35) that for purely physical adsorption processes, the dominant role in reversal of adsorption series is played by the extent of ultrapores in the adsorbent which do not admit large molecules. Dubinin and his co-workers have found with many charcoals in solutions of slightly soluble alcohols that the maximum volumes adsorbed were substantially identical for all the alcohols, being a simple filling of capillary pores by alcohol molecules. Kiselev and Shcherbakova (16) observed this effect for both alcohols and acids; however, they noticed that at low concentrations the adsorption followed direct Traube series, as would be expected for pores accessible to all members of the series. It is apparent that a reversal of Traube's series would be expected from activity considerations in cases of solutions in non-polar solvents, in which the lower members of the series are less soluble than the higher members. This fact could be used to explain several of the "reversals" mentioned in reference (34).

In summary, it has been demonstrated that for a given adsorbent and type adsorbate, the surface excess adsorbed from dilute solutions is primarily a function only of the absolute activity of the solute. It has been shown that Traube's rule is a necessary consequence of this behavior.

D. Adsorption of the Immiscible Alcohols and Acids as a Function of Activity over the Entire Solubility Range

As is shown in Figures 7 to 12, the measured surface excesses of immiscible alcohols and acids invariably rise asymptotically as the saturation concentration is approached. This is in agreement with results obtained by Hansen (2) with similar systems, and is a consequence of the small amount of work required to remove the solute from solution to a separate organic-rich phase. The composition of the adsorbed phase is not necessarily that of the organic liquid saturated with water, for activities and solubilities may be greatly altered by the potential field of the adsorbent. As will be pointed out later, however, the adsorbed phase must

