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INFLUENCE OF POLAR FUNCTIONALITY, SOLVENT AND CHAIN LENGTH ON ADSORPTION OF SEMI-POLAR ORGANIC COMPOUNDS ON INSOLUBLE CALCIUM SALT SURFACES

by

Rasma Sylvia Apinis

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Pharmaceutical Chemistry)
in The University of Michigan
1976

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To

My Mother and Father

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INTRODUCTION

The adsorption of soluble species at liquid-solid interfaces has been of long standing interest and importance. There has been wide application of the adsorption process in the fields of chemistry, engineering and biology, in a wide range of industrial processes and natural systems.

More recently, there has been an interest in the application of the process in the field of oral biology, where the adsorption phenomenon has been recognized as having an important role in certain mechanisms for the protection of tooth enamel. An understanding of the physical-chemical behavior of hydroxyapatite would be important to an understanding of various aspects of its biological behavior, such as demineralization and the development of caries. Work in these laboratories has been carried out which emphasizes such an understanding. It has been shown that certain types of organic compounds such as alkyl amines, when adsorbed onto hydroxyapatite, have a dramatic effect on the rates of enamel demineralization. Others have shown that these compounds result in an inhibition of plaque formation on the surface of the enamel.

Because of the importance of the many empirical uses of the adsorption process, it is apparent, therefore, that it is important to gain a fundamental physical-chemical

understanding of the phenomenon. There have been a great number of investigations performed, from many standpoints, but, because of the complexity of many of the systems, there is still a lack of complete mechanistic understanding of the adsorption of polar organic compounds, such as surface active agents, onto inorganic surfaces. There still exists a need for basic investigations which could potentially lead to a fundamental understanding of the mechanisms involved in the adsorption of organic compounds where only the anchoring group may be varied, or of a series of compounds where the anchoring group is constant and the chain length of the hydrophobic tail is varied. The difficulties associated with the investigation of such questions have been two-fold. There has been a lack of an adequate theoretical framework for these studies, and a lack of good experimental systems that are well-defined and accessible to meaningful interpretation.

There have been recent significant advances by S. G. Ash and D. H. Everett in the statistical mechanics for the adsorption of polymers in which configurations and interactions of different portions of the molecule with the adsorption site have been considered. More recently, Bladon, Higuchi and Molokhia have extended the calculations to include the effect of the solvent. These studies are significant because they provide for the first time a framework for systematic experimental study of the adsorption of polar organic molecules onto adsorbing surfaces,

or meaningful interpretation of such studies.

It was the intent of this investigation to examine a number of factors influencing the adsorption of polar organic compounds from aqueous and non-aqueous solvents onto inorganic surfaces. The work includes a general survey of the adsorption behavior of compounds having a single polar group onto hydroxyapatite and calcium fluoride surfaces. The portion of the investigation dealing with the adsorption of homologous series of n-alkyl polar anchoring compounds in organic solvents involves interpretation of the experimental results in terms of the theoretical results of Bladon, Higuchi and Molokhia. An attempt is made to assess the chain length effect, the effect of the strength of the polar group-surface site interaction energies and the effect of a strongly competing solvent on the adsorption.

A fundamental study such as this helps to give insight into the nature of the forces and interactions acting both within the bulk solution and between the adsorbing species or solvent and the solid adsorbent. It is hoped that this study can be a valuable contribution in the achievement of a mechanistic understanding of adsorption processes. And, it is a long-term hope that studies along these lines would help shed some light on the adsorption behavior of potentially important compounds on hydroxyapatite crystal surfaces, and thus help to understand the kinetic behavior of these crystals under demineralizing and remineralizing

conditions. An understanding such as this would lead to an understanding of the behavior of bones and teeth under biological conditions.

LITERATURE REVIEW

Adsorption from solution by solids has been of great importance in many fields of science and technology, including the health-related sciences. The presence of adsorbed films affects the chemical and physical behavior of a solid, and a large number of systems and processes in nature are controlled to a significant extent by the presence or addition of organic solutes which concentrate at the surface of a solid. Such alterations are important to many chemical systems, and may have considerable biological significance as well. This has been the case in the dental field, where there has been a great deal of interest in the adsorption of various compounds onto human dental enamel and hydroxyapatite, particularly in relation to the subsequent effect on the enamel demineralization as well as plaque attachment.

Thus, the initial incentive and basis of this investigation was to relate the adsorption of certain materials on tooth surfaces to their effectiveness in preventing plaque attachment. This included such potential anti-plaque agents as long-chain alkylamines and fatty acids. The work was done in aqueous media, with hydroxyapatite powder used to simulate the tooth surface. However, the resulting system was a very complex one, with a number of interactions occurring, which made it difficult to carry out a baseline study. Therefore, subsequent work was

performed with non-aqueous, non-polar solvents. This literature review, therefore, covers these various aspects of the study; the oral biology, adsorption studies in aqueous systems on hydroxyapatite and adsorption studies in non-aqueous systems.

Oral biology

At the present time, practically all available data from dental research seems to justify the concept that dental plaque has a primary role, and is actually a prerequisite, not only in dental caries, but also periodontal disease. Intensive studies have been carried out to determine its origin, structure, composition, mechanism of formation and its exact role in the development of caries.[1-15] It is generally accepted that the plaque is a result of microbial metabolism of dietary carbohydrate, especially sucrose,[15] resulting in the formation of lactic, acetic and propionic acids.[11] This excessive accumulation of acid favors dissolution of the calcium phosphate in the underlying enamel, resulting in demineralization. Thus, almost all of the investigations into the prevention of caries have been directed in one of two ways--decreasing the acid solubility of enamel or the prevention of plaque formation on the surface.

A large number of substances have been investigated, which, through interaction with the enamel on the surface of the tooth, make the enamel more resistant to demineralization. The most studied substance in this regard has been fluoride,[16-28] which has been demonstrated to impart

protection against the dissolution of enamel. Green and Walsh[29] observed that measurable protection against demineralization by acid saliva was given by oleic acid and solutions of cetylamine in paraffin. They postulated that the amine end groups were adsorbed at the enamel surface and the hydrocarbon chains were acting as a bridge between the enamel and the paraffin oil, which was enabled to form a fairly stable film. In a subsequent study[30] the same workers tested a number of amines of different chain lengths (C_8 to C_{18}) for their protective effect and found the most effective to be the tetradecylamine, which gave up to 90 per cent protection. The protective activity depended on the chain length and appeared to reside in a monomolecular layer of amine adsorbed onto the enamel surface. In continuing studies, Irwin et al.[31,32] examined primary, secondary, tertiary and quaternary amines, as well as some diamines, as to the efficiency of their protection, and found that primary amines were much more effective than the secondary and tertiary amines, while the quaternary compounds studied gave no protection at all.

Adsorption was suggested as the mechanism of protective action by Weiss and Bibby,[33-35] who studied the adsorption of various proteins onto bovine enamel, and the subsequent reduction of the enamel solubility in acid.

Roseman et al.,[36] through dissolution and adsorption studies with synthetic hydroxyapatite and dental enamel, found that aliphatic amines markedly reduced the dissolu-

tion of both substrates, and that there was a corresponding strong affinity of the amines for apatite and enamel surfaces.

More recently, studies have been aimed at prevention of plaque formation on the surface of the tooth. One approach has been directed against the bacteria in the plaque. In addition to antibiotics,[37-40] other antibacterial agents have been reported to possess plaque-inhibiting capacity. Gjermo et al.[41] studied the plaque inhibiting capacity of eleven antibacterial compounds, and when he compared the in vitro antibacterial activity with the in vivo plaque-inhibiting effect, he found no correlation except in the case of chlorhexidine salts and benzalkonium chloride. He concluded that factors other than general antibacterial activity are important in plaque inhibition. In a later study, Rolla, Loe and Schiott[42] indicated that chlorhexidine gluconate adsorbs onto hydroxyapatite, tooth surfaces and salivary mucins, and that the adsorbed chlorhexidine is released when the concentration in the environment is low. The authors postulated that chlorhexidine could prevent bacterial colonization and the development of dental plaque, either by being slowly released from reservoirs on the tooth surface or simply by being adsorbed onto the tooth surface. In a screening procedure for the plaque inhibiting capacity of various chemicals, Turesky et al.[43] found that only adhesive antibacterial chemicals inhibited plaque formation. Among these were chlorhexidine gluconate and dodecylamine hydrochloride.

Other substances which have been studied in the attempt to inhibit plaque formation include sodium ricinoleate,[44] victamine C, a cationic surfactant,[45] zinc salts[46] and the anionic surfactants, sodium sulforicinoleate and sodium N-lauroyl sarcosinate.[47] Nordbo and Rolla[48] investigated phytic acid and glycerophosphates and found that they reduced plaque formation in vivo. They postulated that due to their high affinity for hydroxyapatite, these compounds compete for the surface with the salivary macromolecules, thus inhibiting their adsorption.

Adsorption on hydroxyapatite

The above-mentioned studies demonstrated the effectiveness of numerous potential adsorbing agents in retarding demineralization or preventing plaque attachment onto hydroxyapatite and enamel surfaces. However, they did not provide information about the mechanism of the adsorption, the nature of the surface or the nature of the interaction with the surface sites. A number of investigators have studied adsorption on hydroxyapatite from solution to determine the nature and magnitude of the interfacial interactions occurring between the surface and selected organic compounds. Ibsen and Urist[49] studied the simultaneous adsorption of citrate and oxytetracycline on hydroxyapatite and concluded that both compounds were competing for the same adsorption site on the surface. This site was suggested to be the calcium atom.

In an attempt to elucidate the mechanism of protein adsorption onto hydroxyapatite, Bernardi and Kawasaki[50] performed chromatography of a number of synthetic polypeptides on a hydroxyapatite column. Their results showed that the carboxyl groups on the polypeptides are responsible for the interaction with hydrohyapatite, since only polymers containing them were retained by the columns. According to the authors, this interaction occurred between the carboxyl groups and the calcium sites of the hydroxyapatite. On the basis of these results obtained with the polypeptides, it was postulated that carboxyl groups are also responsible for protein interaction with hydroxyapatite.

Roseman et al.[36] investigated the adsorption of long-chain amine hydrochlorides on hydroxyapatite and the effect of various factors on this adsorption. In addition to studying the ionic strength effect and the pH effect on the adsorption of dodecylamine hydrochloride, they investigated the adsorption of a homologous series of amine hydrochlorides, and found greater adsorbing tendency, or binding strength, in the higher homologues. The extent and strength of adsorption was related to the effect on the dissolution rate of hydroxyapatite.

The adsorption of 2-butanol and methyl ethyl ketone on hydroxyapatite was studied by Bett, Christner and Hall[51] by means of infrared techniques. They found evidence that the carbonyl group of the ketone was probably

not associated with a single surface species. They suggested that one means of binding was a charge-transfer interaction between the carbonyl group and the surface.

Magrill[52,53] studied the adsorption of sodium phytate on hydroxyapatite and defined two constants, which were characteristic for each phytate solution. One of these was related to a hypothetical initial uptake and was found to decrease by increased phosphate concentrations or by an increase in the pH from 8 to 11. The adsorption isotherm conformed to the Freundlich equation.

Adsorption studies of salivary proteins on hydroxyapatite were carried out by McGaughey and Stowell,[54] who determined the effect of phosphate ion and pH on the adsorption. They found that phosphate ions inhibit the adsorption of proteins, and hydrogen ions enhance the adsorption. There was an interdependence between these two factors; when no phosphate ion was present, the adsorption-enhancing effect of the hydrogen ion was significantly reduced, and removing hydrogen ions (increasing pH) notably increased the adsorption-inhibiting effect of phosphate. The same authors[7] also found that calcium ions enhance the adsorption of salivary proteins by hydroxyapatite, and that hydrogen ions eliminate this effect.

Adsorption in non-aqueous systems

Of the many adsorption studies performed in aqueous systems, few have led to mechanistic understanding of the

process, due to the complex solutions which may result when water is the solvent. Numerous studies have been done in non-aqueous systems to elucidate the basic mechanisms in the adsorption process.

Orientation of adsorbed molecules

There have been a number of studies conducted which have dealt with the question of the orientation of the adsorbed molecules. Contrary to some early assumptions that the perpendicular orientation is normally adopted at the liquid-solid interface, Kipling and Wright[55] concluded that stearic acid is adsorbed onto homogenous carbon surfaces with the hydrocarbon chain parallel to the surface. This was in contrast to the perpendicular orientation of stearic acid molecules in close-packed films on aqueous substrates[56] and on alumina.[57] Recognizing that this difference in the orientation was due to the difference in polarity of the substrates, the authors, in a subsequent study,[58] examined the orientation of stearic acid on solids intermediate in polarity between carbon and alumina. They suggested that in adsorption from solutions in cyclohexane, stearic acid is adsorbed onto silica as dimers with the hydrocarbon chains parallel to the surface, but in a perpendicular orientation as monomers on the surfaces of alumina and titania. It was concluded that the nature of the substrate was a very important determining factor in the question as to which orientation is adopted, with

probably quite small differences in the energies of interaction having a great influence.

This model proposed by Kipling and Wright was later shown to be incorrect by Armistead, Tyler and Hockey,[59] who studied the adsorption of a homologous series of n-fatty acids on silica. They determined that the observed effective area per molecule on the surface was too small to correspond to a flat configuration, and that the variation in the molecular cross-sectional area with chain length was too small to fit the model.

Hasegawa and Low,[60] by means of infrared spectra, also investigated the effect of the nature of the solid on the structure of the adsorbed species, and found that stearic acid is adsorbed onto silica predominantly as monomers at low concentrations. This model also differed from that of Kipling and Wright, who had postulated the adsorption of the acid as dimers. The authors could give no information, however, about the orientation of the adsorbed molecules, because the absorption of the silica obscured the region of the bands of stearic acid necessary to give this information.

Smith[61] postulated that at low surface density, on metal surfaces, long chain carboxylic acids and alcohols lie flat on the surface until they are compressed essentially to a close-packed array. Further compression causes the molecules to kink so that part of the chains are erect. Then, according to the author, the erect por-

tions cluster into nuclei which grow into micelles.

The adsorption of cationic and anionic surfactants onto silica in the presence of organic solvents was studied by Rupprecht.[62] He postulated that the molecules were flat-lying up to a chain length of ten carbon atoms, and that molecules with chains longer than C_{10} assumed a perpendicular orientation on the surface. The conclusion was that the adsorption of the long-chain surfactant molecules may be caused by a dynamic equilibrium between these two states of adsorption, with the longer species preferring a perpendicular orientation.

Polar group effect

Several studies have been conducted which have dealt with the effect of the functional group on the strength and extent of adsorption. In adsorption studies of polar organic compounds on metal surfaces, Cook and Hackerman[63] found that the total amount of adsorption for the series studied was in the decreasing order acids, amines, alcohols and esters. In a similar study, Hackerman and Roebuck[64] obtained adsorption isotherms for a variety of polar organic compounds in benzene on metal powders, in order to find relationships between the functional groups of an organic compound and its adsorbability. Their data showed that acids were adsorbed to a greater extent than the other compounds investigated.

Results of adsorption of polar organic compounds from hydrocarbon solutions on reduced metal surfaces were reported by Greenhill,[65] who noted that monolayer formation was complete at a lower concentration for strongly adsorbed compounds such as stearic acid than for less strongly adsorbed ones like alcohols or esters.

Low and Lee[66] obtained infrared spectra for the adsorption of the C_{18} alcohol, acid and amine from carbon tetrachloride onto silica. From their data they concluded that the acid exhibited lower adsorption and that its interaction with the silanol groups on the surface was weak.

In his adsorption experiments with some cationic and anionic surfactants (including alkylpyridinium chlorides, alkyltrimethylammonium chlorides and sodium alkyl sulfates) onto silica from chloroform, Rupprecht[62] reported that varying the cationic head group on molecules of the same chain length had no effect on the adsorption. The limiting adsorption for the anionic surfactants was lower than that for the cationic, but no direct comparison was made by the author, and no explanation was given.

Solvent Effect

In early adsorption studies dilute aqueous solutions were used, and the effect of the solvent was generally ignored. In one of the earlier investigations of the influence of the solvent, Smith and Hurley[67] studied the

adsorption of fatty acids onto carbon black in several different solvents. From their experimental data, they were able to show that the arrangement of the solvents tried, in order of increasing adsorption of the acids, was acetone, ethyl acetate, benzene, n-heptane, n-hexane, carbon tetrachloride and cyclohexane. However, according to the authors, no explanation for this order seemed apparent.

Crisp[68] regarded the influence of the solvent on adsorption as being due to competition between molecules of solvent and adsorbate for the surface of the adsorbent, even in dilute solutions. As a result, the process of adsorption was viewed as being more complex than that of a one-component system, in that molecules are not simply adsorbed or desorbed, but are exchanged with adsorbed solvent molecules.

Blackburn and Kipling[69] investigated the extent of the effect of molecular interaction, or association, between components in the liquid phase on the adsorption. A study was made of adsorption on charcoal from four systems in which the molecular interaction in the bulk was graded from a small effect in saturated hydrocarbons to strong hydrogen bonding in an aqueous system. They concluded that hydrogen bonding between two components in the liquid phase resulted in only a slight departure from the behavior which would have been expected in the absence of any association.

In selective adsorption studies of benzene and n-hexane solutions of n-fatty acids onto silica, Armistead et al.[59] determined that the adsorption in benzene was approximately one third the adsorption in hexane solutions. However, because this was not primarily a study of the solvent effect, no explanation for the observed difference was presented.

Similar results were obtained by Mathews and Colwill,[70] who observed less adsorption of n-butylamine onto silica from toluene solution than from n-heptane. They attributed the lesser amounts of adsorption from toluene to adsorption of both amine and solvent.

In two separate studies, Vetrova et al.[71,72] determined adsorption isotherms for fatty acids on silica gel from carbon tetrachloride and benzene, respectively, and found that the adsorption was reduced in the benzene. Zelizny et al.[73] also investigated the effect of the solvent on adsorption, and showed that all the n-fatty acids studied exhibited decreasing adsorption from heptane, carbon tetrachloride and benzene.

Ash[74] discussed the influence of the solvent on adsorption in terms of the combined effects of the solvency and affinity of the solvent for the surface. The more energetically favorable adsorbate-solvent contacts are, the lower will be the adsorption, and vice versa. However, the change in adsorption with solvent cannot always be explained solely in terms of changing solubility, and the

affinity of the solvent for the surface must also be considered. The less affinity a solvent has for the surface, the greater would be the adsorption of the solute. The author suggests that because the solvency and affinity lists are in inverse order, one effect tends to cancel the other. Thus, an explanation of the solvent dependency of adsorption has to be in terms of specific molecular effects. It was proposed that the use of mixed solvents could be a useful technique in interpreting the effect of different solvents on the adsorption.

In studies on the influence of solvents of varying polarity on the adsorption of ionic surfactants on silica, Rupprecht[62] found that polar organic solvents reduced or completely prevented the adsorption of both cationic and anionic surfactants. He concluded that the controlling factors in the adsorption process were both solvation effects around the surfactant molecules and solvent competition for adsorption sites on the silica. Both of these effects resulted in reduced adsorption of the solute.

Chain length effect

The regularities which are often found in the simpler physical properties of homologous series also extend to their behavior at interfaces. Traube,[75] in studies on the surface tension of aqueous solutions of organic solutes, found that surface activity increased strongly and regularly as any series was ascended. Because surface activity

is related to adsorption at the interface, Traube's rule has been extended to adsorption from aqueous solutions and has been expressed in terms of the regular increase in the strength of adsorption of successive members of a homologous series, as measured by the work required to remove one mole from the surface layer to the bulk of the solution.

Numerous investigations have been performed on the extent of adsorption of members of a homologous series by a given solid and from the same solvent. Freundlich's[76] early work on adsorption of the lower fatty acids from aqueous solution by charcoal showed increasing adsorption with increasing chain length. Since Freundlich's adsorption studies dealt with a non-polar solid and a polar liquid, Holmes and McKelvey[77] anticipated a reversal of Traube's rule in adsorption from a relatively non-polar solvent by a polar solid. This they found in adsorption of fatty acids from toluene by silica gel.

In adsorption studies of fatty acids on sugar charcoal from aqueous solutions, Nekrassow[78] obtained results which showed a reveral of Traube's rule. He attributed this reversal to the polar nature of the charcoal, which had been prepared under strongly oxidizing conditions. This would result in increasingly effective competition by water for sites on the surface. According to Bruns,[79] however, this reversal was due to exclusion of the larger molecules from narrow pores on the surface, rather than

polarity of the surface. Iliin[80] also attributed the apparent reversal of Traube's rule, which was observed in adsorbing fatty acids onto certain types of charcoal, to the ultrapore structure which limits the entry of the larger molecules.

Smith and Hurley[67] carried out adsorption experiments with fatty acids onto carbon blacks, which were assumed to be non-porous, and observed that acetic acid was adsorbed to a considerably greater extent than the longer-chain homologues. The only conclusions made were that some of the acids are not adsorbed in a perpendicular orientation, since their effective cross sections were much greater than 20.5 $\mathring{A}^2$.* Hansen and Craig[81] determined isotherms for the adsorption of homologous series of alcohols and acids from aqueous solution by non-porous carbon blacks. When the isotherms were plotted as a function of concentration, Traube's rule was followed in a qualitative sense, but when plotted as a function of activity (which was equated with reduced concentration), at low absolute activities the isotherms were congruent. The authors explained these results by citing Hansen, Fu and Bartell's comment[82] that the work required to remove a solute from solution as pure solute depended only on the activity of the solute. Thus, if the adsorbent acted on the same

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* 20.5 $\mathring{A}^2$ is the generally accepted value for the cross-sectional area of carboxylic acids, based on condensed film studies.[56]

functional group, congruency of adsorption isotherms in a homologous series would result. The authors, on this basis, predicted a reversal in the adsorption of the lower fatty acids and alcohols from hydrocarbon solvents by non-porous adsorbents, since the activity coefficients would decrease on ascending the series.

Elder and Springer[83] suggested that whereas acetic and formic acids may adsorb more strongly on silica gel because of hydrogen bonding, the decrease in total adsorption of higher members of the series is due to their increased molecular size, not to the effect of the non-polar chain. The results of Bartell and Fu[84] for the adsorption of organic acids on silica gel from carbon tetrachloride led to the same conclusions, for although the adsorption maxima were higher for the smaller acid molecules, there appeared to be little change in energy from formic to butyric acid. More recent work by Armistead et al.[85] showed that the molar heat of adsorption of fatty acids on silica from benzene is independent of their hydrocarbon chain length as well as the surface coverage.

Linner and Williams,[86] though suggesting that if the amount of fatty acids adsorbed at a standard concentration decreased as the chain length increased it constituted a "reversal of Traube's rule," interpreted the effect as being due to a difference in the available surface area.

In adsorption studies of a homologous series of

alcohols on alumina from a benzene solution, Crisp[68] found practically no change in the molar free energy of adsorption nor in the heat of adsorption between octyl alcohol and melissyl alcohol (C_{31}). From this, he concluded that only the polar groups were taking part in the adsorption, and that the condition of long-chain molecules adsorbed onto alumina from non-polar solvents is analogous to their adsorption at an oil-water interface, except that at the solid interface they are localized to fixed sites. He also suggested that any instances of the supposed reversal of Traube's rule were a result of confusion between the total amount adsorbed, which may decrease with chain length increase, and the energy of adsorption, which may either be independent of chain length or may increase with it. He doubted, on the rather scanty evidence available, whether in any series the energy of adsorption decreased with increasing chain length. In this he was following Langmuir's[87] interpretation of Traube's rule and considering only those cases in which the same area of solid is available to all members of the homologous series.

Ganichenko et al.[88] studied the adsorption of a homologous series of alcohols onto silica gel from carbon tetrachloride solution and found that the amount of the maximum adsorption decreased with an increase in the length of the hydrocarbon chain. This was explained on the basis of the orientation of the alcohols, which was reported to change with the growth of the length of the hydrocarbon

radical. The alcohol molecules were apparently being positioned at a certain angle to the surface, with the longer chain molecules occupying more space on the surface. Vetrova et al.,[71] in adsorption studies of n-fatty acids onto silica gel from carbon tetrachloride solutions, also observed a decrease in the maximum amount adsorbed with an increase in the chain length. They interpreted these results as being due to the fact that as the molecular weight of the acids increases, the dispersion interaction of the hydrocarbon radicals with each other and with the surface of the adsorbent grows, and the molecules assume a more inclined position. Zelizny et al.[73] noted the same chain length effect with fatty acids on silica gel from various solvents, and also concluded that the molecules were inclined toward the surface of the silica gel at a certain angle.

Allen and Patel[89] determined both the heats of adsorption at monolayer coverage for long-chain fatty acids in heptane on polar surfaces, and the amounts of fatty acids adsorbed. They found that the number of molecules adsorbed decreased as the carbon chain length increased, rapidly at first and then more slowly. On the basis of their data, they suggested a possible orientation at the surface and concluded that the decrease in the adsorption with increasing chain length was due to interference of the chains with each other, and mutual repulsion.

In adsorption studies of a series of n-alkyl amines

from n-heptane solutions onto silica, Mathews and Colwill[70] found that the quantity of amine adsorbed decreased with increasing length of alkyl chain. The results were interpreted by assuming that the adsorbed molecules have their alkyl chains inclined to the adsorbent surface at an angle which is determined by the nature of the solvent and of the surface.

Adsorption studies by Armistead et al.[59] showed that lengthening the hydrocarbon chain of n-fatty acids decreased the limiting adsorption from hexane on silica. In benzene, however, the adsorption isotherms were independent of chain length, with the exception of the C_6 and C_8 acids. The authors concluded that the limiting adsorption could not be attributed to either the close packing of the hydrocarbon molecules with their chains parallel to the surface or to the saturation of a fixed number of adsorption sites on the surface.

Van Cauwelaert et al.[90] observed by means of infrared spectroscopy that as the chain length of n-alkyl amines was increased, there was less interaction with the hydroxyls on the surface of silica. The authors concluded that steric effects due to the different apparent molecular areas of the amines were the determining factor in the number of hydroxyls which interact, and not the strength of the interaction.

In studies of the adsorption of methyl esters of n-fatty acids on silica from benzene and carbon tetra-

chloride, Mills and Hockey[91] found that both the selectivity of the adsorption process and the limiting adsorption decreased with increasing chain length of the ester. They postulated that this variation was a result of the change in solvation of the alkyl chain as it passes from the solution into the interfacial phase. That is, the solvated hydrocarbon chains of the solute are more "ordered" in the interfacial phase than in the bulk solution and this "ordered" layer has a structural coherence which is responsible for the limiting adsorption values being lower than those corresponding to full utilization of all the adsorption sites.

Theoretical model

A statistical-mechanical model for multilayer polymer adsorption has been developed by Ash, Everett and Findenegg[92] which predicts total polymer adsorption and the amount of each configuration in each layer near the surface. The model considers the orientation and configuration in terms of the interaction of different portions of the molecule with the surface sites and with each other. The results of this work provide interesting examples of the interplay of energy and entropy terms in determining the preferred configurations of adsorbed molecules. However, due to the model design, solvent effect could not be considered and evaluated. More recently, Bladon, Higuchi and Molokhia[93] made appropriate modifications in the model

which would make it possible to assess the solvent effects on the adsorption behavior of the polymers.

The specific polymers examined were the asymmetric dimer (A-B) and the asymmetric tetramer (A-B-B-B) in a solvent (C). The 'A' segments include the polar head group of the molecule and the 'B' segments make up the hydrocarbon chain.

The parameters required for the model to define the system are the nearest neighbor interaction energies between all combinations of the various contacting, non-bonded segments (including the solvent), and the interaction energies between the surface and each segment type in each layer near the surface. The interaction energies between the segments aredenoted as E_{ab}, E_{ac}, E_{cc}, etc., and that between the surface and the segments as X_A, X_B and X_C.

The assumptions of the model are: (1) the segments of the polymer and the solvent monomers are approximately the same size, (2) the segments of the polymer and the solvent monomer occupy only the lattice points of a given geometric array (close-packed hexagonal), (3) the energies of interaction between non-bonded segments are angularly independent, are additive in nature, and extend no further than the nearest neighbors, and (4) the surface has a homogeneous interaction energy for each segment type.

With this model, by varying each segment-to-segment interaction energy independently, analyses could be made of the effect that each interaction energy has on the

surface excess, and on the energy, entropy and number of each molecular configuration in each layer near the surface.

Figure 1 shows the possible dimer configurations and Figure 2 shows the possible tetramer configurations. The term, ω_s, is defined as the number of ways of forming a polymer molecule of configuration 's' in the presence of only solvent monomer molecules.

ω_s $\omega_1 = 6,\ \omega_2 = 3,\ \omega_3 = 3$

Figure 1. Configurational species of asymmetric dimers (A: polar segment, B: nonpolar segment).

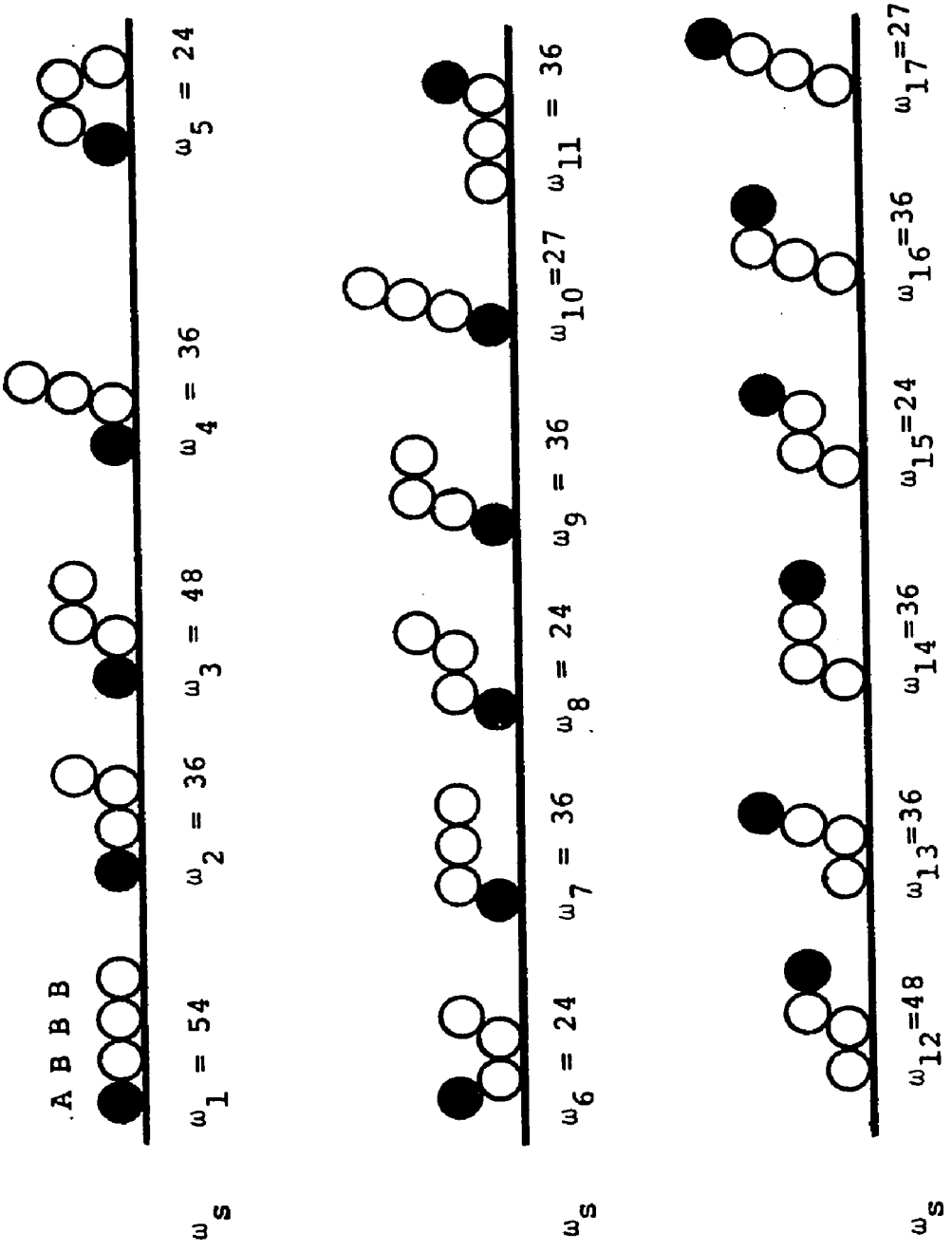

Figure 2. Configurational species of asymmetric tetramers (A: polar segment, B: nonpolar segment).

STATEMENT OF THE PROBLEM

The preceding review of the literature has shown that a large number of systems of widely differing types have been studied experimentally, but that a fundamental understanding of the adsorption phenomenon has developed slowly. The earlier experiments did not provide the best foundation for building a theory of adsorption, and workers have lacked a meaningful theory as a basis for analyzing their results. Thus, in spite of all the studies done, many basic questions still have gone unanswered, indicating the need for a mechanistic, physical-chemical, systematic approach to the problem.

The purpose of this investigation was to study the adsorption of various n-alkyl compounds with a polar anchoring group onto hydroxyapatite and calcium fluoride, and to examine the various factors which are able to influence the adsorption process, both in aqueous and non-aqueous systems. By studying these factors and their role in the adsorption process, it was the intention to elucidate the adsorption mechanism.

Specifically, the various factors which were to be investigated included, in the aqueous system, polar group effect, electrolyte effect, pH effect, common ion effect and chain length effect; and in the non-aqueous systems, the polar group effect, solvent effect and chain length effect.

It was also the intention of this work to attempt to establish a relationship to the theoretical results of Bladon et al., which predict both the effect that the solvent has on the adsorption and the influence of the chain length.

Even though the aqueous system is of greater interest biologically, and the results are of both theoretical and practical significance, the aqueous solvent and the hydroxyapatite surface present such a complex system that a physical interpretation of the adsorption process was not conclusive. Therefore, even though the work with the aqueous systems was done first, the results are presented as a general survey of the adsorption process in the second part of this thesis, since a basic mechanistic interpretation was not possible. The non-aqueous sytems, being less complex, lend themselves more easily to interpretation, and are more appropriate for analysis by the theoretical model of Bladon et al. Therefore, these studies are presented and discussed first.

ADSORPTION IN NON-AQUEOUS SYSTEMS

As a result of the adsorption studies in aqueous systems we were able to elucidate some of the mechanisms involved, and identify several different factors which influence the adsorption process. However, as will be seen, the use of water as a solvent results in fairly complex systems, and there were a number of interactions and complicating factors involved. As a result, it was difficult to isolate any one single factor, and explain its effect on the adsorption process conclusively.

Therefore, to eliminate some of these complicating factors, and in this way be better able to study the adsorption mechanism and gain a better understanding of the interactions involved, it was decided to use a simpler, more basic system, even though the aqueous studies may be of greater clinical significance. To avoid the complex solutions of the aqueous system, organic solvents were used, and calcium fluoride (as well as hydroxyapatite) was used as the adsorbing surface. Calcium fluoride was selected because it has a more uniform, homogeneous surface than hydroxyapatite, and it has a well-defined crystalline structure. These factors make it more possible to assess the types of interactions involved, and the possible types of surface sites. Hydroxyapatite was also studied in the non-aqueous systems, because it is a biologically important mineral, and any information which could con-

tribute to an understanding of its behavior and properties would be beneficial.