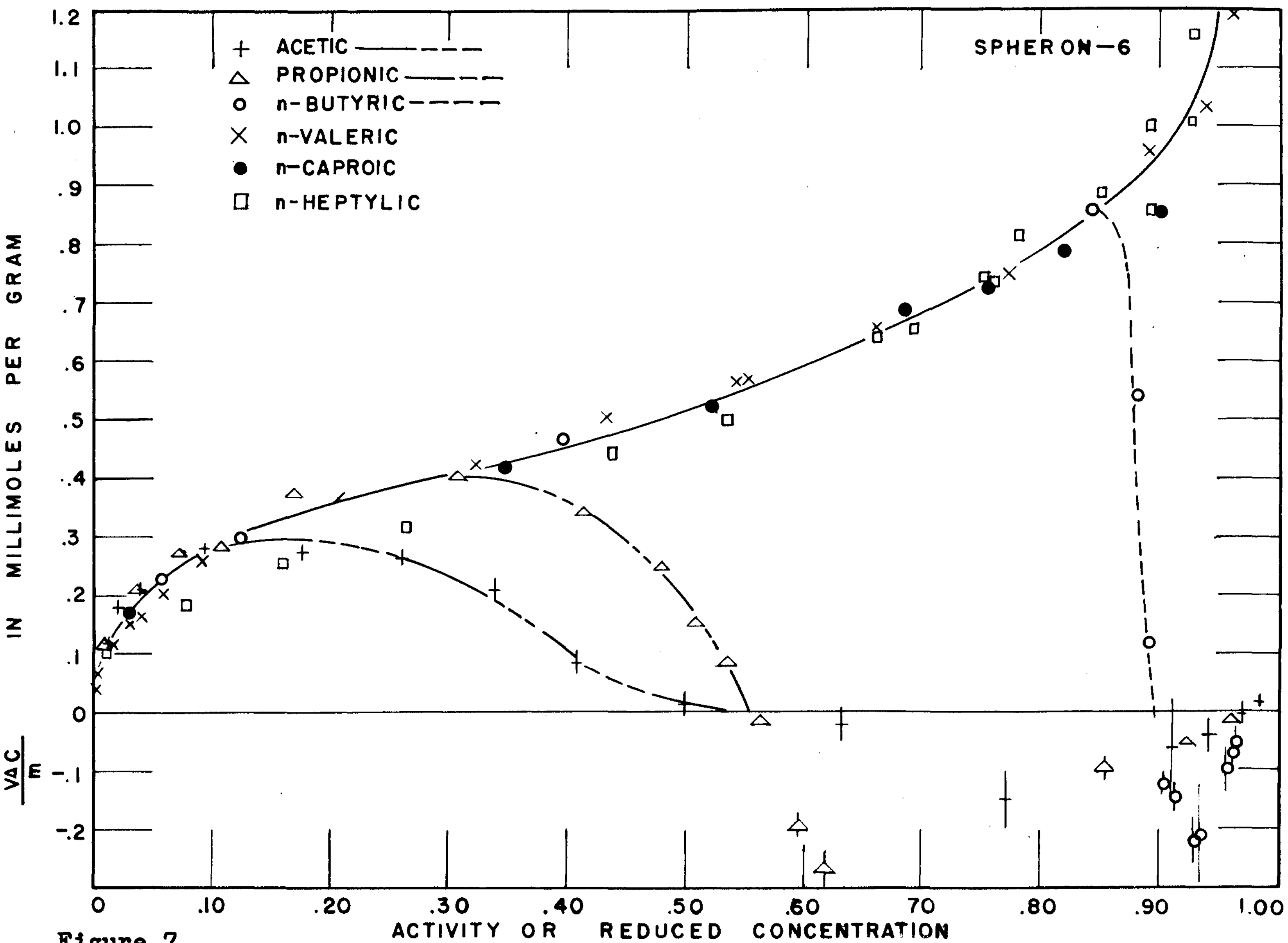

Figure 7

ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON SPHERON-6

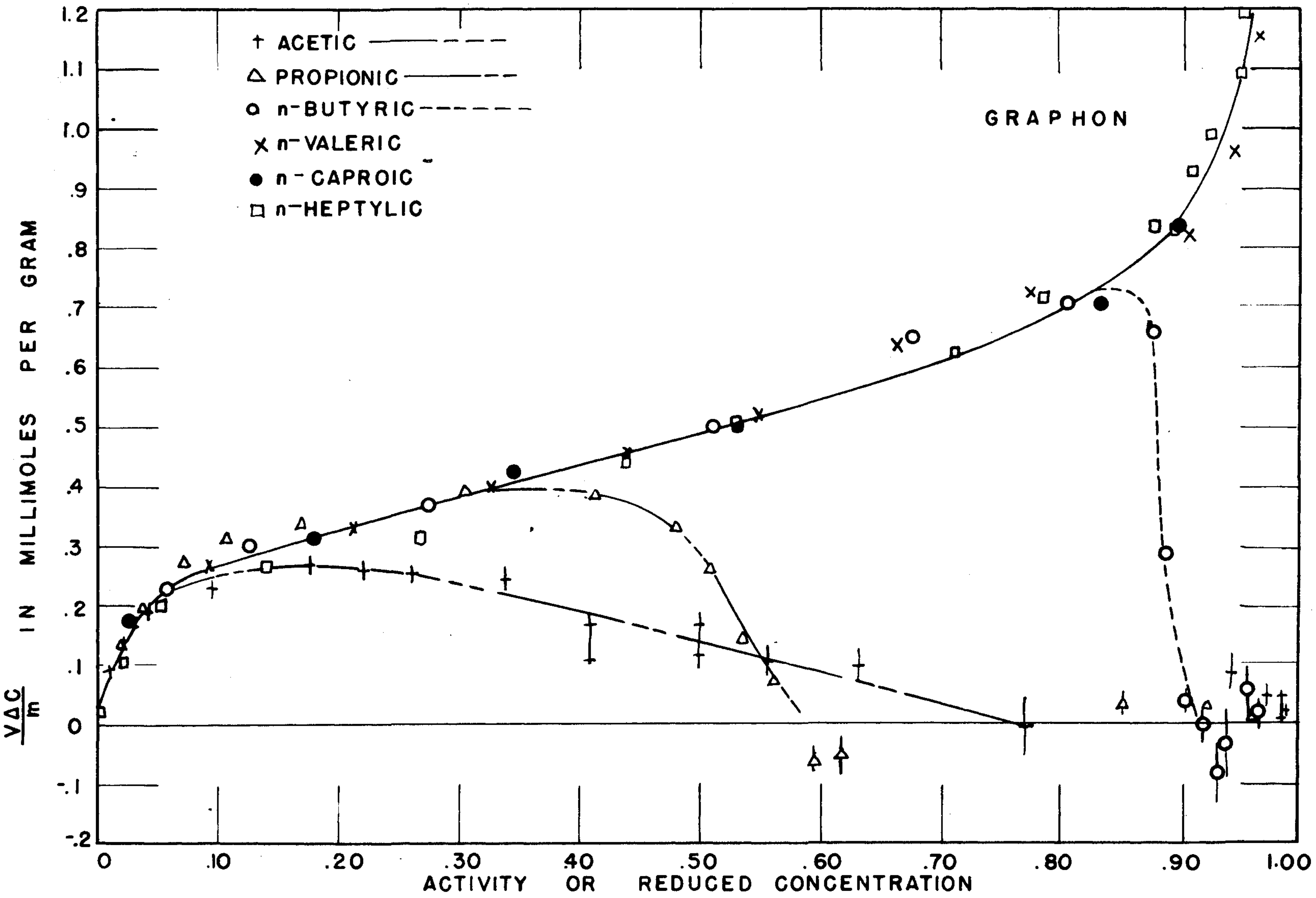

Figure 8.

ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON GRAPHON

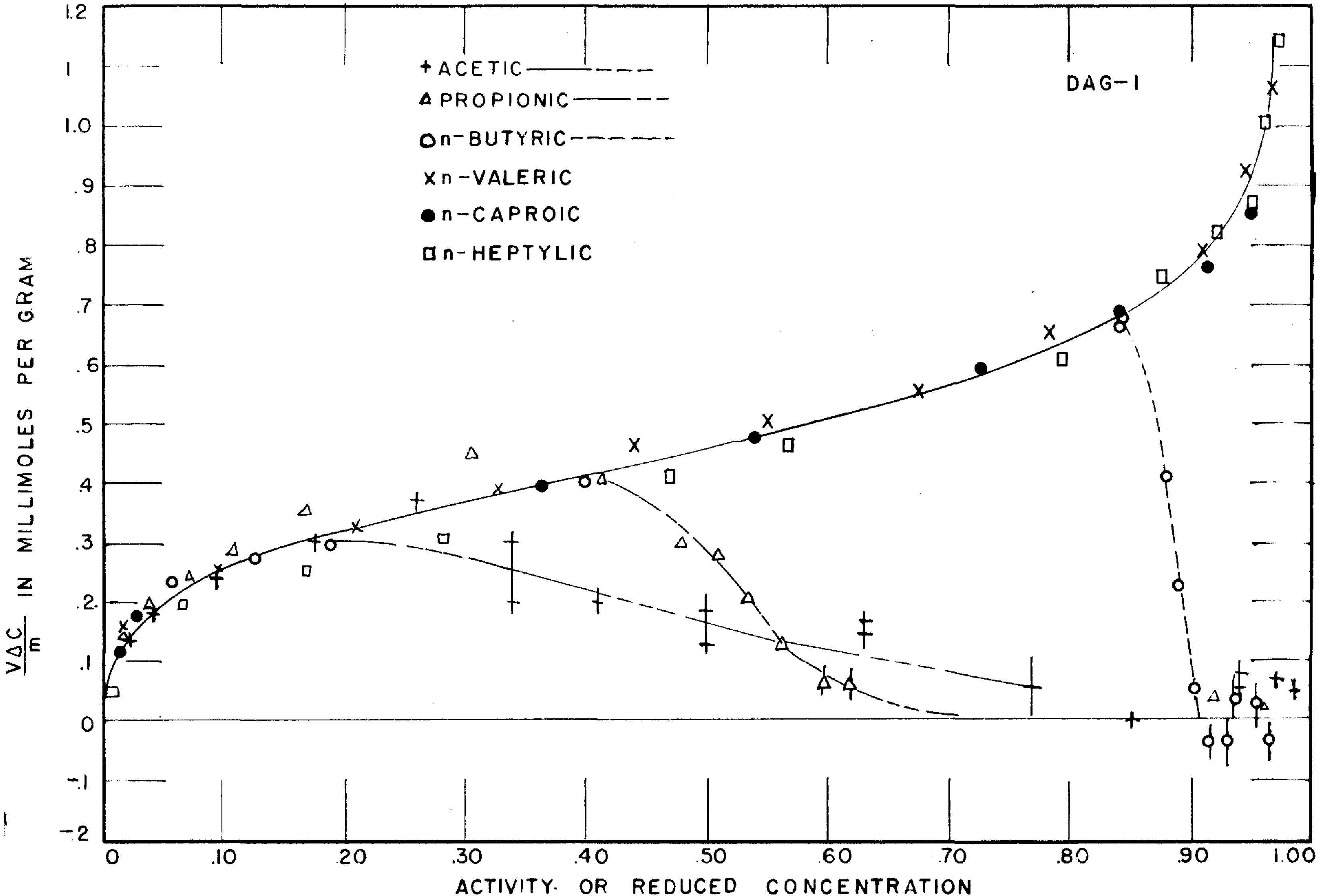

Figure 9.

ADSORPTION OF FATTY ACIDS FROM AQUEOUS SOLUTION ON DAG-1

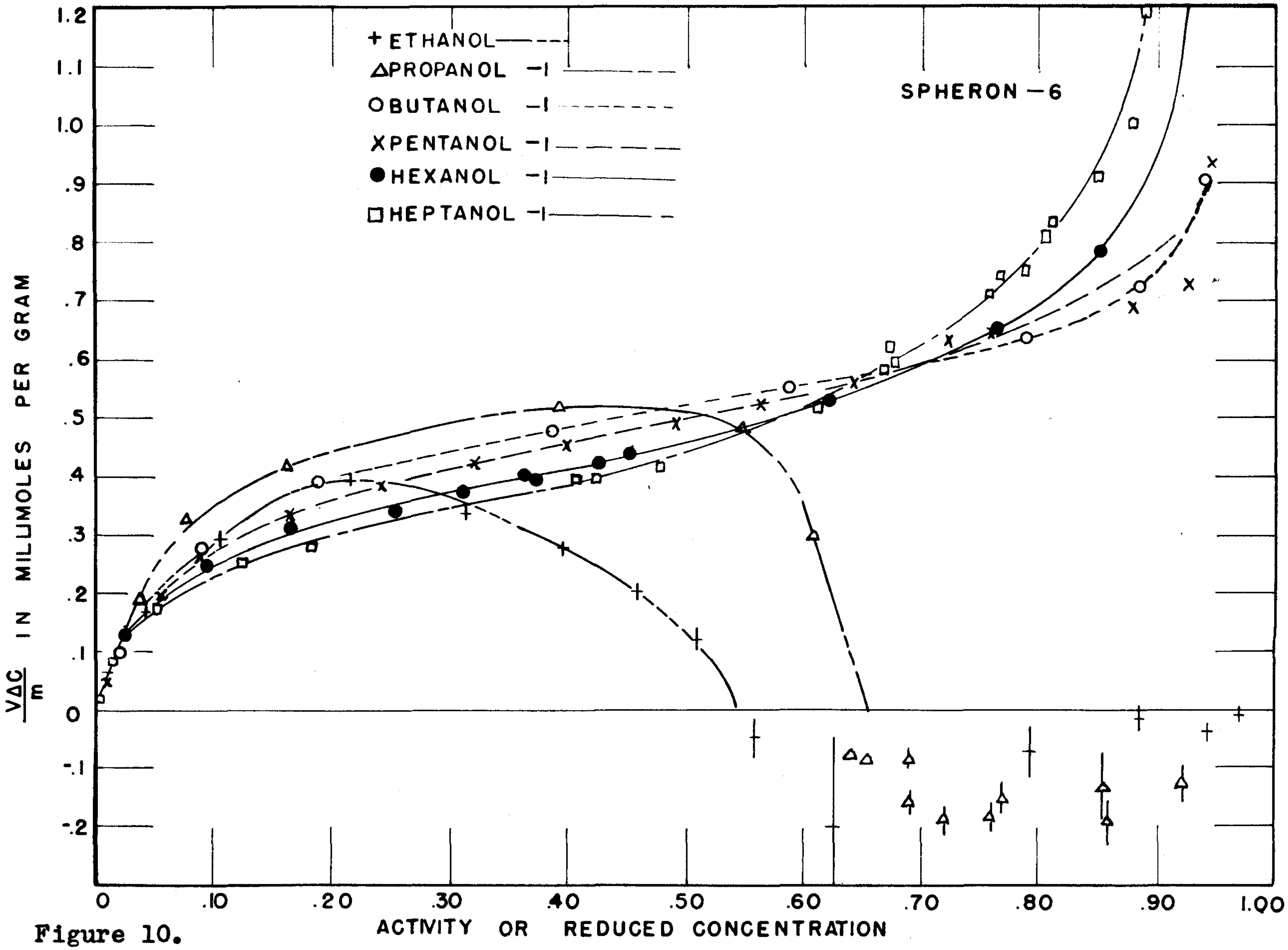

Figure 10.

ADSORPTION OF NORMAL ALCOHOLS FROM AQUEOUS SOLUTION ON SPHERON-6

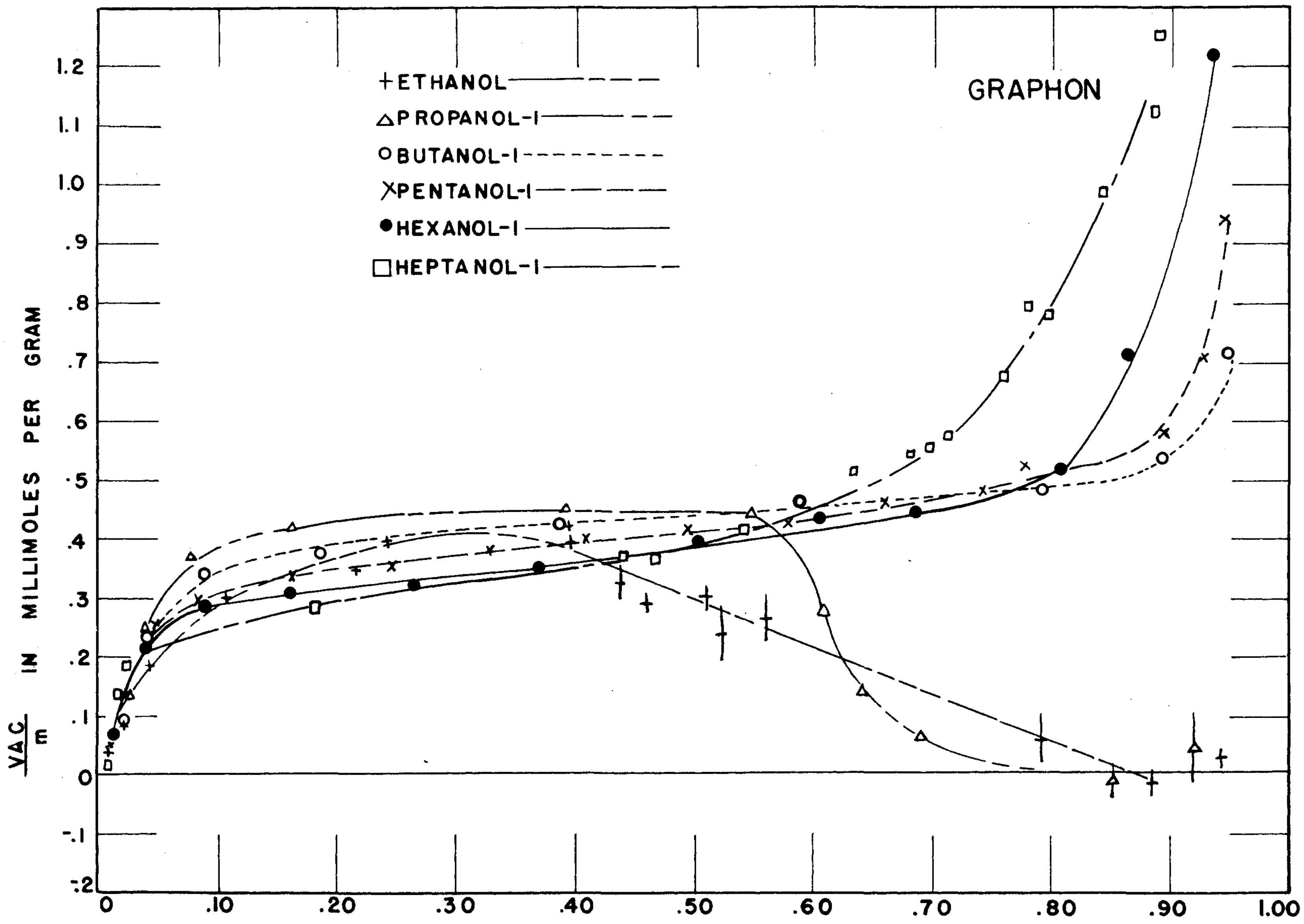

Figure 11.

ADSORPTION OF NORMAL ALCOHALS FROM AQUEOUS SOLUTION ON GRAPHON

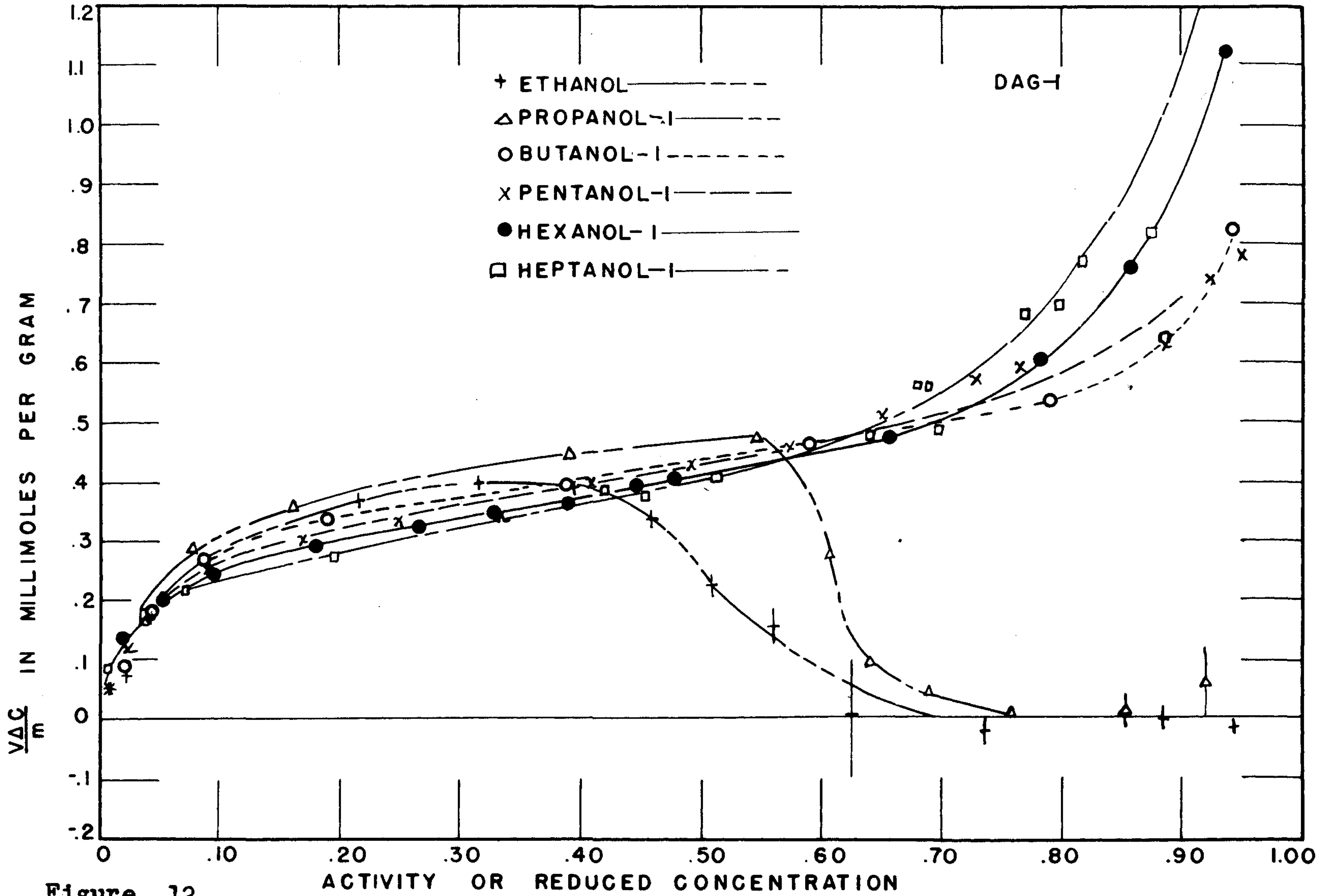

Figure. 12.