It was also the intention of going to this system to obtain experimental data which could be correlated to, or be discussed in terms of, a theoretical model, developed by Bladon, Higuchi and Molokhia.

Experimental

Materials

In adsorption studies, very small quantities of an impurity can have a dominating influence in the results, and can lead to incorrect and unreproducible experimental data. Because of this, the importance of manipulating the materials carefully was recognized, and an effort was made to be certain of the chemical purity of the materials.

Three types of compounds were used in these adsorption studies. These were amines, acids and alcohols of varying chain length, and included butylamine,[1] hexylamine,[2] octylamine[3] and dodecylamine;[3] butyric acid,[3] octanoic acid,[2] decanoic acid,[4] lauric acid[2] and myristic acid;[3] and hexyl alcohol,[2] lauryl alcohol[1] and cetyl alcohol.[1] All of the amines and alcohols were purified by

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[1] J. T. Baker Chemical Co., Phillipsburg, N.J.
[2] Eastman Kodak Co., Rochester, N.Y.
[3] Aldrich Chemical Co., Inc., Milwaukee, Wis.
[4] Matheson, Coleman and Bell, Norwood, Ohio

reduced pressure distillation under dry nitrogen and were stored under nitrogen. The acids were used as received. The purity of all these compounds was checked by means of thin layer chromatography prior to use.

Radioactive compounds used included butyric acid,[1] octanoic acid,[2] lauric acid,[2] myristic acid,[3] hexyl alcohol,[1] lauryl alcohol[3] and cetyl alcohol.[3] These were kept in a hexane solution and stored under nitrogen in a refrigerator. The purity of these compounds was also determined by thin layer chromatography, and the plates were scanned by the Packard Radiochromatogram Scanner.

The solvents used in these studies were acetone and hexane. These were distilled prior to use and stored under nitrogen.

The adsorbents used were commercially available Victor hydroxyapatite[4] and calcium fluoride. The hydroxyapatite has a high surface area, 70 M^2/gm,[94] making it advantageous for use in adsorption studies. Its calcium to phosphate ratio has been reported to be 1.66.[94]

The selection of calcium fluoride as the adsorbing surface was governed by a number of factors. It is a polar adsorbent and contains calcium, both of which give it characteristics similar to those of hydroxyapatite. The

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[1] American Radiochemical Corporation, Sanford, Fla.
[2] ICN Isotope and Nuclear Division, Irvine, Calif.
[3] New England Nuclear, Boston, Mass.
[4] Stauffer Chemical Co., Victor Division, New York, N.Y.

results obtained with the calcium fluoride, then, could be used to help explain the results of the hydroxyapatite adsorption studies. However, the calcium fluoride has a simpler, more uniform surface than hydroxyapatite, and this makes it more possible to assess basic interactions involved in the adsorption. Ideally, a surface would be desired which would be completely homogeneous with only a single adsorption site. However, no such material exists, which still possesses the polar character of the calcium fluoride. Even silica, which is used very widely in adsorption studies, is not an ideal surface, since it has a "mixture" of different crystal faces exposed to the surface,[95] producing a non-uniform surface.

The samples of the calcium fluoride used were prepared by A. Molokhia and J. Bladon according to the following published procedure:[96] a slurry of calcium carbonate[1] in boiling double distilled water is slowly titrated with 48% hydrofluoric acid[2] with constant stirring. When effervescence ceases, the precipitated calcium fluoride is filtered while hot, and washed with dilute acetic acid until carbon dioxide bubbles are no longer visible. The precipitate is then washed three times with boiling double distilled water, and dried at 300°C. A 200-mesh sieve was used to

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[1] Baker Analyzed Reagent, J. T. Baker Chemical Co., Phillipsburg, N.J.

[2] Analytical Reagent Grade, Mallinckrodt Chemical Works, St. Louis, Mo.

break down the powder aggregates into small particles with a narrow size distribution. The powder was stored in a dessicator for the adsorption studies. The surface area of the sample was 21 M^2/gm, as determined by BET nitrogen adsorption.

Procedure

In the case of the studies performed with hydroxyapatite, 10 ml of a known concentration of adsorbate solution were added to 200 mg of the powder in 100 ml volumetric flasks. For the calcium fluoride studies, 400 mg of powder were used and 3 to 5 ml of solution were added, depending on the compound being studied. For the alcohol and acid experiments, the solutions added were a mixture of the radioactive and the non-radioactive compounds, since the assay was a radioactive one. These were prepared by making a stock solution of the hot plus cold compound, and then making appropriate dilutions of this solution with the purified solvent. In this way, the same specific activity was maintained in each solution.

In all cases, the flasks were tightly sealed with Parafilm to prevent any evaporation of the solvent during the shaking. The flasks were shaken by means of a wrist-action shaker in a constant temperature water bath maintained at 30°C. The length of the equilibration period was 20 hours, except in the case of the alcohols, which will be discussed later. The rate of shaking was main-

tained constant in all experiments.

Because of the possibility of potential oxidation of the alcohols during the experiment, certain special procedures had to be taken for these compounds in the experimental procedure. After the powder was weighed into the 100 ml volumetric flasks, it was heated for several hours in a vacuum oven at 200°C. This was to de-gas the powder. Nitrogen was flushed into the oven and over the powder in the flasks at the end of the heating period. The experimental solutions, which were prepared with solvent also flushed with nitrogen, were added to the flasks, and after their addition, nitrogen was once more flushed into the flasks and over the solutions.

The shaking time in the case of the alcohols was reduced to two hours, since this, also, helped lessen the chance of any oxidation occurring. Equilibrium time was determined to be less than one hour.

At the end of the equilibration period, the solutions were placed in polyethylene centrifuge tubes with screw caps for centrifugation at 3000 rpm for 5 minutes. Aliquots were taken from the supernatant for assay.

The supernatant solutions of the alcohols were also checked for any oxidation or degradation products which may have occurred during the shaking by means of thin layer chromatography. The plates were checked visually, with iodine vapor, and radioactively, by means of radioscanning as well as cutting the plates into sections and

determining the counts in each region by means of liquid scintillation. No oxidation or degradation products were found when the experiments were done under the above conditions.

To investigate the possibility of any oxidation products having been adsorbed onto the surface, the alcohols were de-sorbed, and again, a TLC was carried out, and checked in the same way. Here, too, no evidence of any interfering substance was found.

Assay

The amines were assayed by means of a non-aqueous titration method. To 2 ml of the supernatant solution were added 10 ml of glacial acetic acid. The solution was then titrated with freshly diluted 0.001 N perchloric acid in glacial acetic acid, using 0.1% crystal violet in glacial acetic acid as the indicator. A magnetic stirrer was used during the titration to ensure rapid mixing. For each experiment, a standard curve was also obtained, where solutions of known concentrations were titrated and the results plotted. The concentrations of the unknown solutions were then determined, using the slope of this standard plot of concentration versus volume of titrant in the calculations.

The assay for the acids and alcohols was a radioactive one. Initial counts for each sample were obtained

by withdrawing a 1 ml sample from the solutions before shaking, and adding it to 10 ml of scintillation solution in a scintillation vial. The scintillation cocktail was prepared by making a 500 ml solution of 2.5 grams of PPO (2,5-diphenyloxazole)[1] and 50.0 grams naphthalene[2] in p-dioxane.[3] Final counts for the samples were obtained similarly, where a 1.0 ml aliquot of the supernatant solution was withdrawn, and also added to 10 ml of the scintillation solution. The samples were counted in the Beckman Liquid Scintillation System. The final concentration for each sample was then determined by means of a standard curve, which was constructed using solutions of known concentrations of labelled compounds and non-labelled compounds. The amount adsorbed was found by taking the difference between the initial and final concentrations.

Preliminary results

Results leading to treatment of calcium fluoride

Adsorption experiments were initially performed using samples of calcium fluoride which had not been heated to 300°C. These experiments were done using the homologous series of amines in hexane and acetone, and dodecyl alcohol

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[1] Scintillation Grade, Packard Instrument Co., Inc., Downers Grove, Ill.

[2] Eastman Kodak Co., Rochester, N.Y.

[3] Spectroquality, Matheson, Coleman and Bell, Norwood, Ohio

in hexane and acetone. The results are presented in Table I.

Table I

Results of Preliminary Adsorption Studies with Non-heated Calcium Fluoride

Adsorbate	Limiting Adsorption Value (millimoles/gram) Hexane	Acetone
Butylamine	0.140	0.05
Octylamine	0.090	0.05
Dodecylamine	0.090	0.05
Dodecylalcohol	0.040	- -

From these results it was thought that there were two types of adsorption sites on the calcium fluoride, and that the amines were adsorbed onto both of these sites in hexane. Upon the use of acetone as the solvent, one of these sites was poisoned, making it unavailable for adsorption by the amines, and the other site was apparently unaffected. The alcohol, on the other hand, was only adsorbed onto one of these sites, and this was the site that was eliminated when acetone was added.

The same experiments were performed using a new sample of calcium fluoride, which had been heated to 300°C, and the following results were obtained:

Table II

Results of Preliminary Adsorption Studies with Heated Calcium Fluoride

	Limiting Adsorption Value (millimoles/gram)	
Adsorbate	Hexane	Acetone
Butylamine	0.08	- -
Octylamine	0.04	- -
Dodecylamine	0.04	- -
Dodecylalcohol	0.04	- -

It was apparent that heating the sample had removed one of the available adsorption sites for the amines but had had no effect on the alcohol adsorption. This indicates that the surface area was not changed by the heating. The heating apparently removed the site that was previously non-poisonable by the acetone, in the case of the amines, for the relatively higher adsorption of the butylamine observed in hexane was still seen in the heated sample. The removed sites may have been water adsorbed onto the surface.

After these preliminary experiments, the subsequent work was all done using the calcium fluoride samples which had previously been heated to 300°C.

Results leading to the procedure employed with the alcohols

Because the presence of even very small amounts of impurities in the adsorbate solution may have a great effect on the adsorption measurements, it was deemed important to assess the purity of the compounds used, as well as their stability during the duration of the adsorption experiments. Consequently, thin layer chromatography was used to determine these factors. In the process, it was found that the alcohols used, hexyl, lauryl and cetyl, underwent some reaction to produce a decomposition compound or an oxidation product during the shaking portion of the adsorption experiment, when done for the usual 18 hours, under air. This second product appeared as an additional spot on the TLC plates. As a result, more extensive checking was done with these compounds to assess the influence of the various factors which may have contributed to the presence of the impurity.

The solvent system used in the thin layer chromatography was a solution of chloroform and methanol in the radio 95:5. After development, the plates were allowed to dry, and placed in an iodine chamber, to permit visible determination of the spots. The plates were then scanned on the Packard Radiochromatogram Scanner, Model 7201, to determine the relative amounts of activity in the spots, as well as to determine the presence of any radioactive compound which may not have shown up with the iodine. And finally, the sections of the plates where spots appeared,

or locations which showed activity under the scanner, were cut up and placed into scintillation cocktail in scintillation vials to be counted on the Beckman Liquid Scintillation System. (A blank piece of the plate was also counted in the same manner, in order to get accurate background counts.) In this way, an accurate determination could be made of the amount of the impurity present, if any, in relation to the pure compound. All samples checked in this manner were run in at least duplicate sets.

The R_f value of the pure alcohol under the conditions used was found to be 0.55. When a second spot was seen, it had an R_f value equal to 0.67, so the impurity was evidently a compound less polar than the alcohol.

The various factors investigated as to the magnitude of their effect, if any, on the stability of the alcohols included the effect of shaking under nitrogen as opposed to shaking in air, the effect of the length of the shaking time and the effect of heating and de-gassing the powder prior to use. In each case, a TLC was run on a sample of the solution before the experiment and one on a sample taken from the supernatant after the experiment. In this way, it was made certain that there was no impurity present in the solutions used to do the experiments.

The results of the above evaluation are presented in Table III.

Table III

Effect of Various Factors of the Stability of n-Alkyl Alcohols

Conditions	Per Cent of Impurity
Shaken in air for 20 hours	6.20
Shaken under nitrogen for 20 hours	1.49
Shaken under nitrogen for 12 hours	1.39
Shaken under nitrogen for 6 hours	0.52
Shaken under nitrogen for 2 hours	<0.10[1]
Shaken under nitrogen with degassed powder for 12 hours	1.25
Shaken under nitrogen with non-degassed powder for 12 hours	1.39

[1] The counts for the section of the plate where the impurity should have been were so low, it was not possible to determine with accuracy what the exact amount present was.

From these results, it is clear that the two important factors to be considered are the length of the shaking time and shaking under nitrogen rather than in air. Degassing and heating the powder to 200°C immediately prior to use also results in greater stability of the compound, although the effect is less marked. Thus, all these factors were taken into consideration, and were used in determining the procedure used for the experiments with the alcohol compounds.

Results

Effect of the polar group

To study the effect of the type of polar anchoring group on the adsorption, a series of three twelve-carbon compounds was studied: dodecylamine, dodecyl alcohol (lauryl alcohol) and dodecanoic acid (lauric acid). The experiments were performed both in hexane and acetone, with hydroxyapatite and calcium fluoride as the adsorbents. Hexane was chosen because it would be a non-competing solvent for the polar inorganic surface, and acetone was selected because it was a more polar solvent, and may have an effect on the adsorption. The results of these experiments are presented in Figures 3, 4 and 5. The adsorption of dodecylamine, dodecylalcohol and dodecanoic acid onto hydroxyapatite from hexane is shown in Figure 3. It can be seen that the acid and amine both have a much steeper initial slope in their isotherms than does the alcohol, indicating a stronger affinity for the surface. It is difficult to distinguish between the initial slopes of the lauric acid and the dodecylamine, since they are both so very steep. The alcohol and the amine both reach the same plateau, 0.17 millimoles/gram, whereas the acid is adsorbed to a greater extent, 0.32 millimoles/gram.

Figure 4 shows the adsorption of the same three compounds onto hydroxyapatite with acetone as the solvent. It is clear that the acetone has a pronounced effect on

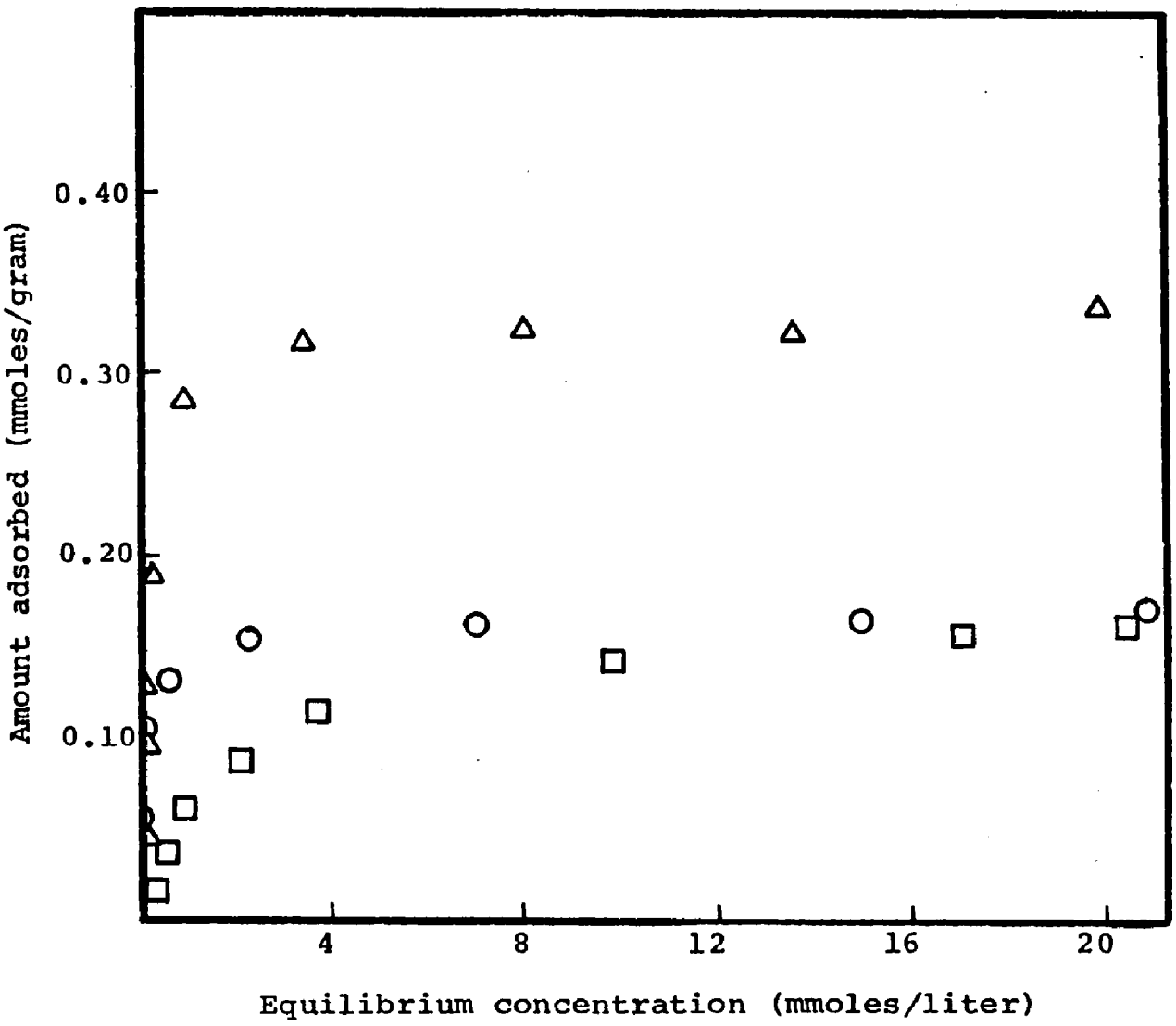

Figure 3. The adsorption of polar organic compounds of the same chain length, but with different anchoring groups, from hexane on hydroxyapatite