ADSORPTION OF NORMAL ALCOHOLS FROM AQUEOUS SOLUTION ON DAG—I necessarily extend more than one molecular diameter from the adsorbent surface.

The best curves drawn through the individual points for valeric, caproic, and heptylic acids practically coincide over most of the activity range with each of the three adsorbents, as is shown in Figures 7 to 9. The only marked exception is heptylic acid at lower concentrations, the deviation being greatest on Spheron-6.

While the adsorption of the acids appears to be independent of chain length, Figures 10 to 12 show a systematic variation in adsorption of alcohols with increased chain length. At low concentration the order of increasing adsorption is that of decreasing chain length; the isotherms cross, however, at a reduced concentration of about .65 and the order is reversed above this concentration. Arguments involving such properties as molecular volumes could be invoked to explain the variations observed in the alcohols. At high concentrations, the order of the alcohols might be explained by a greater degree of cooperative adsorption as the chains increased in length. The term cooperative adsorption is applied to an adsorptive process assisted by lateral interaction of the adsorbed molecules, and it would seem logical that this interaction may be proportional to the chain length. Any arguments involving molecular dimensions invoked for the alcohols should apply almost equally well to the acids, however, where little or no similar variation is observed.

For both the alcohols and acids, the adsorption on a particular adsorbent is seen to be primarily a function only of solute activity over the entire solubility range. Deviations from this rule are far greater with the alcohols than with the acids, and the alcohol deviations appear to be systemmatic.

E. The Form of the Isotherms of Soluble Acids and Alcohols

It is immediately obvious from Figures 7 to 12 that the isotherms of soluble acids and alcohols are fundamentally different in form from those of the slightly-soluble ones. This is a necessary consequence of the method of measurement, and would be true even if one component alone were adsorbed in the pure state at the solid surface. The isotherms shown indicate the "apparent adsorption", or surface excess, and, since the values are obtained by measuring changes in solution concentration, at high concentrations it would be physically impossible to obtain large positive surface excesses of the predominating component. For instance, in a solution which is 99 mole per cent alcohol and 1 mole per cent water, 50.5 per cent of the alcohol (half the volume of the original solution) would have to be removed (adsorbed as pure alcohol) in order to reduce the concentration of alcohol in the remaining solution by one mole per cent. Obviously, it would be impossible with soluble systems to obtain measured surface excesses which rise asymptotically in the manner of those for the slightly-soluble members of the series; in the slightly-soluble systems, the measured surface excesses do not differ greatly from the total amount of sorbate present at the surface (surface excess plus amount which would be present with no adsorption), since the solutions are dilute even at saturation, and the high measured values and asymptotic rise are, therefore, realizable.

As has been pointed out by Williams (8) and Ostwald and de Izaguirre (6), and well illustrated by Heymann and Boye (7), in adsorption from solution it is not "dry" or pure sorbate which constitutes the adsorbed phase; the solute is also adsorbed. Consequently, two types of apparent adsorption isotherms can occur from miscible binary liquid systems. After the isotherm for the component which is preferentially adsorbed passes through a maximum, it can drop off and approach the abscissa in a gradual or asymptotic manner, if this component is strongly adsorbed preferentially over the entire concentration range, or it can cross the concentration axis and pass through a minimum, showing apparent negative adsorption of this component, before finally reaching the zero value required as the concentration approaches pure liquid. The latter type is observed when both components are adsorbed with forces of the same order of magnitude. Both of these types are observed in Figures 7 to 12, the isotherms of both acids and the alcohols on both Graphon and

DAG-1 being of the first type, while those with Spheron-6 are the second type. These differences will be discussed below in conjunction with the observed adsorption of water from the organic phases of slightly-soluble acids and alcohols.

It should perhaps be noted that Elton (15) has recently published an argument which purports to show that if both components of a binary mixture have positive adsorption potentials, preferential adsorption of one component over the entire concentration range cannot occur. Elton's argument was developed from the equations for equilibrium between the adsorbed layer and the solution, the activities being related by

$$a_A^s / a_A = \exp \left\{ \left[(\mu_A)_0 - (\mu_A^s)_0 \right] / RT \right\} \qquad (3)$$

where $(\mu_A)_0$ is the chemical potential of component A in an arbitrarily defined standard state in solution, and $(\mu_A^s)_0$ is the corresponding chemical potential in a suitable standard state in the surface layer. A similar equation holds, of course, for component B of the binary system. The term $(\mu_A)_0 - (\mu_A^s)_0$ may be considered as the adsorption potential of component A. By analogy to work of Fu, Hansen, and Bartell (12), Elton writes, in the limit as X_A tends to zero,

$$(X_A^s / X_A)_0 = (a_A^s / a_A)_0 \qquad (4)$$

where X_A and X_A^s are the mole fractions of component A in the solution and the adsorbed phase, respectively. Again, a similar equation could be written for component B. Elton also states that for plots of X_A^S vs X_A to show complete preferential adsorption of component A, the adsorption potentials of A and B must be opposite in sign, and these requirements inserted into Equation (3) and its corresponding equation for component B lead one to the conclusion that, if both components have positive adsorption potentials, no complete preferential adsorption can occur. Elton's Equation (4), however, assumes the activity coefficient of the surface phase and the activity coefficient of the bulk phase to be similar functions of concentration. This assumption is not necessarily true and, in fact, is probably not true since the activity coefficients of the adsorbed phase calculated by Fu, Hansen, and Bartell are not monotonic while the coefficient in bulk solution is a monotonic function of concentration. Also, in asserting that complete preferential adsorption cannot occur unless the adsorption potentials are opposite in sign, Elton neglects the fact that adsorption of the two components is competitive, and one component can be adsorbed by displacing the other. The complete preferential adsorption of miscible alcohols and acids on Graphon and DAG-1 indicated in this work does not imply a negative adsorption potential for these adsorbents towards water; it does, however, show that this potential is small compared with the adsorption potentials of aliphatic acids and alcohols.

Isotherms similar in form to those indicated for acetic acid and propionic acid in Figure 9, showing positive adsorption of the acid over the complete isotherm, were found by Nestler and Cassidy (36) for adsorption on activated charcoal of acetic, propionic, and butyric acids from solution. Schmidt-Walter (37) also had found the complete isotherm for the adsorption of acetic acid on charcoal from aqueous solution to be of this type. These results indicate that the charcoals used did not contain micropores of such size as to admit water and exclude the alcohol molecules, and also that the charcoal surfaces had much lower affinity for water than for the alcohols.

The isotherms shown in Figures 7 and 10 for the soluble alchols and acids on Spheron-6 are, in contrast to those with the other adsorbents, of the sigmoid type, showing definite negative adsorption of the organic component at high concentrations. When one considers the ability of a single adsorbent to selectively adsorb one component from a binary mixture at low concentrations of that component and also selectively adsorb the other component when it is present in low concentrations, he soon arrives at one of two apparently logical explanations of such behavior. One might assume either that there exists a preferred composition of the adsorbed phase, and the change in bulk concentration is merely the result of adsorption of a phase of this composition, or that there are different areas on the adsorbent surface which have widely different affinities for the two components. Work of Bartell and Lloyd (38) indicates that the former explanation is not correct, for different preferred compositions would be required for the same binary system on different adsorbents. If the latter explanation is correct for the systems used in this work, the mole fractions at which the isotherms crossed the concentration axis should be approximately the same with the different organic acids and alcohols. Unfortunately, these particular isotherms are not sufficiently accurately defined in this region for a rigid test of the latter assumption. Data discussed below, however, give definite indication that there are areas on Spheron-6 which have specific affinity for each of the components of these aqueous systems.

In Figures 7 to 12, the courses of the isotherms for the miscible systems are not delineated over the complete activity range. In the high activity ranges (approaching pure alcohol or acid), the points are so scattered that, in most cases, the isotherms are not well defined in this region. This is partly due to the lower sensitivity of the analytical method in these regions, as indicated by the analytical uncertainties shown on the graphs, and partly due to the unusually poor reproducibility of points at these high concentrations, as has been described previously. None of the individual points shown, however, is physically impossible.

In Figures 7 and 10, the "negative adsorption" values of -.25 millimoles for propionic acid, -.20 millimoles for butyric acid, and -.18 millimoles for propanol at activities of 0.62, 0.93, and 0.86, respectively, would correspond, respectively, to the adsorption of an amount of water equal to about 1/2, 3/4, and 3/8 of a close-packed monolayer of water at the surface, assuming a molecular area for water of nine square Angstroms. These are the extreme cases of negative adsorption observed. The least likely of the scattered points at high concentration shown in Figures 8, 9, 11, and 12, indicating complete positive adsorption of the miscible acids and alcohols, is the value of 0.06 millimoles for acetic acid at activity 0.985 (concentration of 17.123 moles per liter) in Figure 9. In order for the volume of liquid contained in the surface layer to be able to furnish sufficient water molecules to the bulk solution to bring about the observed change in bulk concentration, all the water would have to be removed from a surface layer nine Angstroms thick, these molecules serving to dilute the bulk solution. An adsorbed layer of this thickness is not unreasonable, corresponding to only two molecular layers of acetic acid, but this is an absolute minimum value since the calculation is based on the assumption that pure acetic acid constitutes the adsorbed phase, and it seems very unlikely that this should be the case. Actually, it seems more likely that the observed apparent positive adsorption at very high concentrations of soluble acids shown in these figures is due, rather than to the preferential adsorption of large amounts of acid, to the possible extraction of a small amount of water from the surface of the adsorbent itself, the water from this source thus serving to dilute the solution. Reference to the earlier discussion of the nature of the adsorbents used serves to show that this explanation is by no means unreasonable, and it is apparent that such small amounts of extractable water introduced on the adsorbent would affect the surface excess values obtained by the usual procedure only at high solution concentration.

While the high-concentration ends of the adsorption isotherms of the soluble acids and alcohols are not well defined for the reasons stated, the general form of the complete isotherm is indicated and fairly well documented in all cases.

F. General Comparison of Alcohols and Acids in Their Adsorptive Behavior

Comparison of Figures 7 with 10, 8 with 11, and 9 with 12, using a median isotherm of those shown for the various immiscible alcohols in each case, shows the adsorption of alcohols and acids to be almost identical with each other over the entire activity range. The composite acid isotherm on Graphon is not quite so flat as that for the alcohols, having slightly lower adsorption at low concentrations and higher adsorption at reduced concentrations between 0.5 and 0.8. All three adsorbents show the acid adsorption slightly higher than that of the alcohols at reduced concentrations around 0.65, but for Spheron-6 and DAG-1 both the shapes and corresponding magnitudes of the isotherm for the acids are nearly identical with those of the isotherm for the alcohols.

While only two types of molecules have been tested, these data indicate that variation of the functional group on an aliphatic chain has only a secondary effect on the amount of adsorption at carbon surfaces from aqueous solutions of the organic substance at a given absolute activity. Specific interaction between organic adsorbate and carbon surface, if any, would appear to involve primarily the alkyl group rather than the functional group. Investigation of adsorbates having a wider variety of functional groups would be desirable, however, before making this generalization with complete confidence.

G. Adsorption of Water from Organic Phases. The Marked Difference in the Adsorbents in their Affinity for Water

In measurements of the adsorption of water from the organic phases of the alcohols and acids which are not completely miscible with water, it was seen that neither Graphon nor DAG-1 exhibited any preferential adsorption of water at any concentration, while Spheron-6 did show a definite adsorption of water in all cases. These results are given in

Tables 13 to 16, and are in qualitative agreement with the isotherms of the miscible systems, shown in Figures 7 to 12, in which only Spheron-6 shows a definite "negative adsorption" of the organic component at very high concentrations, and which indicate that the adsorption potential for organic molecules is much higher than that for water at the surfaces of Graphon and DAG-1.

The adsorption of water from the organic phases shown by Spheron-6 followed, in all cases, isotherms of pronounced Langmuir type. This is in sharp contrast to the isotherms for the adsorption of the organic components from aqueous solutions, which are sigmoid in shape, rising steeply as saturation concentration is approached. No rise in the water isotherms is observed even at water concentrations above 99 per cent saturation. The Langmuir character of these isotherms, that is, the rise in adsorption to a constant limiting value as the concentration increases, indicates that there is a definite and limited area with specific affinity for water molecules. From the present data, one cannot rule out the possibility that Spheron-6 contains minute cracks, as has been suggested by Pierce and his co-workers (39) in the interpretation of their data for the adsorption on Spheron-6 of water and ethyl chloride from the vapor phase. Such cracks or capillaries would have to be smaller than implied by Pierce, however, for they would have to be of such size as to admit water molecules while excluding even nitrogen molecules, since surface areas measured by nitrogen adsorption agree with microscopic areas. It has been claimed by Maggs (40) that pore constrictions of such dimensions do exist in coals, much of the internal surface area being made inaccessible to nitrogen at the low temperatures at which measurements of surface areas by nitrogen adsorption are made. Thus, it could be argued that Spheron-6 contains minute pores of such size that water molecules can be admitted, but alcohol and fatty acid molecules are excluded, and it is the filling of these pores with water which gives rise to the Langmuir-type isotherms observed. To explain the different behavior of Graphon, which was made by strong heating of Spheron-6, one needs only to assert that the pores of Spheron-6 are destroyed by the heating process.

An alternative explanation of the Langmuir form of these isotherms is to assume the existence of specific sites on the surface of Spheron-6 which have a strong affinity for water molecules, and when all these sites are occupied, no further specific adsorption of water occurs. High temperature evacuation studies of Anderson and Emmett (3), the results of which are shown in Table 22 for Spheron-6, show that oxygen complexes do exist on the carbon surface, as had been postulated previously by numerous workers (references obtainable from Anderson and Emmett's article). A certain number of these complexes could logically be of a type which would have a strong attraction for a water molecule. Oxygen complex structures similar to the functional grouping of phthallic anhydride may constitute the active sites required to give the Langmuir-type water isotherms which are observed.