Key: △ dodecanoic acid

○ dodecylamine

□ dodecyl alcohol

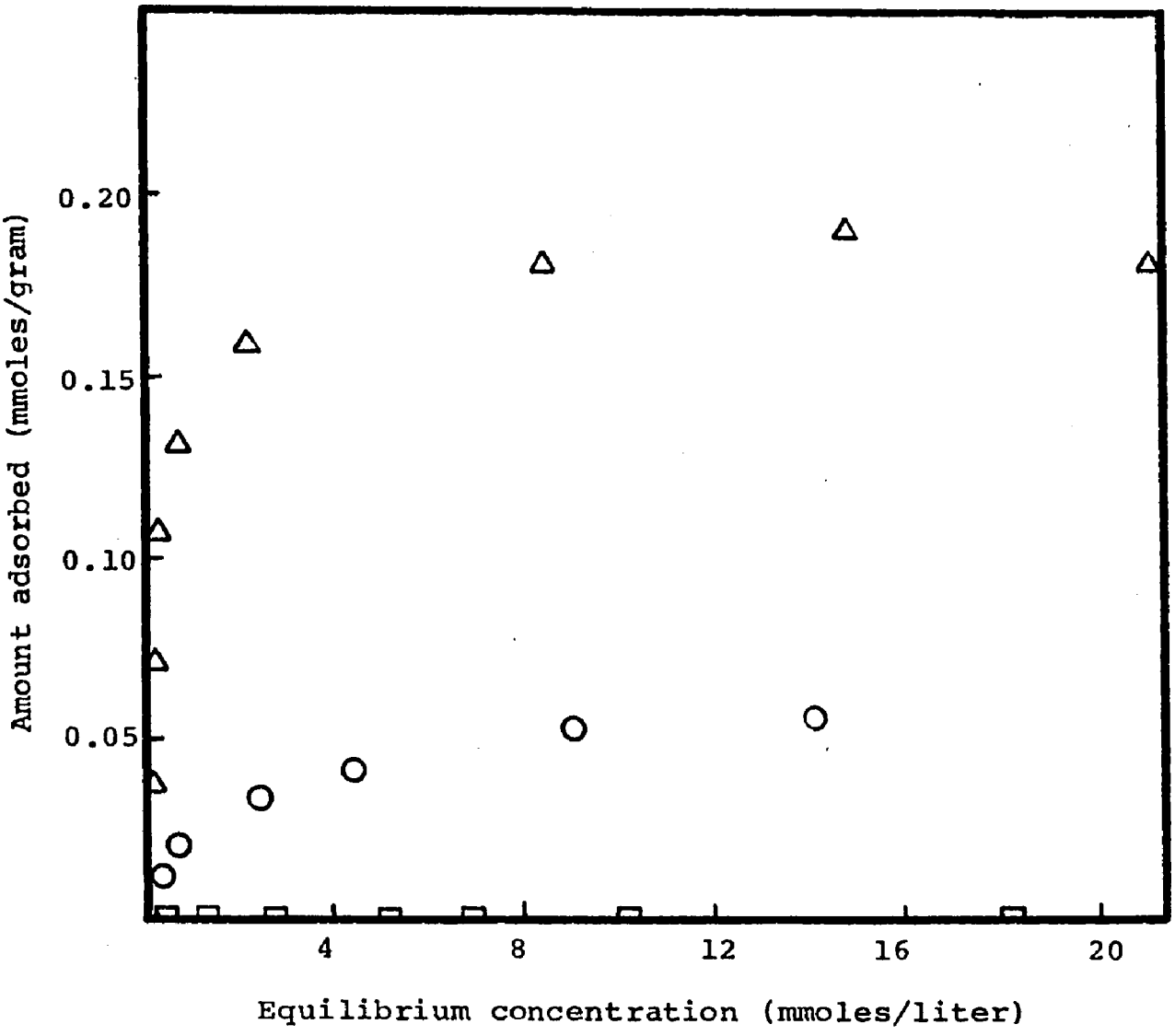

Figure 4. The adsorption of polar organic compounds of the same chain length but with different anchoring groups from acetone on hydroxyapatite.

Key: △ dodecanoic acid

○ dodecylamine

□ dodecyl alcohol

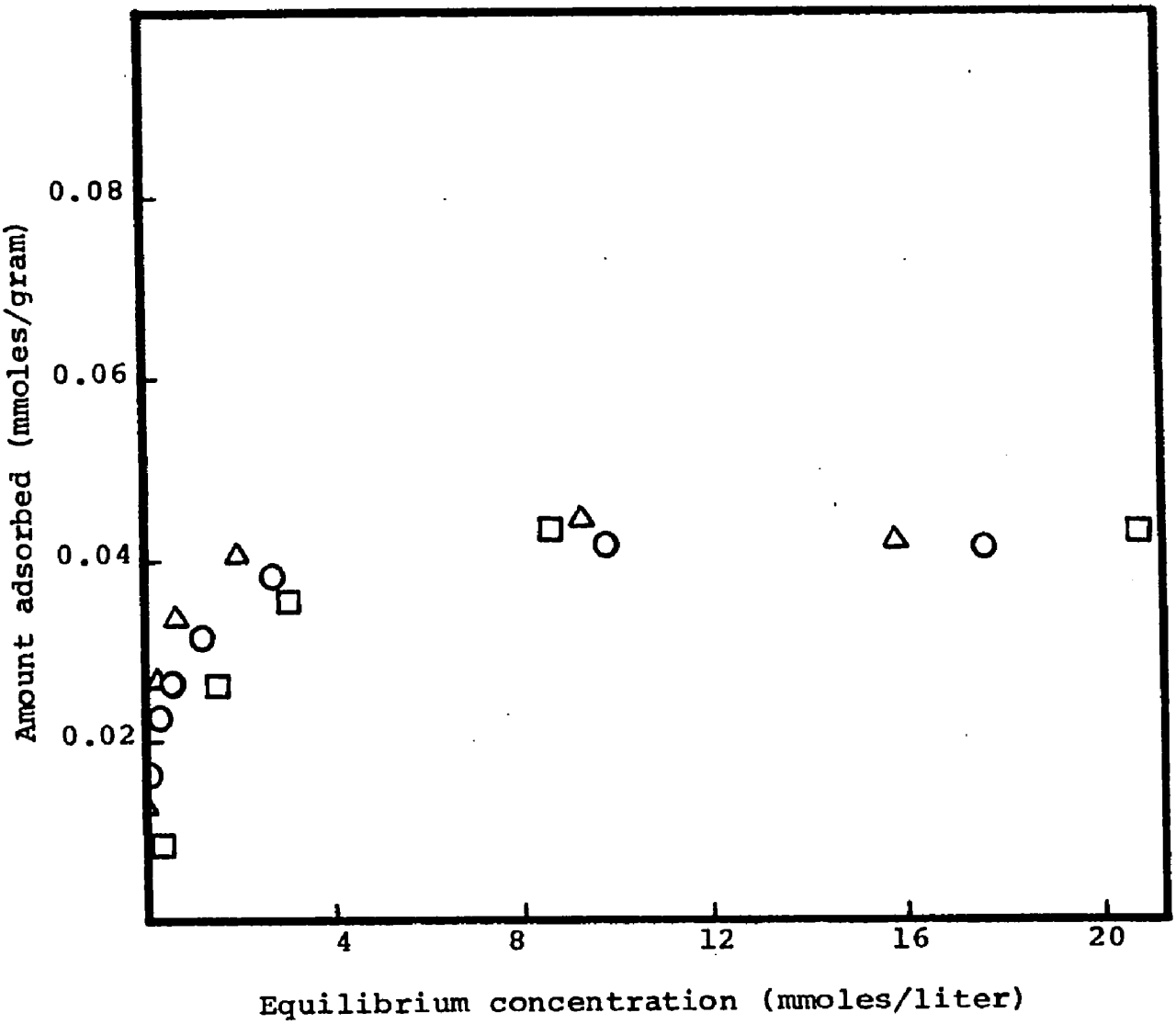

Figure 5. The adsorption of polar organic compounds of the same chain length but with different anchoring groups from hexane on calcium fluoride.

Key: △ dodecanoic acid

○ dodecylamine

□ dodecyl alcohol

the adsorption, when it is compared to that in hexane. In all cases adsorption was reduced, and in the case of the lauryl alcohol it was eliminated. It is interesting to note that the adsorption of the amine and the acid was reduced by the same amount, 0.12 millimoles/gram.

The adsorption of the amine, acid and alcohol on calcium fluoride from hexane is shown in Figure 5. The point of interest in this case is that, even though the isotherms of the three compounds do not have the same initial slope, they all reach the same limiting adsorption. The acid has the greatest initial slope, and the alcohol has the lowest. When the same experiments onto calcium fluoride are performed in acetone rather than hexane, no adsorption of any of the three compounds is seen, again pointing out the strong effect that the acetone has on the adsorption.

From these figures it is evident that the type of polar anchoring group on the molecule can have a pronounced effect in determining the extent of adsorption, depending on the adsorbing surface. It is also clear that acetone has a marked effect on the adsorption, this effect being one of interference with the adsorption. In each case the adsorption is either reduced or entirely prevented by the acetone, depending on the adsorbing surface and the type of polar group on the molecule.

Solvent effects

Since the use of a more polar solvent, acetone, was shown to have such a marked inhibitory effect on the adsorption, it was decided to investigate in more detail the effect of the solvent by adding varying amounts of acetone to the hexane solvent.

These experiments were performed using the same three compounds, dodecylamine, lauryl alcohol and lauric acid, onto hydroxyapatite and calcium fluoride surfaces. The experimental results are presented in Figures 6 through 13. Figure 6 shows the effect of adding varying amounts of acetone to hexane on the adsorption of dodecylamine on hydroxyapatite. Figures 7 and 8 show the same effect for lauryl alcohol and lauric acid, respectively.

The same qualitative description may be applied to the adsorption results obtained from all three compounds. The addition of acetone to hexane, even in small percentages, had an inhibitory effect on the adsorption. In each case, with hydroxyapatite as the adsorbent, as the per cent of acetone was increased, the amounts adsorbed decreased. In the case of the lauryl alcohol, the incorporation of 5 per cent of acetone was sufficient to completely prevent adsorption of the alcohol. The situation was different, however, for the amine and the acid. Here, above a certain amount of added acetone, there was no further change in the adsorption. Instead of going to

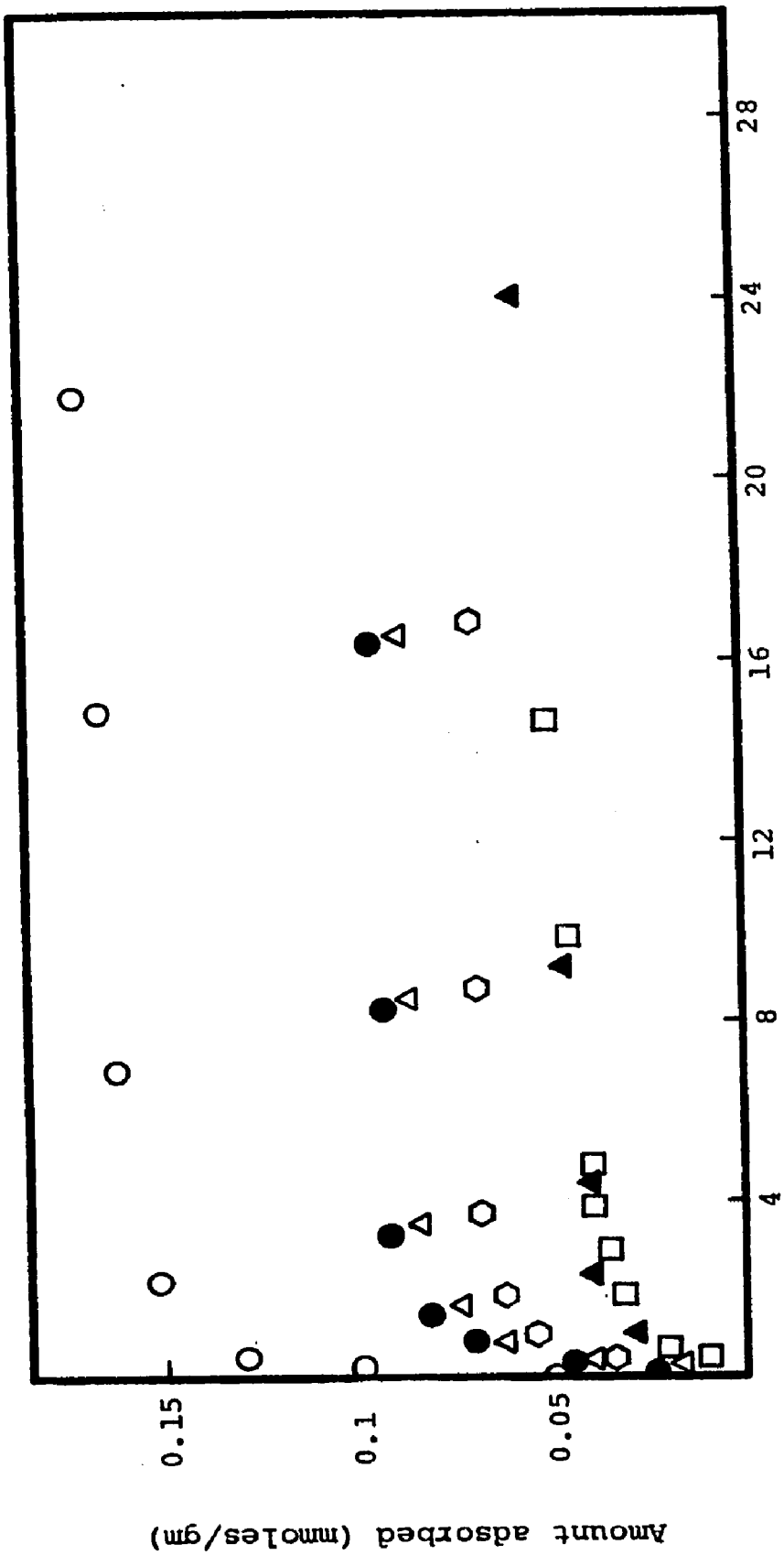

Figure 6. Effect of solvent on the adsorption of dodecylamine from acetone-hexane mixtures on hydroxyapatite.

Key: Concentration of acetone in hexane

○ none △ 2% ▲ 10%

● 1% ⬡ 5% □ 100%

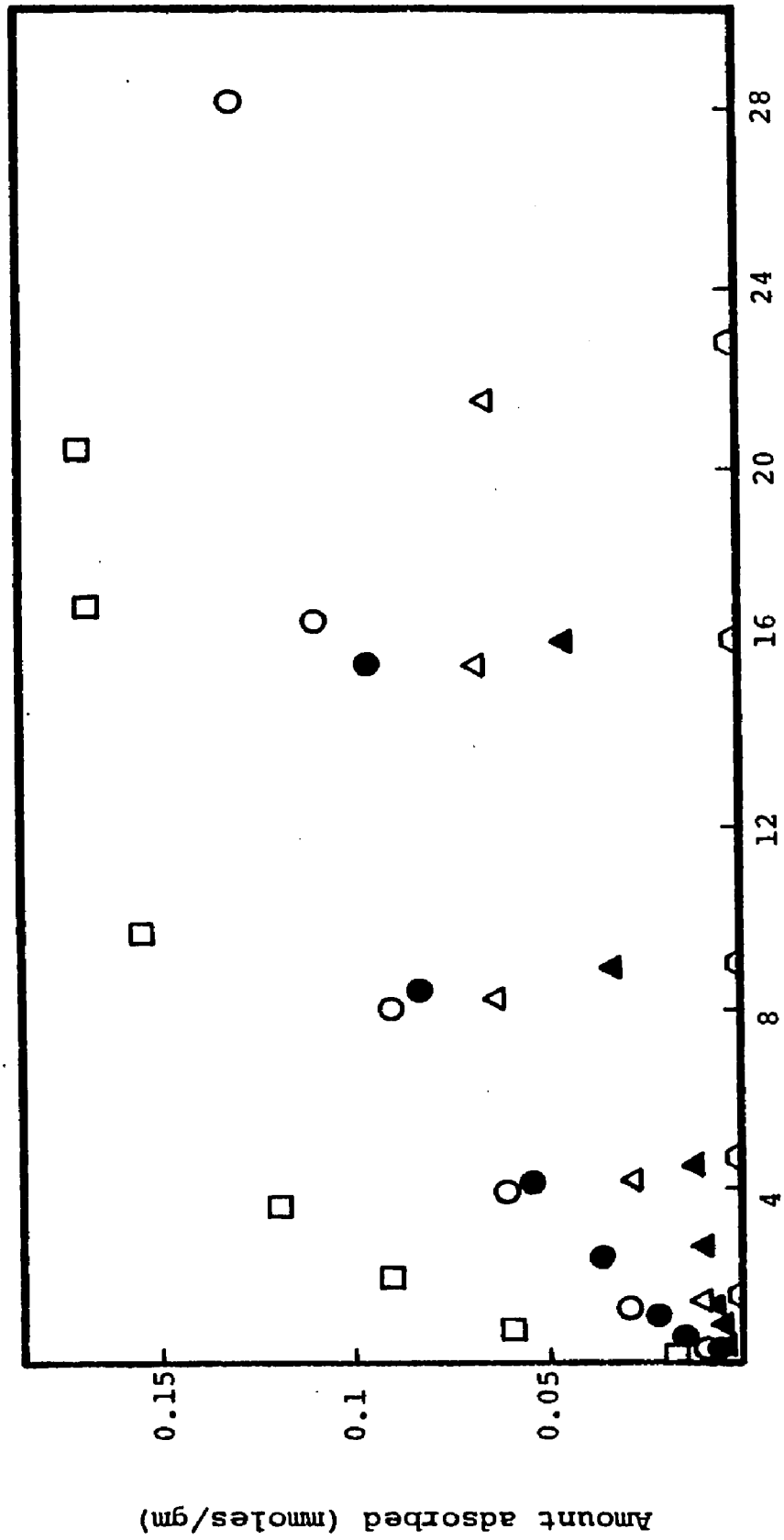

Figure 7. Effect of solvent on the adsorption of lauryl alcohol from acetone-hexane mixtures on hydroxyapatite.