Table 22

Gases evolved from Spheron-6 *(cc., S.T.P., per gram)

Temp. °C.	H_2	CO	CO_2	H_2O (g)
25-300	0.04	0.13	0.62	2.16
300-600	0.16	7.71	2.98	2.48
600-900	17.60	19.35	1.58	2.87
900-1200	35.42	2.62	0.12	0.06
Total	53.22	29.81	5.30	7.57

*From the data of Anderson and Emmett, J. Phys. Chem. 56, 753 (1952)

The inability of Graphon to adsorb water from solution as does Spheron-6 would indicate that, while the surface of Graphon probably retains some oxygen complexes, the type of complex which possesses specific affinity for water is removed by graphitization. As was pointed out by Pierce and Smith (41), the initial heats of adsorption of nitrogen or hydrocarbons on Graphon is less than that on Spheron-6, indicating that graphitization may also destroy the sites which are most active toward adsorption of these substances. The difference between Graphon and Spheron-6 in their water affinities as observed in this work is in agreement with recent results of Pierce, Smith, Wiley, and Cordes (39) concerning the adsorption of water vapor by these adsorbents. Their investigation showed that Graphon adsorbed almost no water vapor at relative humidities less than 0.95, while Spheron-6 adsorbed appreciable amounts at relative humidities as low as 0.55. As seen above, this difference in adsorbent properties can be explained to nearly equal satisfaction whichever of the two mechanisms one postulates for the adsorption of water by Spheron-6; in one case, graphitization merely closes minute pores in the adsorbent, while in the other case it removes active surface oxides. Work of Anderson and Emmett (42) showed that Spheron-6 which had been "degassed" by evacuation in an induction furnace at temperatures up to 1200° C., and which was believed by the authors to be fairly free of oxygen complexes, adsorbed less water vapor than before "degassing", and showed no adsorption of water at relative pressures less than 0.3. These authors again point out the fact that the removal of oxygen complex from the surface of carbon black tends to decrease the amount of water adsorbed at a given reduced pressure and increase the relative humidity required to produce a given adsorption. In the production of Graphon from Spheron-6, then, it is probable that surface oxides are removed by the graphitization, and this alone suffices to explain the observed difference between these adsorbents in their affinities for water.

In either of the above explanations of the Langmuir character of the water isotherms for Spheron-6, the condition described would require that the same limiting amount of water be adsorbed from all the different organic liquids in all cases in which the adsorbent received no special treatment. Examination of Tables 13 to 16 does not show this to be true. The discrepancy is believed to be due to inaccuracy in measurement, since the interferometric method of analysis is relatively insensitive for these systems and especially because of large uncertainties in the interferometer zero-point readings for the organic liquids, as described elsewhere in this dissertation. Different relative humidities during weighing of the samples may also have influenced these results, since more water may have been adsorbed from the atmosphere during weighing on humid days.

H. Effect of Evacuation of Adsorbent Immediately Before Use

Early preliminary experiments showed no difference in adsorption of butanol from 0.6 molar aqueous solutions when the adsorbent was evacuated immediately before exposure to the solution. Later experiments with solutions containing very small quantities of water in the various alcohols and acids, however, gave quite erratic results, and it was believed that this was largely due to the adsorption of varying quantities of water from the atmosphere during the weighing and transferring of the adsorbents before exposure to the solutions. The amount of water introduced into the system in this manner would be entirely negligible when the solution under investigation contained more than a few per cent water, but would have significant effect upon measurements with solutions of very low water content. Tables 13 and 15 show that evacuation of Spheron-6 at about 180° C. immediately before addition of solution increased the amount of water adsorbed. It is interesting to note that, while there was a significant difference when Spheron-6 was evacuated, there was little or no change in adsorptive properties upon evacuation of the adsorbents Graphon and DAG-1. Systems which were examined for such changes include four concentrations of water in hexanol on DAG-1 and eight on Spheron-6, three concentrations of water in butanol on DAG-1 and seven on Spheron-6, four concentrations of water in propanol on DAG-1, three on Graphon, and six on Spheron-6, and four concentrations of water in butyric acid on DAG-1, five on Graphon, and seven on Spheron-6. In no case was there indication of adsorption of water from the alcohol or acid on either Graphon or DAG-1, but water was adsorbed by Spheron-6 from the organic liquid in all cases.

It is seen that in the adsorption of water from butanol on Spheron-6, evacuation of the adsorbent increased the amount of water adsorbed by a constant difference of about 0.125 millimoles per gram, the original adsorption having reached about 0.95 millimoles per gram. This difference corresponds to sufficient water to cover about 12 per cent of the adsorbent surface. In the adsorption of water from hexanol by Spheron-6, evacuation raised the points about 0.3 to 0.4 millimoles per gram, with the original adsorption about 0.7 millimoles per gram. Caution must be used in attaching too much significance to these values, because of the uncertainties mentioned above; the general effect of increased water adsorption, however, is definite and real. The failure of evacuation to cause any change in water adsorption isotherms of Graphon or DAG-1 is simply a result of the inability of these substances to adsorb water vapor from the atmosphere to any appreciable extent, so no removable water was introduced into the systems on the non-evacuated adsorbent in these cases. As mentioned above from the work of Smith, _et al_., Graphon adsorbed almost no water vapor at relative humidities less than 0.95, while Spheron-6 adsorbed appreciably at relative humidities as low as 0.55. This latter figure was often exceeded to varying degrees in the laboratory during the course of this work. In no case was the Graphon exposed to relative humidities approaching 0.95.

As a check on the lack of any effect by such evacuation upon the isotherms for adsorption of alcohols and acids from solutions of higher water content, one point on the isotherm for aqueous pentanol (reduced concentration about 0.5) adsorbed on Spheron-6 was repeated with evacuated adsorbent. This point was found to fit nicely on the original isotherm.

The increased adsorption of water on Spheron-6 after mild evacuation was probably merely a replacement at the surface adsorption sites of water which was pumped off in the evacuation. The data taken by Anderson and Emmett (3) during evacuation of Spheron-6 at increasing temperature (see Table 17) show that, while considerable quantities of water vapor are pumped off at low temperatures, most of the CO_2 comes off at 300-600° C., the CO at 600-900° C., and the H_2 at 900-1200° C. at the temperature at which our samples were evacuated (ca 180° C.), therefore, the effect of evacuation was probably mostly a simple removal of water vapor, leaving the surface oxides relatively undisturbed. Thus the evacuated samples not only retained their ability to adsorb water, but adsorbed additional water to replace that which had been pumped off.

I. General Comparison of Adsorptive Behavior of Different Carbon Adsorbents

The specific surface areas of Spheron-6, DAG-1 and Graphon are in the ratio 1.00 : 0.90 : 0.69. If, for a given adsorbate at a given concentration, intensive characteristics of the adsorption regions were identical for these adsorbents then the measured surface excesses should have been in the same ratio. Deviations from this ratio should then be attributed to variation in specific surface characteristics of the adsorbents.

The marked differences in the adsorption of water by these adsorbents at low water concentrations have already been noted and explanations for these differences in terms of specific surface characteristics have been advanced. Comparison of surface excesses of alcohols and acids at low activities presented graphically in Figures 1B-6B shows that, in the adsorption of acids over the low activity range, isotherms for the three adsorbents are substantially identical; alcohol adsorption isotherms over this same range on Spheron-6 and DAG-1 are substantially identical while the isotherms on Graphon lie somewhat above those on the other two adsorbents. In view of the different surface areas of the adsorbents these facts again reflect differences in specific surface characteristics of the adsorbents. In particular, Graphon adsorbs considerably more organic adsorbate on a surface excess per unit area basis than the other two adsorbents, reflecting a greater energy of interaction between adsorbate and surface in the Graphon case. This also suggests that the graphitization may have destroyed surface oxide complexes existing on Spheron-6, as suggested by the work of Anderson and Emmett (3), for such complexes could be presumed to hold water in preference to organic solute by hydrogen bonding. On this basis it is necessary to assume that DAG-1 has a specific surface character intermediate between Spheron-6 and Graphon, or else that its effective area for adsorption of organic solutes is less than that for adsorption of nitrogen. Adsorption of organic solutes at absolute activities greater than 0.1 involves increasingly multimolecular adsorption, as will be shown in the next section of this thesis. It might therefore be expected that at higher activities the adsorption isotherms would reflect less and less specific surface characteristics as increasing numbers of adsorbate molecules are held at distances several Angstroms from the carbon surfaces. Comparison of Figures 7 to 12 shows that the adsorption of both alcohols and acids by Spheron-6 is higher than the adsorption of these same adsorbates by Graphon and DAG-1 in the high activity range, as would be expected from surface area considerations. Isotherms for adsorption by Graphon, however, appear to lie slightly above corresponding isotherms for adsorption by the higher area adsorbent DAG-1, which is difficult to explain without attributing inaccessible regions (micropores) to the latter adsorbent.

In general, the varying specific surface characteristics of the three carbon adsorbents markedly affect the adsorption of water from binary solutions of low water concentration; the effect of these characteristics on the adsorption of organic solutes from dilute aqueous solution appears to be significant but small compared to the absolute activity factor previously discussed.

J. Multimolecular Adsorption

Since the surface areas of the three adsorbents are 114.0, 78.7, and 102.4 square meters per gram, respectively, for Spheron-6, Graphon, and DAG-1, it is readily calculated, assuming a minimum molecular area of 20.5 square Angstroms for all the acids and alcohols, that a close-packed monolayer of acid or alcohol would contain 0.924 millimoles per gram of Spheron-6, 0.638 millimoles per gram of Graphon, and 0.830 millimoles per gram of DAG-1. The molecular cross-sectional area assumed is that found for fatty acids by the film-balance technique, as reported by Adam (14). The value similarly found for alcohols is 21.6 square Angstroms, so the above quantities can be used a maxima for the amount of acid or alcohol contained in a monolayer. Comparing these maxima with the measured surfaces excesses shown in Tables 1 through 12, and plotted in Figures 7 through 12, it is seen that these maxima are exceeded by measured values in the following systems:

Spheron-6	Graphon	DAG-1
	Butanol-1	
Pentanol-1	Pentanol-1	
Hexanol-1	Hexanol-1	Hexanol-1
Heptanol-1	Heptanol-1	Heptanol-1
	n-Butyric Acid	

Spheron-6	Graphon	DAG-1
n-Valeric Acid	n-Valeric Acid	n-Valeric Acid
	n-Caproic Acid	n-Caproic Acid
n-Heptylic Acid	n-Heptylic Acid	n-Heptylic Acid

For these systems, then, multilayer adsorption is a necessary assumption. Since the isotherms of all the slightly soluble acids and alcohols exhibit a rapid rise as saturation concentrations are approached, even though in a few instances the highest surface excess measured did not yet exceed the maximum possible monolayer content, multilayer adsorption is clearly indicated for all these cases.

The most remarkable point noted here is the presence of n-butyric acid in the above list. Although, as is pointed out in the introduction of this work, there is good evidence for the existence of multilayer adsorption of one component from solutions in systems which are entirely miscible with each other, as well as from solutions in which the solute exhibits limited solubility in the solvent, these values observed for the adsorption of n-butyric acid on Graphon from aqueous solution constitute the only known instance in which the adsorption of a soluble component actually exceeds the maximum amount that could be packed into a close-packed monolayer. Since the adsorption is demonstrably multimolecular in this one instance of a soluble acid, this observation can be taken as strong additional evidence that the adsorption of all the acids and alcohols, when considered over the entire activity range, is fundamentally of a multimolecular nature.

K. Indicated Thicknesses of Adsorbed Layers

In the foregoing discussions, it has been pointed out that the fundamental difference in form of the isotherms for completely soluble acids and alcohols and those of limited solubility is due, not to a difference in actual adsorptive behavior of the acid, but rather, to the fact that for miscible substances at higher concentrations a large quantity of solute would be present in the volume immediately surrounding the solid surface even if no adsorption occurred, and this quantity is not considered in a measurement of the surface excess. It has been shown that adsorption from both types of systems is fundamentally multimolecular in character. It also has been shown that for very dilute solutions, in which the measured surface excess is essentially equal to the total amount of solute present at the surface for all the members of a homologous series, both immiscible and miscible, the measured surface excesses on a given adsorbent are primarily a function only of the adsolute activity of the solute in solution for a particular homologous series.

These observations suggest that, for a particular complete series and given adsorbent, the total amount of solute in the adsorption volume may be a function only of the absolute activity of the solute over the entire activity range.

The assumption that this is true would make possible the calculation of indicated thickness of the adsorbed layers for all the soluble acids and alcohols investigated. The term "thickness" of the adsorbed layers is used to designate the distance from the solid surface to the point in the solution at which the solution composition no longer changes with increasing distance from the surface; that is, the distance over which the adsorptive forces are effective in changing the solution composition. This treatment would assume, of course, that this distance is uniform over the entire surface, and would be an independent means of evaluating k in the equation $U = \Gamma + kC$, discussed in the introduction above. Since the concentration of organic solute is low over the complete activity range in the cases of limited solubility, the total amount of solute in the adsorption layer is nearly the same as the surface excess over the whole range in these cases, the greatest difference being of the order of magnitude of the uncertainty in the surface excess isotherms; therefore, these measured surface excesses might be used directly as a reference for computing an indicated adsorption thickness for the soluble systems. Under the assumption just mentioned, the adsorption thickness would be the distance from the surface required to furnish an adsorption volume equal to that which would, at the bulk concentration, contain as much solute as would need to be added to the observed surface excess at any particular activity to make the resulting total amount of solute in the adsorption volume the same as is shown by the reference isotherm. The experimental data were analyzed under this assumption, and at one time during the course of this work it was believed that this would prove a valid method for estimating layer thicknesses of the soluble acids and alcohols, estimated thicknesses from such calculations being of magnitudes of a few molecular lengths. In final analysis, however, this was found not to be true. Final calculations of layer thicknesses consistent with the above assumption gave values which were not physically reasonable, many such values being less than that of a single molecular diameter.

If one were to assume, as Kiselev (20) has suggested, that k of the equation $U = \Gamma + kC$ can be evaluated from the slopes of the isotherms after their slopes become negative by using the relation

$$k = - \frac{d\Gamma}{dC},$$

he would, using the above adsorption data plotted against concentration, arrive at the following values for k, all numbers being given in Angstroms. For acetic acid, 3.0 on Graphon and ca 3.7 on Spheron-6; Propionic acid, ca 5.7 on all adsorbents, butyric acid, 10.0 on DAG-1 and ca 13. on Spheron-6; ethanol, 3.9 on DAG-1; propanol, ca 5.3 on DAG-1 and about twice this value on Spheron-6. The omissions in this list are due to non-linearity of the observed isotherms even in rough approximation, so no single value is indicated. The treatment itself, however, assumes U, the total amount of solute in the adsorption volume, to be constant; that is, that a plot of U against C would give a Langmuir-type isotherm. Although Kiselev believed this to be the case, and the value of U to be determined by the number of molecules contained in a close-packed monolayer, the present work indicates that U is definitely not constant, being a function of the solute activity. Evaluation of k by this method is, therefore, not a valid approach.

Since no way has yet been found for computing the thickness of the adsorbed layer from data of adsorption from solution, one cannot separate the composite isotherms into its constituent solute isotherm and solvent isotherm, nor determine the composition of the adsorbed phase from these data alone. It is probably impossible to compute this thickness without related independent data from other sources. All treatment currently found in the literature for computing the composition of the adsorbed layer are based upon the assumption of monomolecular adsorption. This assumption does not have general validity.

While adsorbed layer thickness cannot be obtained from these data alone it is possible that definite evidence can be brought to bear upon the problem of molecular orientation at the adsorbent surface under the conditions of adsorption from dilute solutions. Dr. R. S. Hansen has calculated partial isotherms based upon the above adsorption data in the low activity ranges, assuming the organic molecules to be spherical in shape and the fraction of carbon surface covered at these activities, in the Langmuir sense, to be a function only of the activity of the solute. Introducing a $v^{2/3}$ multiplicative correction factor to the $(\Gamma + kC)$ values, where v is the molar volume of the organic liquid, and $v^{2/3}$, therefore, is proportional to the molecular area, and plotting these values against the solute activity, Hansen obtained nearly congruent isotherms for the various acids and the various alcohols. In general, the congruency of isotherms was improved over those shown in Figures 1 to 6. Thus, if the fractional area covered by organic molecules is a function only of the solute activity, the spherical model must be very nearly a true representation. The observed slight variations from congruency would be expected because of the inexactness of the spherical approximation to molecules which are actually ellipsoidal. Independent evidence that the fractional area covered is a function only of solute activity would be necessary for definite conclusions in this regard, but the model does provide satisfying self-consistency in interpretation of the experimental data.