Key: Concentration of acetone in hexane

□ none ● 1% ▲ 3%

○ 0.5% △ 2% ⬡ 5%

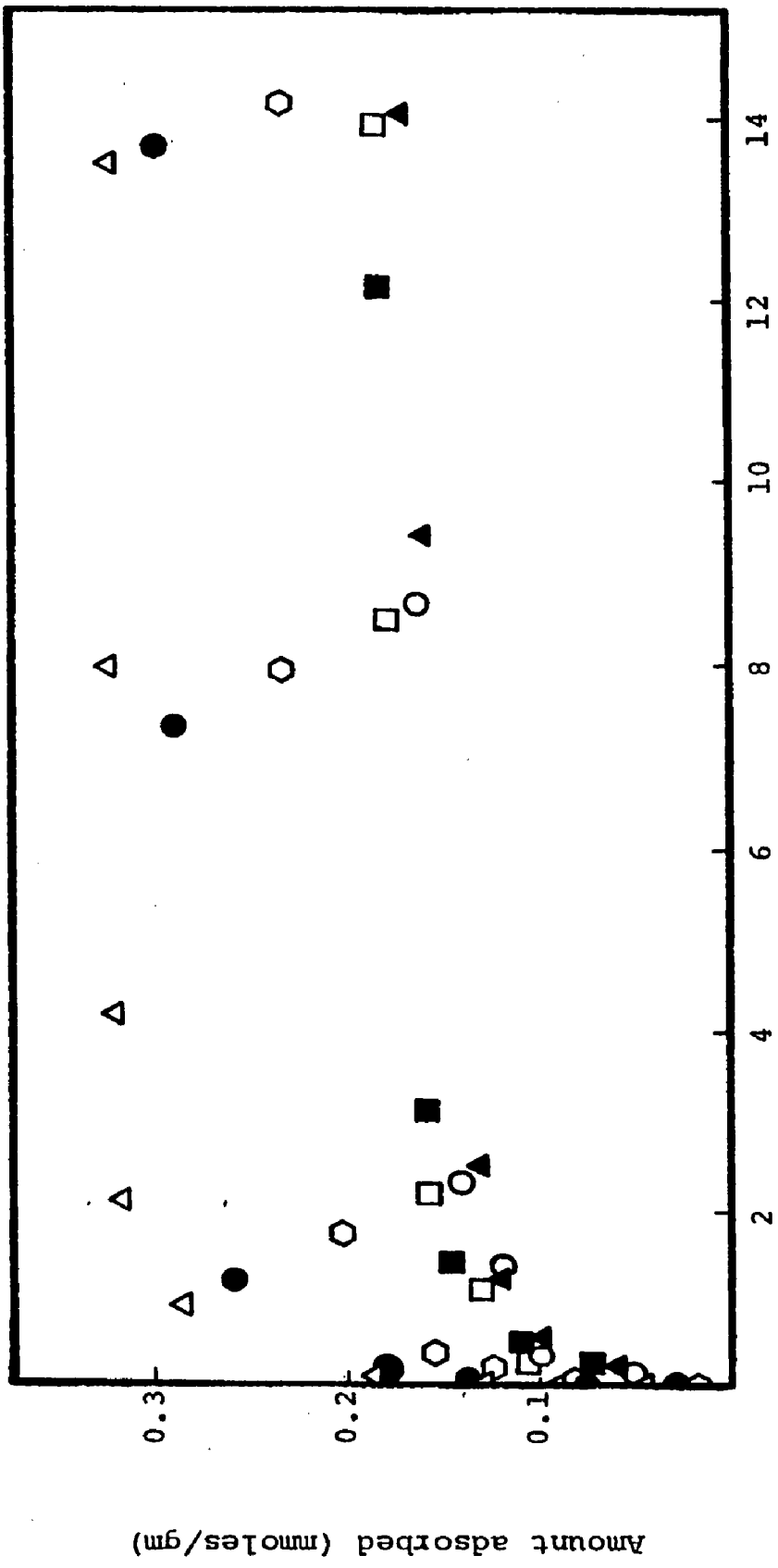

Figure 8. Effect of solvent on the adsorption of lauric acid from acetone-hexane mixtures on hydroxyapatite.

Key: Concentration of acetone in hexane

△ none ⬡ 5% ▲ 25% □ 100%

● 1% ■ 10% ○ 50%

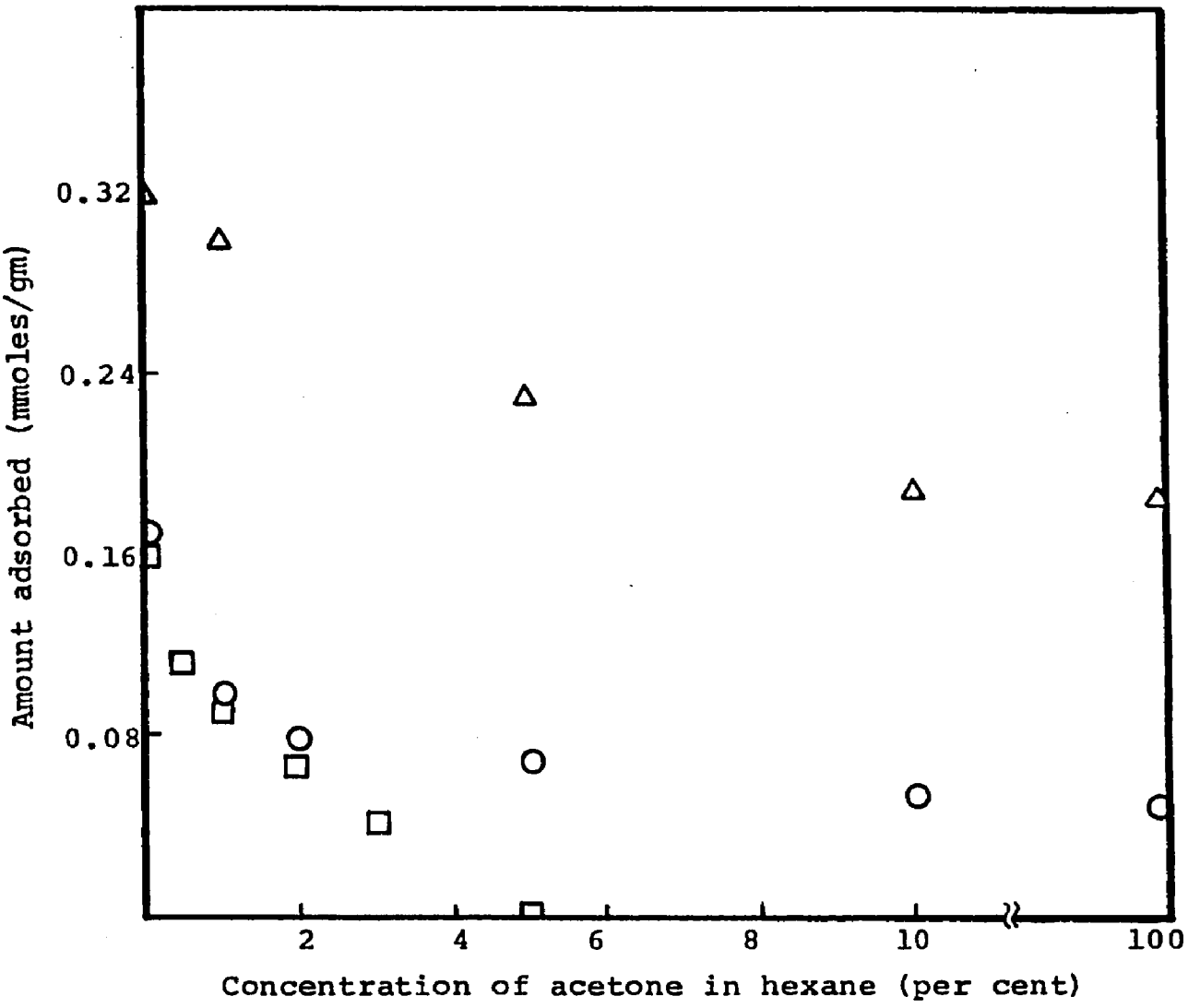

Figure 9. Effect of acetone on the limiting adsorption values of lauric acid, dodecylamine and lauryl alcohol on hydroxyapatite from acetone-hexane solvent mixtures.

Key: △ lauric acid

○ dodecylamine

□ lauryl alcohol

zero, the adsorption reaches a minimum limiting value at an acetone concentration of 10 per cent. That is, amounts of acetone greater than 10 per cent produced no further decrease in the adsorption, up to 100 per cent acetone.

The inhibitory effect of acetone on the equilibrium adsorption levels of the three compounds on hydroxyapatite is demonstrated in Figure 9. The initial slopes of these curves indicate that the initial degree of inhibition of the acetone was greater for the amine and the alcohol than for the acid, implying that the acid has a greater affinity for the site for which the acetone competes. The initial slopes of the alcohol and the amine are almost identical, which seems to indicate that they exhibit the same sensitivity to the addition of the acetone in their adsorption. This would mean that they have the same affinity for the site from which they are displaced by the acetone. However, the maximal effect on the adsorption in the case of the amine required more than the addition of 5 per cent acetone, indicating that it does have a somewhat greater affinity for this site than does the alcohol.

The adsorption isotherms of the dodecylamine, lauryl alcohol and lauric acid from the mixed solvent systems on calcium fluoride are presented in Figures 10 through 12. The effect of adding various proportions of acetone to hexane on the adsorption of dodecylamine is demonstrated in Figure 10. Figures 11 and 12 show the same effect on the adsorption of lauryl alcohol and lauric acid. Here,

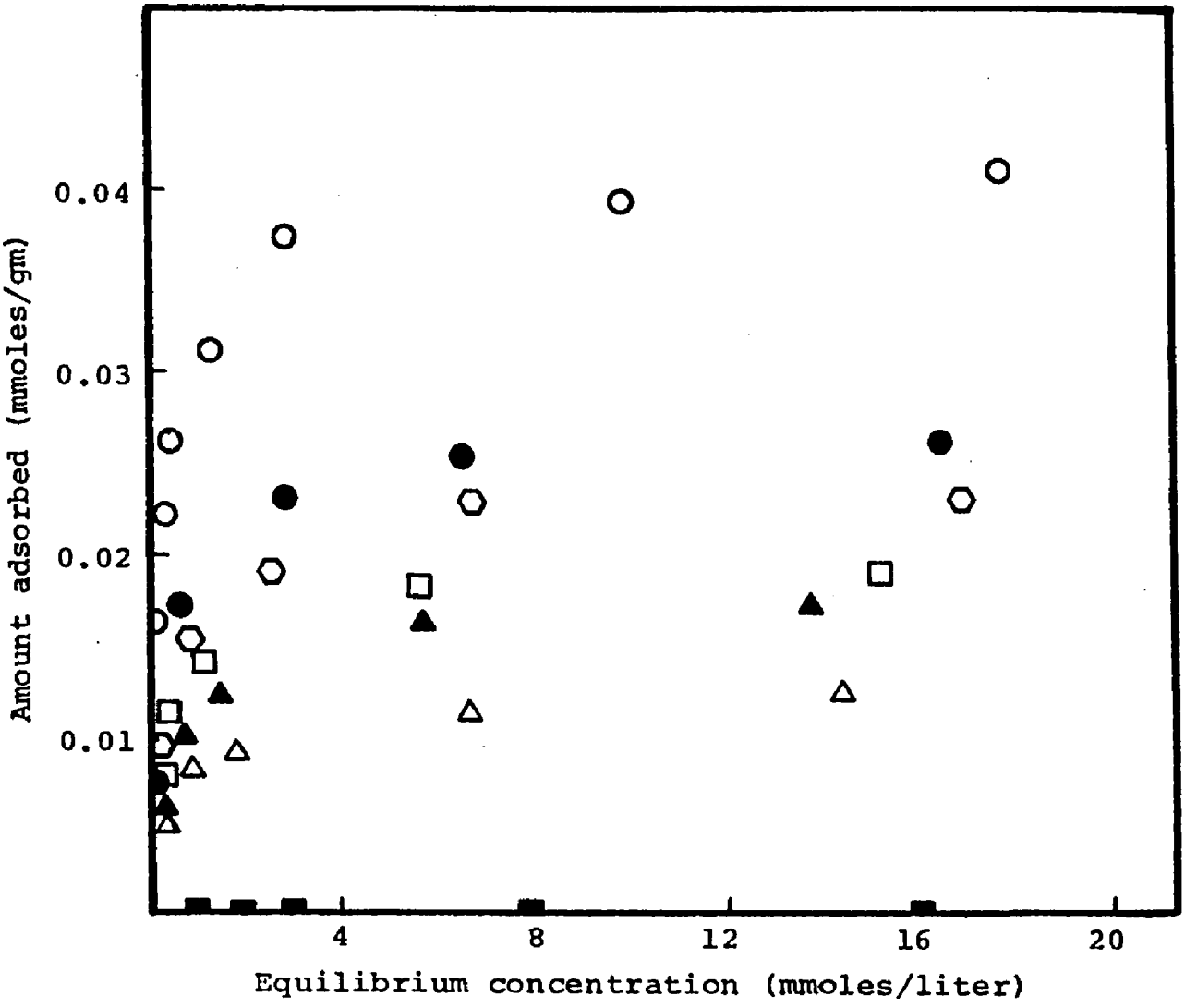

Figure 10. Effect of solvent on the adsorption of dodecylamine from acetone-hexane mixtures on calcium fluoride.

Key: Concentration of acetone in hexane

○ none ⬡ 0.5% ▲ 2.0% ■ 10.0%

● 0.25% □ 1.0% △ 4.0%

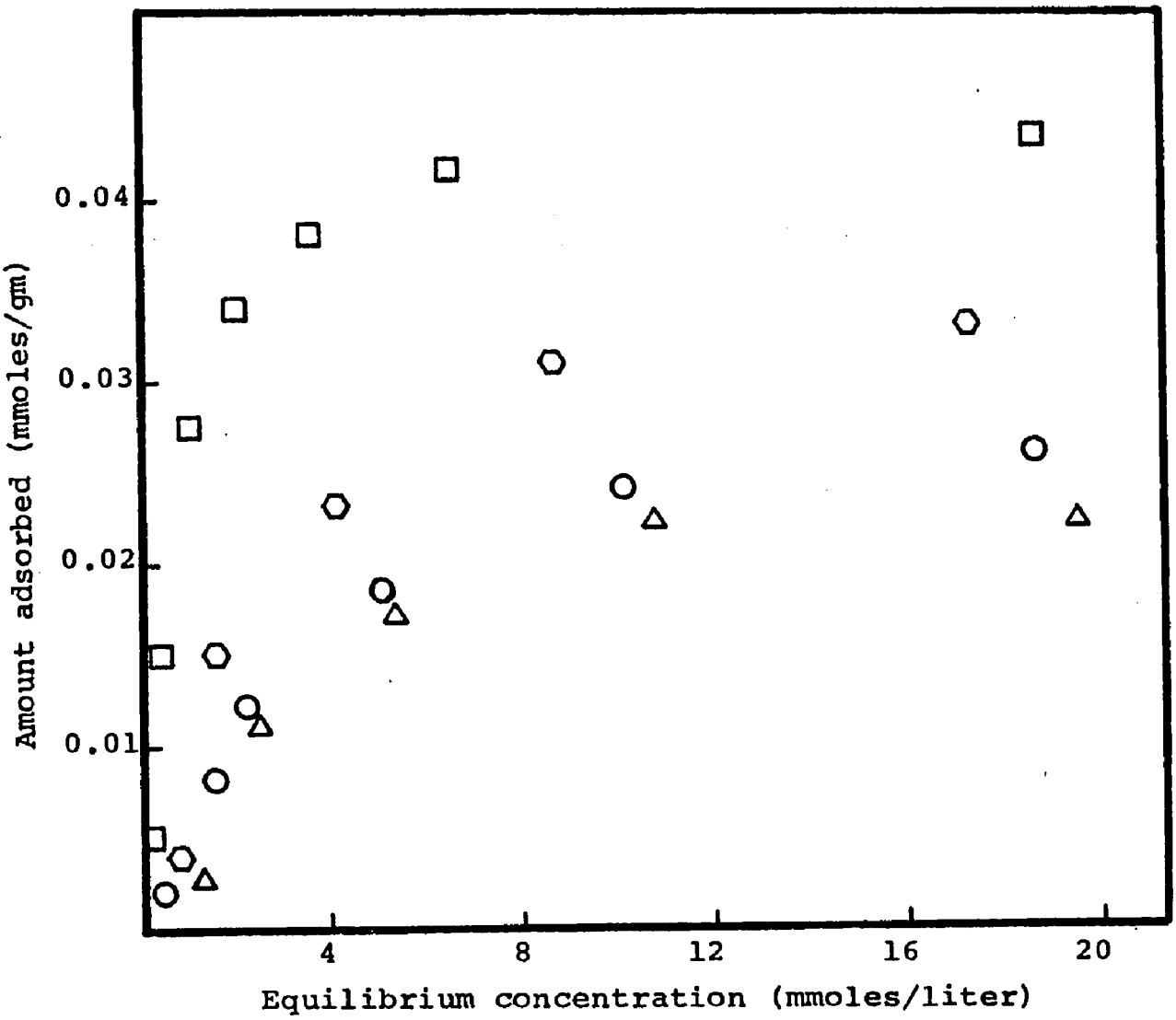

Figure 11. Effect of solvent on the adsorption of lauryl alcohol from acetone-hexane mixtures on calcium fluoride.