VII. SUMMARY

The adsorption of the normal aliphatic alcohols and the normal fatty acids containing two to seven carbon atoms from their aqueous solutions on three different non-porous carbon adsorbents has been investigated. In this investigation, absolute solute activity extended in every case from zero to at least 0.88.

Adsorption from the aqueous phases of those of the alcohols and acids which are not totally miscible with water invariably showed a rapid rise in the amount of adsorption as the solution concentration approached the saturation value. This rise reflects the dependency of the adsorption upon the amount of work required to remove the sorbate from solution, and the adsorption values reached in these measurements demonstrate that the adsorption must necessarily be multimolecular.

For a given adsorbent and type adsorbate, the surface excess obtained from dilute aqueous solutions of all members of the series, both miscible and immiscible, depended primarily on the absolute solute activity. In the activity range $0.005 \leq a \leq 0.10$ the individual isotherms varied only five to ten per cent for different members of the series. Traube's rule is a necessary consequence of this behavior.

For a given adsorbent the surface excesses of the slightly soluble acids and alcohols depended primarily on the activity over the entire activity range. The miscible acids and alcohols followed the same surface-excess versus activity curve for ranges which were more extensive the higher the position in the homologous series. Deviations from the mean were significantly greater with the alcohols than with the acids, and appeared to be systematic.

For the miscible systems, Graphon and DAG-1 showed positive adsorption of the organic component over the entire concentration range; Spheron-6 showed S-shaped isotherms, with negative adsorption of the organic component at high concentrations. Correspondingly, measurements of the adsorption of water from the organic phases of the immiscible alcohols and acids showed no preferential adsorption of water at any concentration by either Graphon or DAG-1, while Spheron-6 did show a definite adsorption of water in all cases. The water adsorption isotherms on Spheron-6 were of the Langmuir type. Apparently a portion of the surface of Spheron-6 consists of sites, perhaps particular types of oxygen complexes, which possess specific affinity for water molecules. These sites are removed in the process of graphitization of the Spheron-6 carbon black.

For the immiscible alcohols or acids, variations in adsorption at a given activity on the different adsorbents were only five to fifteen per cent, the adsorption on Spheron -6 being slightly greater than on the other adsorbents. Since the specific surface area of DAG-1 was somewhat lower, and that of Graphon considerably lower than the specific surface area of Spheron-6, the results indicate that graphitization increases the specific adsorption of organic substances.

A mean isotherm for the immiscible alcohols was almost identical with the corresponding isotherm for the acids. This lack of dependence of surface excess on functional group and the very weak dependence upon the nature of the solid carbon surface indicate that interaction between surface and organic component must be primarily with the alkyl groups common to both acids and alcohols.

Attempts to compute thicknesses of adsorbed layers from solution adsorption data alone have proved unsuccessful. For such computations, independent related data giving information such as actual potential functions or, perhaps, vapor phase adsorption, would be required.

Solubilities of water in the alcohols and acids and solubilities of the alcohols and acids in water have been determined. Some of these are new measurements; the others have been independently determined, and the values compared with values published in the literature.

The adsorption of alcohols and acids from aqueous solution on non-porous carbons has been found to be a rapid process. Equilibrium was established in less than two minutes. There was no indication of a further rise in adsorption after this time.

VIII. LITERATURE CITED

1. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* *60*, 309 (1938).
2. R. S. Hansen, *Thesis*, Univ. of Michigan, Ann Arbor (1948).
3. R. B. Anderson and P. H. Emmett, *J. Phys. Chem.* *56*, 753 (1952).
4. J. J. Kipling, *Quarterly Reviews* *5*, 60 (1951).
5. H. G. Cassidy, "Adsorption and Chromatography", Inter-Science publishers, New York (1951).
6. W. Ostwald and R. deIzaguirre, *Kolloid-Z.* *30*, 279 (1922).
7. E. Heymann and E. Boye, *Kolloid-Z.* *63*, 154 (1933).
8. A. M. Williams, *Medd. Vetenskapsakad. Nobelinst.* *2*, No. 27 (1913).
9. F. E. Bartell and C. K. Sloan, *J. Am. Chem. Soc.* *51*, 1643, (1929).
10. W. Bachmann, *Z. Anorg. Chem.* *79*, 202 (1913).
11. A. M. Bakr and J. E. King, *J. Chem. Soc.* (London) *119*, 454 (1921).
12. Y. Fu, R. S. Hansen, and F. E. Bartell, *J. Phys. Chem.* *52*, 374 (1948) and *53*, 454 (1949).
13. M. Polanyi, *Z. Phyzik* *2*, 111 (1920).
14. F. E. Bartell and G. H. Scheffler, *J. Am. Chem. Soc.* *53*, 2507 (1931).
15. G. A. H. Elton, *J. Chem. Soc.* (London), 1955 (1952).
16. A. V. Kiselev and K. D. Shcherbakova, *Compt. Rend. Acad. Sci. URSS* *45*, 241 (1944).
17. O. M. Dzhigit, M. M. Dubinin, A. V. Kiselev, and K. D. Shcherbakova, *Compt. Rend. Acad. Sci. URSS* *54*, 141 (1946).
18. O. M. Dzhigit, A. V. Kiselev, L. N. Terekhova, and K. D. Shcherbakova, *J. Phys. Chem. (USSR)* *22*, 107 (1948) as abstracted in *CA* *42*: 5298 d (1949).

19. A. V. Kiselev, Doklady Akad. Nauk. S.S.S.R. 61, 657 (1948). Translated for private use by Mr. and Mrs. John Anderson.

20. A. V. Kiselev, Zhur. Fiz. Khim. 23, 452 (1949). Translation borrowed from Research Library, Brookhaven National Laboratory, Upton, N. Y.

21. W. F. K. Wynne-Jones, Phil. Mag. 12, 907 (1931).

22. H. Lund and J. Bjerrum, Ber. 64 B, 210 (1931).

23. F. C. Collins and V. Lantz, Ind. and Eng. Chem., Anal. Ed. 18, 673 (1946).

24. E. A. Guggenheim and N. K. Adam, Proc. Roy. Soc. 139 A, 218 (1933).

25. A. Giacalome, F. Accascina, and G. Carnesi, Gazz. Chim. Ital. 72, 109 (1942).

26. E. R. Jones and C. R. Bury, Phil. Mag. 4, 841 (1927).

27. J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, J. Chem. Soc. (London)674, (1933).

28. D. J. Donahue and F. E. Bartell, J. Phys. Chem. 56, 480 (1952).

29. R. B. Anderson and W. K. Hall, J. Am. Chem. Soc. 70, 1727 (1948).

30. J. Traube, Annalen 265, 27 (1891).

31. I. Langmuir, J. Am. Chem. Soc. 39, 1890 (1917).

32. C. Brown, J. Phys. Chem. 54, 1278 (1950).

33. F. A. Miller, unpublished work.

34. E. Heymann and E. Boye, Kolloid-Z. 59, 153 (1932).

35. B. Iliin, Z. Physik. Chem. A 155, 403 (1931).

36. F. H. M. Nestler and H. G. Cassidy, J. Am. Chem. Soc. 72, 680 (1950).

37. D. Schmidt-Walter, Kolloid-Z. 14, 242 (1914).

38. F. E. Bartell and L. E. Lloyd, J. Am. Chem. Soc. 60, 2120 (1938).

39. C. Pierce, R. N. Smith, J. W. Wiley, and H. Cordes, *J. Am. Chem. Soc.* *73*, 4551 (1951).

40. F. A. P. Maggs, *Nature* *169*, 793 (1952).

41. C. Pierce and R. N. Smith, *J. Phys. Chem.* *54*, 784, 795 (1950).

42. R. B. Anderson and P. H. Emmett, *J. Phys. Chem.* *56*, 756 (1952).

43. N. K. Adams, "The Physics and Chemistry of Surfaces", 3rd Ed., Oxford University Press, London (1941).