Key: Concentration of acetone in hexane

□ none ○ 2%

⬡ 1% △ 4%

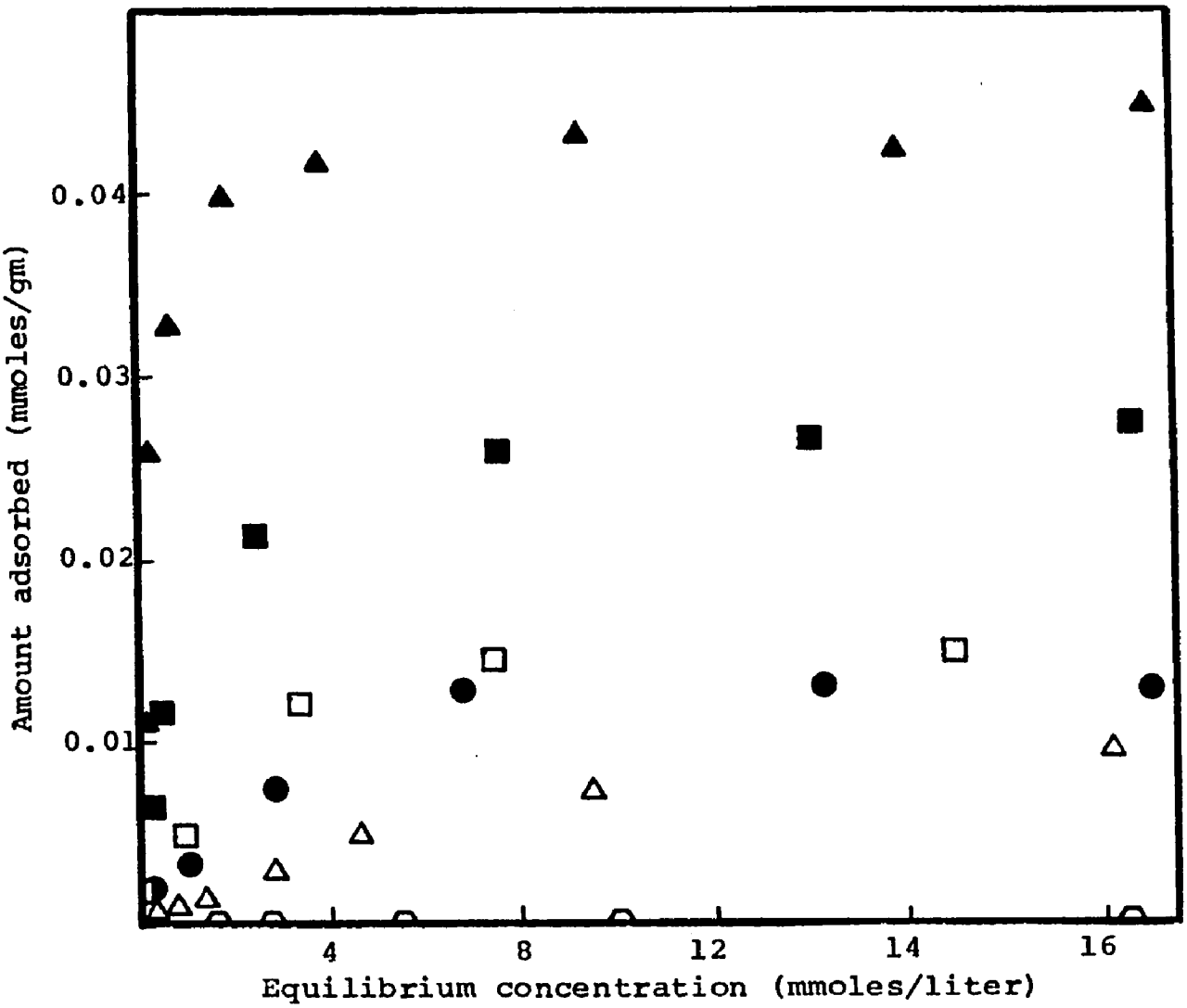

Figure 12. Effect of solvent on the adsorption of lauric acid from acetone-hexane mixtures on calcium fluoride.

Key: Concentration of acetone in hexane

▲ none □ 2% △ 5%

■ 1% ● 3% ⬡ 8%

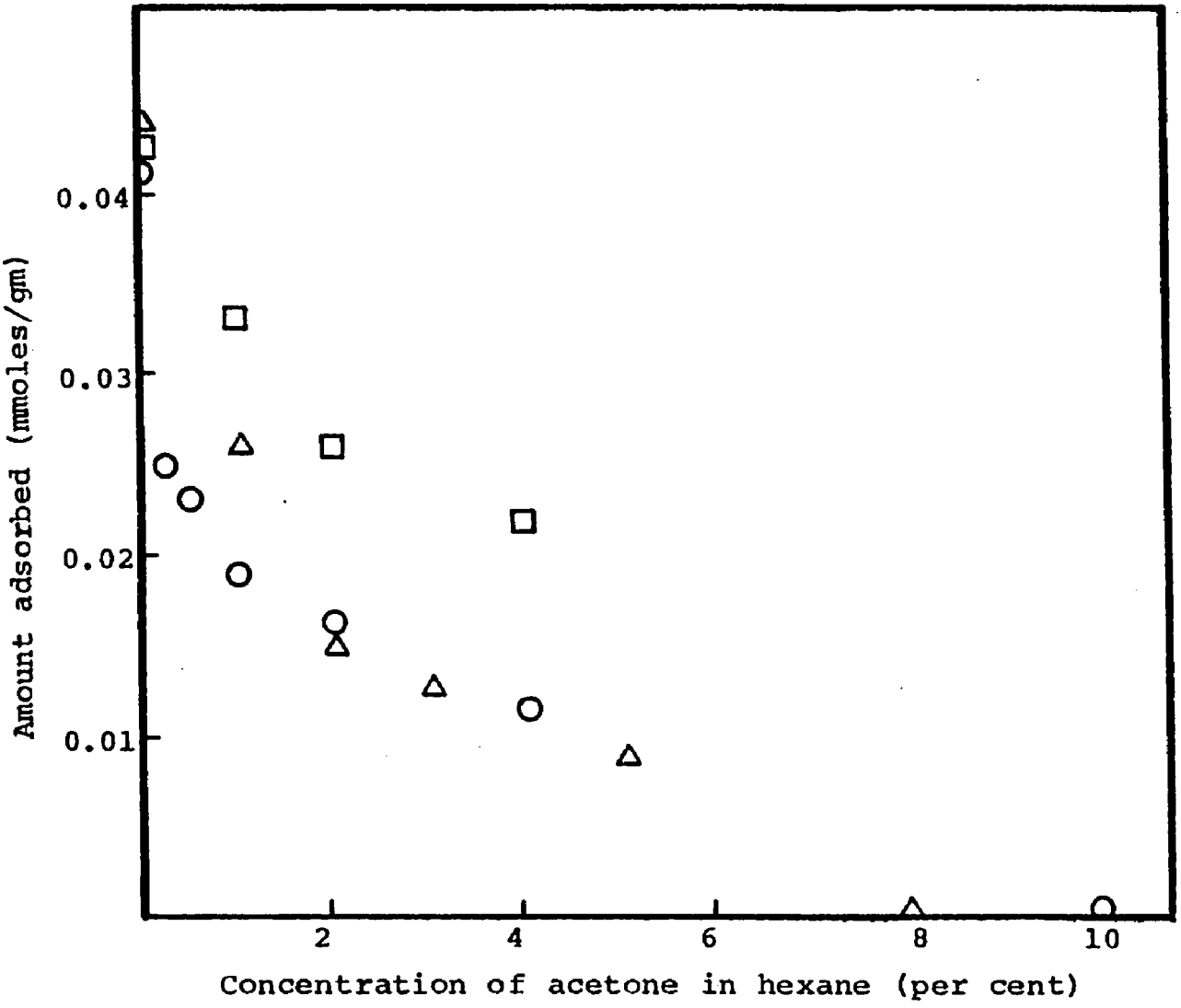

Figure 13. Effect of acetone on the limiting adsorption values of lauric acid, dodecylamine and lauryl alcohol on calcium fluoride from acetone-hexane solvent mixtures.

Key: △ lauric acid

○ dodecylamine

□ lauryl alcohol

again, the same general trends may be observed. As the concentration of acetone in hexane is increased, the amounts of the other compounds adsorbed as well as the initial slopes decreased, indicating inhibition of adsorption by the more polar solvent, acetone. It is interesting to note that at the higher acetone concentrations, where the inhibition is quite strong, there appear to be deviations from the Langmuir shape in the isotherms, in the case of the alcohol and the acid. At acetone concentrations of 5% for the acid and 4% for the alcohol, a slight S-shape appears to be developing in the curves.

In each case, when the concentration of acetone became high enough, zero adsorption of the compounds was approached. For the lauric acid, this concentration was 8% acetone, and for the dodecylamine, 10% acetone.

The inhibitory effect of acetone on the limiting adsorption values is presented in Figure 13. Here, the plateau values of the adsorption isotherms are presented as a function of the percentage of acetone in the hexane solvent. There is a relatively rapid initial decrease in the adsorption levels at low concentrations of added acetone, with the degree of inhibition increasing less rapidly at higher levels of acetone.

Chain length effect

The effect of varying the length of the hydrophobic chain on the molecule while keeping the polar anchoring

group constant was studied by using homologous series of n-alkanoic acids, n-alkyl amines and alcohols. The adsorption experiments were carried out in n-hexane and acetone, with hydroxyapatite and calcium fluoride as the adsorbents. The results of these experiments are presented in Figures 14 through 21.

The adsorption isotherms of n-alkanoic acids of varying chain length are shown in Figures 14, 15 and 16. Figure 14 shows the adsorption of octanoic, decanoic, lauric and myristic acids onto hydroxyapatite from hexane. The same four compounds adsorbed onto hydroxyapatite from acetone give the results seen in Figure 15, and Figure 16 shows the adsorption isotherms of butyric, octanoic, lauric and myristic acids onto calcium fluoride from hexane. When acetone was used as the solvent, no adsorption on calcium fluoride occurred. From these results, it is clear that there appears to be no significant chain length effect on the adsorption of the acids, from either solvent or on either surface. This is true when speaking of both the initial slopes and the plateau regions.

All of the n-alkanoic acids are very strongly adsorbed onto hydroxyapatite from hexane, as evidenced by the extremely steep initial slopes. This steepness makes it difficult to detect any small differences between the initial slopes of the different compounds, if any exists. When acetone is the solvent, the compounds are less strongly adsorbed, and to a lesser extent.

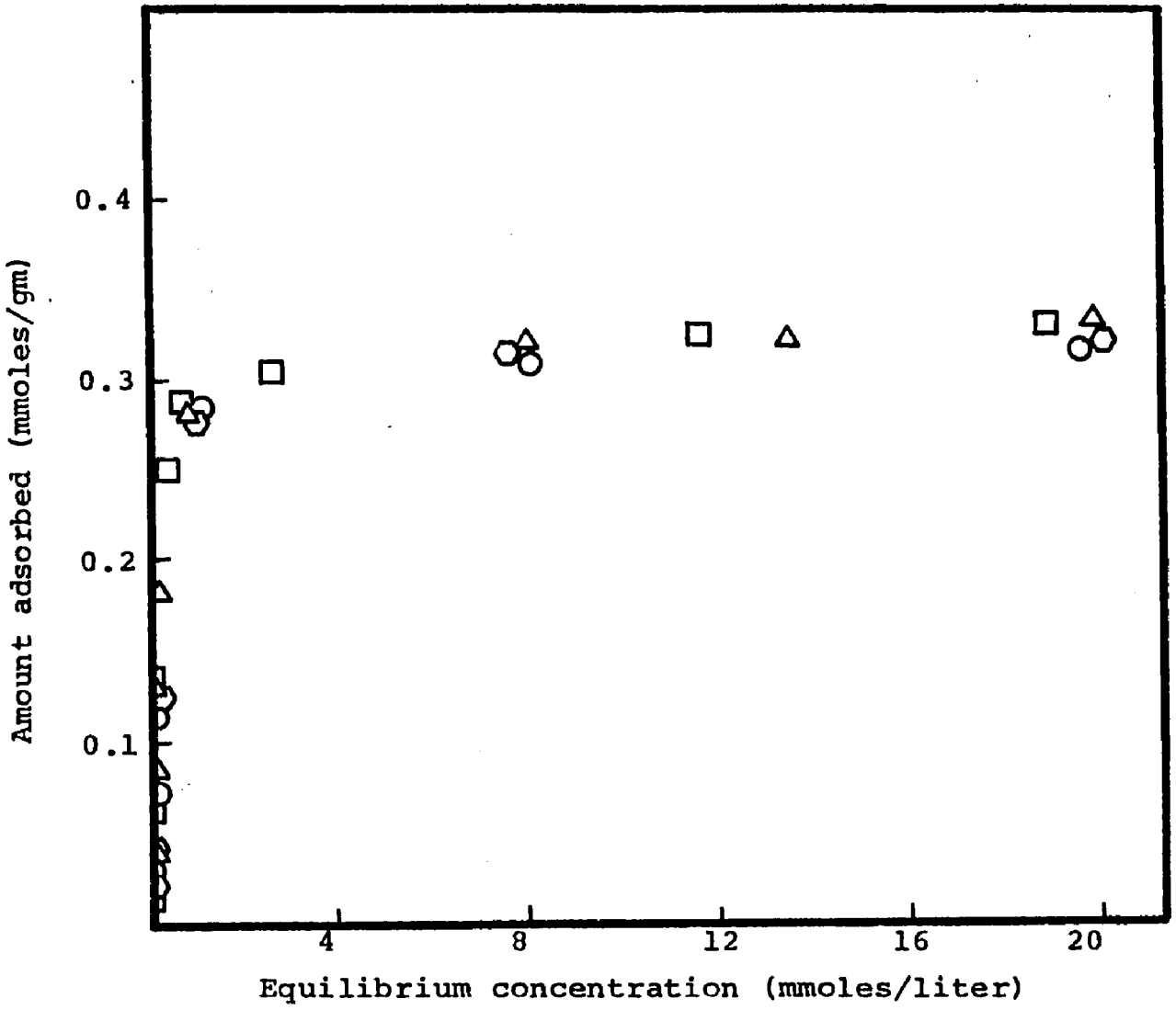

Figure 14. The adsorption of n-fatty acids of varying chain lengths from hexane on hydroxyapatite.

Key: ⬡ octanoic acid △ lauric acid

O decanoic acid □ myristic acid

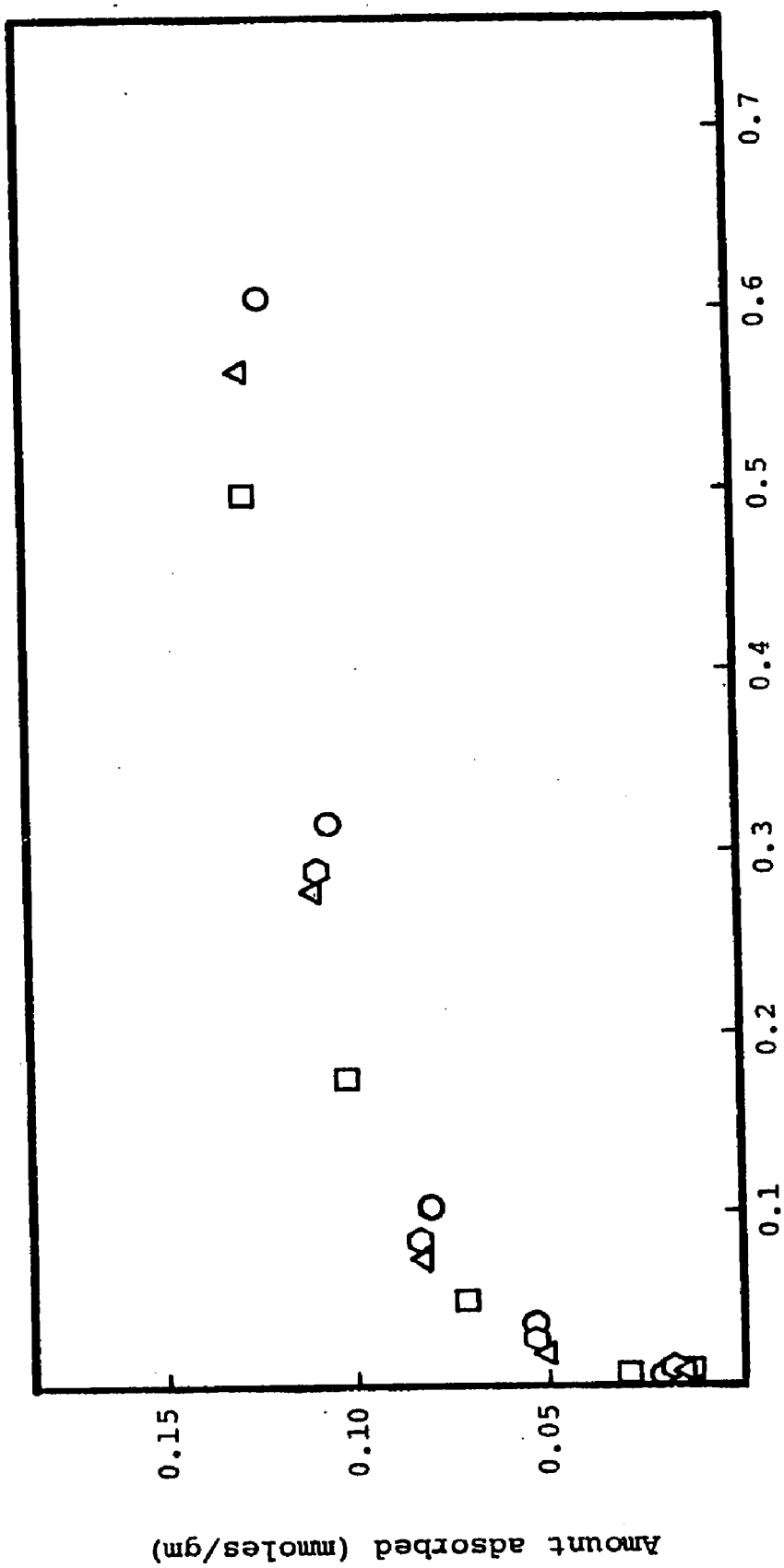

Figure 15. The adsorption of n-fatty acids of varying chain lengths from acetone on hydroxyapatite.

Key: ○ octanoic acid △ lauric acid
⬡ decanoic acid □ myristic acid

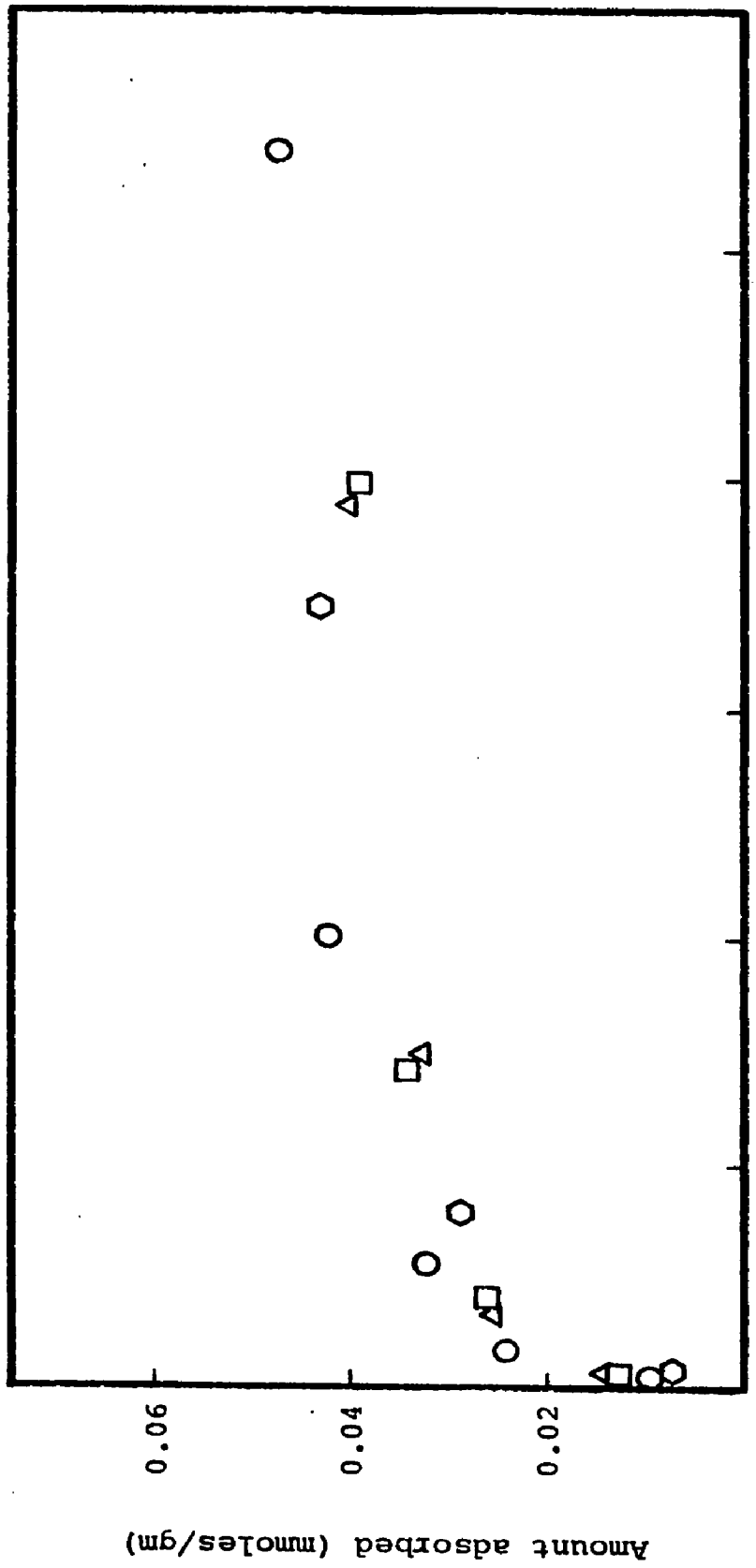

Figure 16. The adsorption of n-fatty acids of varying chain lengths from hexane on calcium fluoride.

Key: ⬡ butyric acid ◁ lauric acid
○ octanoic acid □ myristic acid

The adsorption isotherms of various n-alkylamines of differing chain lengths are presented in Figures 17, 18 and 19. Figure 17 shows the adsorption of butylamine, octylamine and dodecylamine on hydroxyapatite from hexane. Although no differences can be detected in the initial slopes, because they are all so steep, it is clear that the butylamine is adsorbed to a significantly greater extent than the octylamine or the dodecylamine. The octylamine has a slightly higher adsorption than the dodecylamine, 0.185 millimoles/gram as opposed to 0.170 millimoles/gram, and even though this difference is small, it was consistently observed in several experiments.

When the same experiment was performed in acetone (Figure 18), in addition to the overall adsorption of all three compounds being reduced, the chain length effect was also diminished. The butylamine still shows a slightly higher adsorption than the octylamine, but the difference is much less, and there is essentially no difference between the octylamine and the dodecylamine, neither in the initial slopes nor in the plateau region.

To get an indication of the adsorption behavior of the butylamine on the site that the acetone eliminates on hydroxyapatite, the adsorption in acetone was subtracted from the adsorption in hexane, and the resulting curve is presented in Figure 19. It can be seen that the butylamine exhibits the same characteristics in the adsorption that it did in the hexane, which means that this unusually

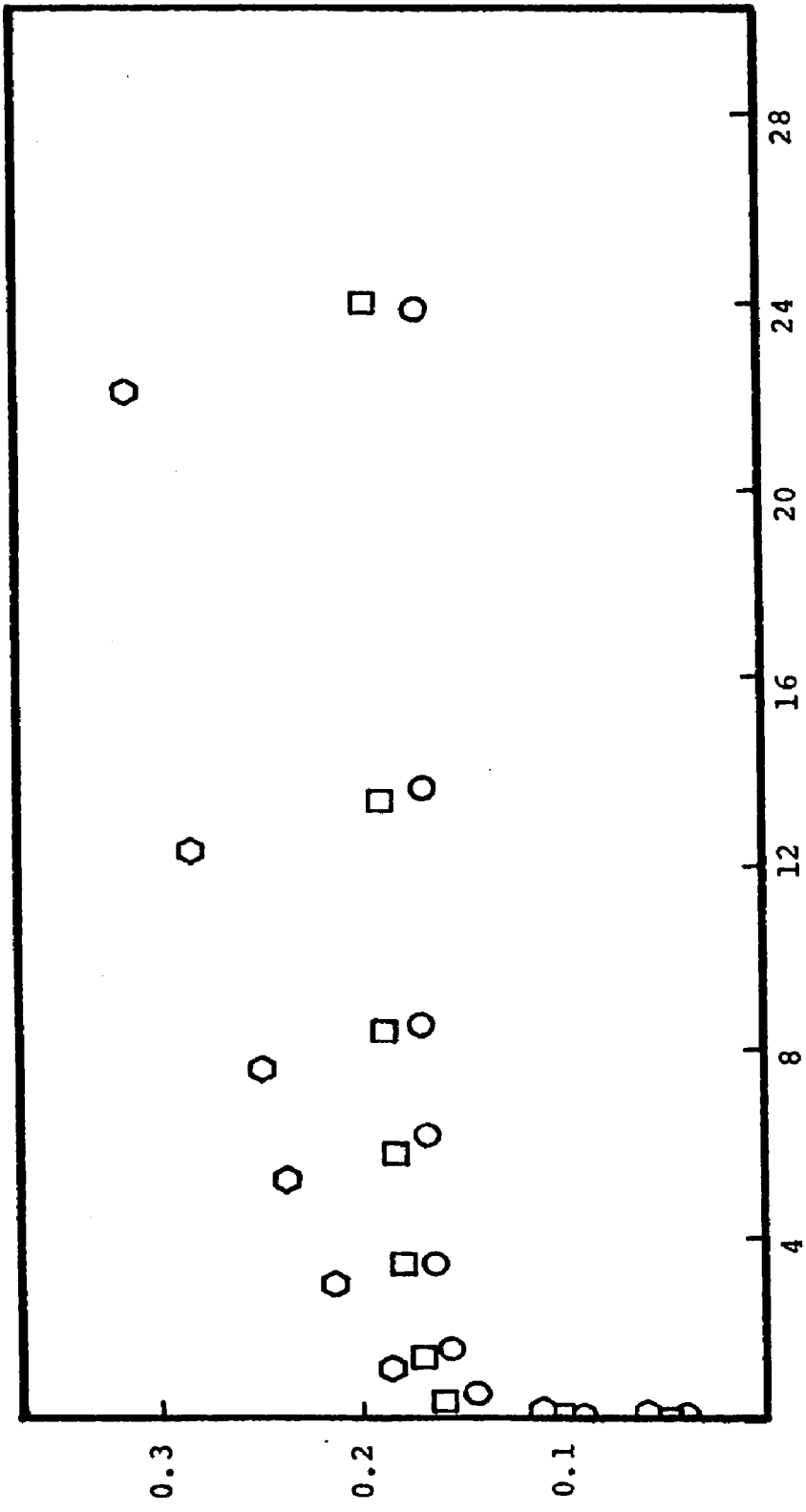

Figure 17. The adsorption of n-alkylamines of varying chain lengths from hexane on hydroxyapatite.

Key: ⬡ butylamine
□ octylamine
○ dodecylamine

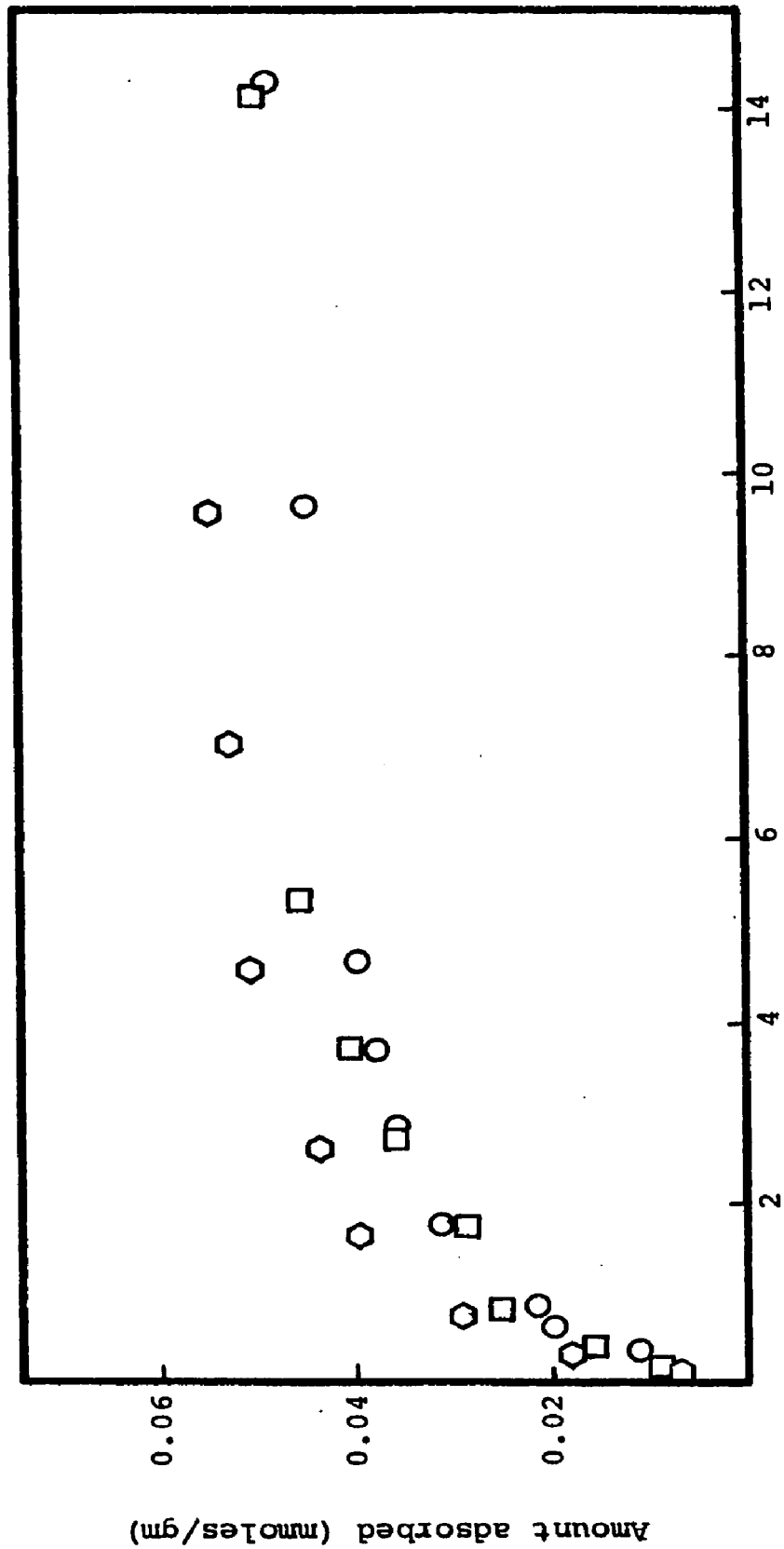

Figure 18. The adsorption of n-alkylamines of varying chain lengths from acetone on hydroxyapatite.

Key: ⬡ butylamine
□ octylamine
○ dodecylamine

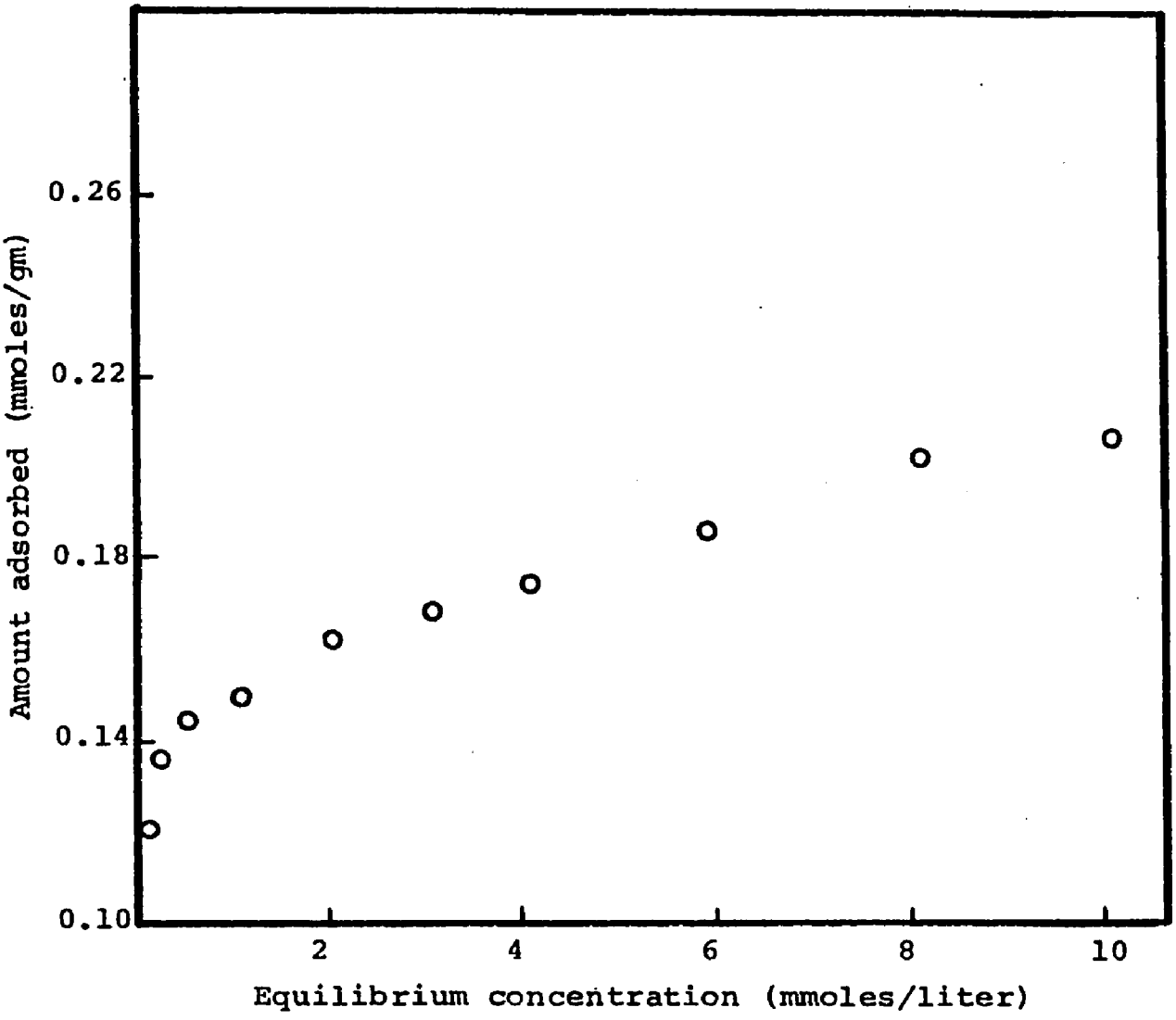

Figure 19. The adsorption isotherm representing the difference between butylamine adsorption on hydroxyapatite from hexane and that from acetone.

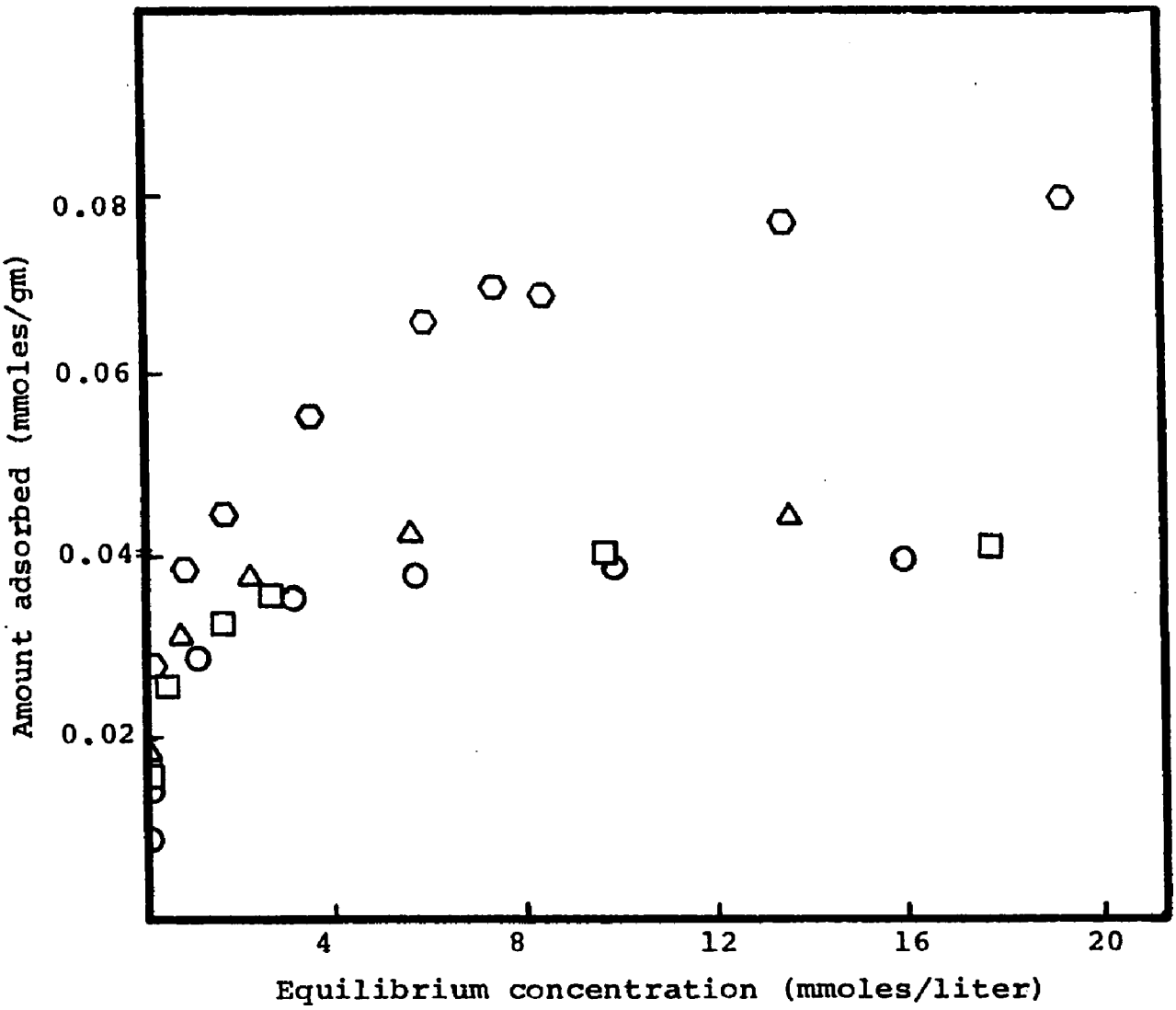

Figure 20. The adsorption of n-alkylamines of varying chain lengths from hexane on calcium fluoride.

Key: ○ butylamine □ octylamine

△ hexylamine ○ dodecylamine

high adsorption is occurring on the site that is poisoned by the acetone.

Figure 20 shows the results obtained when butylamine, hexylamine, octylamine and dodecylamine were adsorbed onto calcium fluoride, with hexane as the solvent. Here again, because the initial slopes are so steep, it is difficult to detect any differences. Temporarily disregarding the butylamine adsorption, which will be discussed later, it is clear that there is a slight chain length effect apparent at the limiting adsorption values. This difference in the plateaus between the hexylamine, octylamine and dodecylamine is small, but it is reproducible and real. The hexylamine shows a slightly higher adsorption than the octylamine and the dodecylamine, which are almost the same.

It is interesting to compare the adsorption isotherm of the butylamine onto calcium fluoride to the curve which represents the difference between the butylamine adsorption onto hydroxyapatite from hexane and that from acetone (Figure 19). It is clear that the curves are very similar in their shape and characteristics. This seems to indicate that the amine is adsorbing onto the same kind of adsorption site in each case.

A greater general chain length effect on the adsorption of molecules of comparable chain length as the amines was observed when alcohols were adsorbed onto calcium fluoride from hexane. The results are seen in Figure 21. In this case, hexyl, dodecyl and cetyl (C_{16}) alcohols were

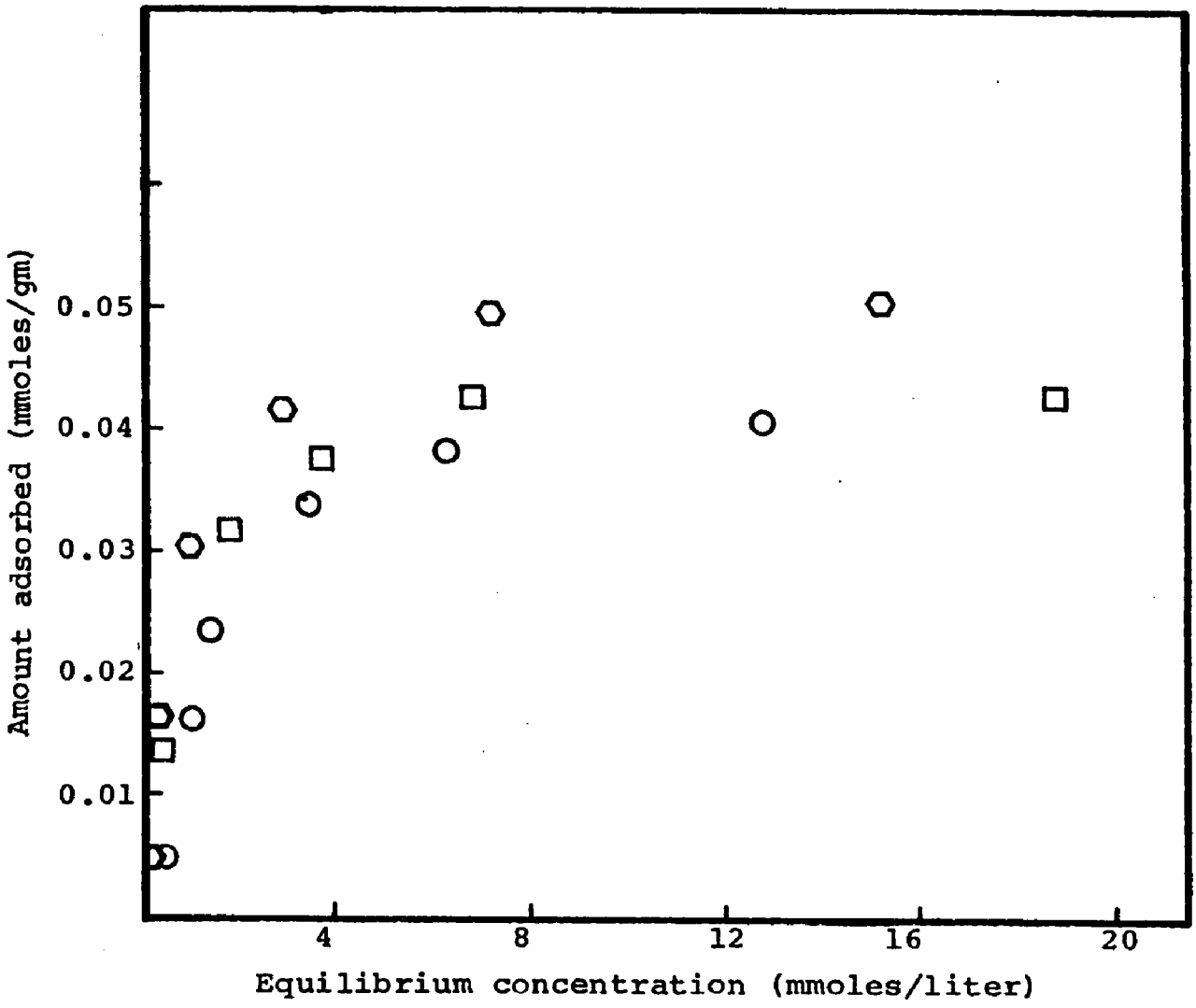

Figure 21. The adsorption of alcohols of varying chain lengths from hexane on calcium fluoride.

Key: ⬡ hexyl alcohol

□ lauryl alcohol

○ cetyl alcohol

used, and it can be seen that the difference between the six carbon and the twelve carbon alcohol is greater than that between amines of the same chain length. It is also clear from these results that as the chain length is increased the differences in the adsorption isotherms are decreased. That is, the plateaus come closer together as the chain length increases.

As was the case with the acids and the amines, no adsorption occurred when acetone was used as the solvent.

Chain length effect in mixed solvents

When adsorption studies were done in mixed solvent systems of acetone in hexane, some deviations from the theoretical curves based on the Langmuir equation were found. It was thought that these deviations may be a result of a decrease in the effective X (interaction energy) of the solute, due to the coverage of the surface by acetone. A lowering of the X would result in a greater chain length effect, according to the model, and the adsorption would be reduced. To investigate this possibility, a series of experiments were performed using hexyl, lauryl and cetyl alcohols in various concentrations of acetone in hexane, with calcium fluoride as the adsorbent. The results are presented in Figures 22, 23 and 24. The concentrations of acetone used were 1, 2 and 4 per cent, respectively. Figure 25 shows the equilibrium adsorption levels for each compound as a function of the acetone con-

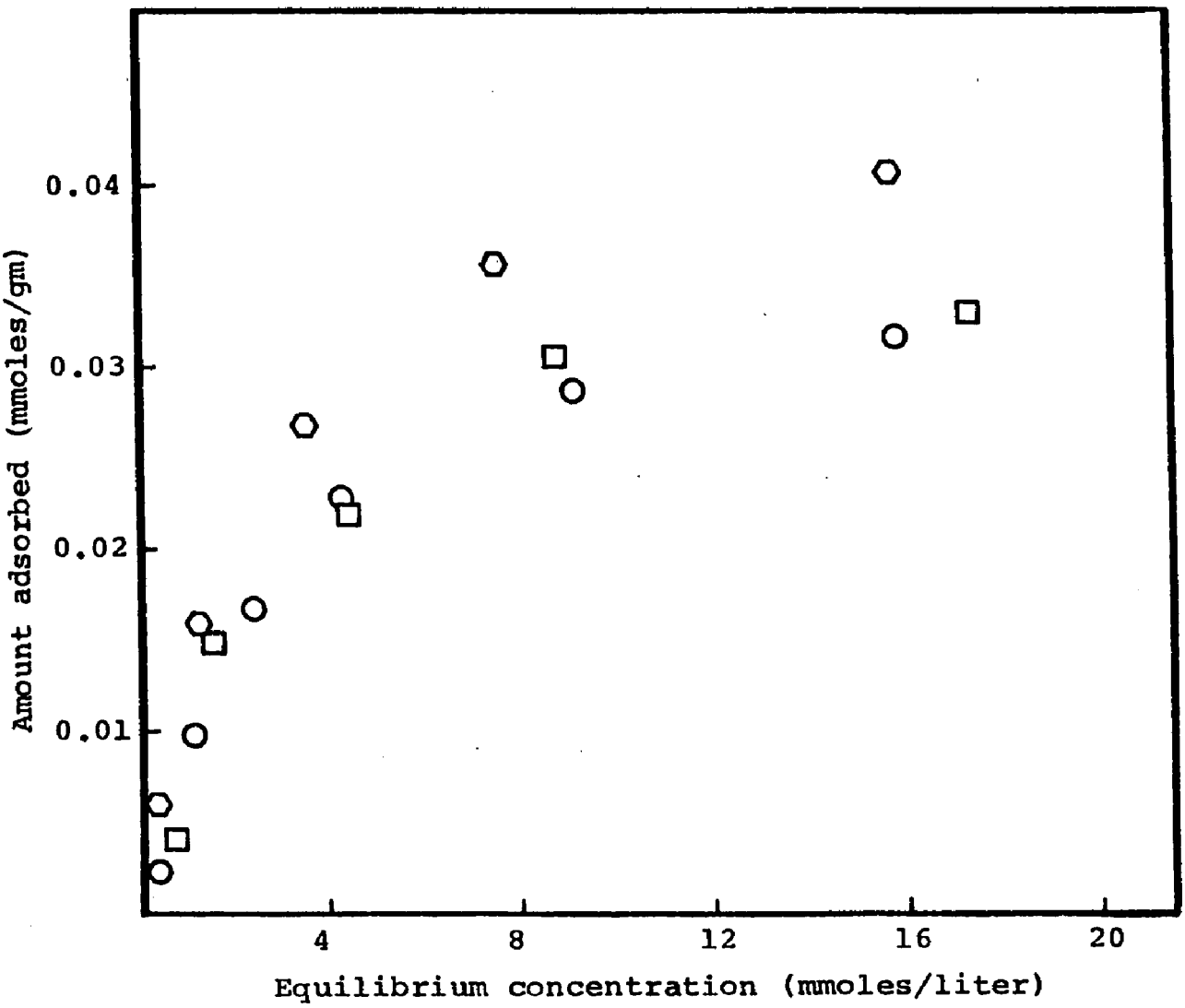

Figure 22. The adsorption of alcohols of varying chain lengths from 1% acetone in hexane on calcium fluoride.

Key: ⬡ hexyl alcohol

□ lauryl alcohol

○ cetyl alcohol

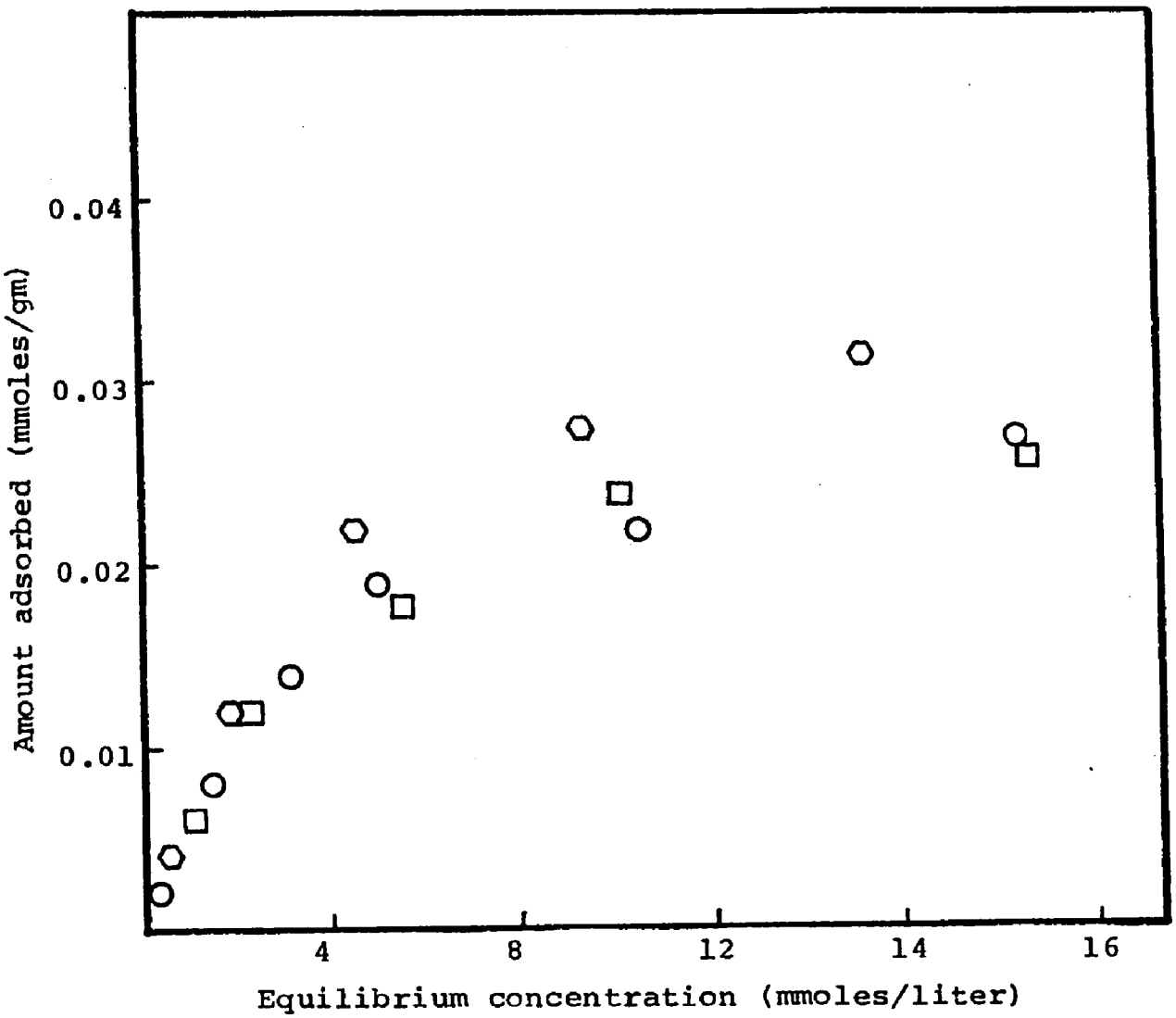

Figure 23. The adsorption of alcohols of varying chain lengths from 2% acetone in hexane on calcium fluoride.

Key: ⬡ hexyl alcohol

□ lauryl alcohol

○ cetyl alcohol

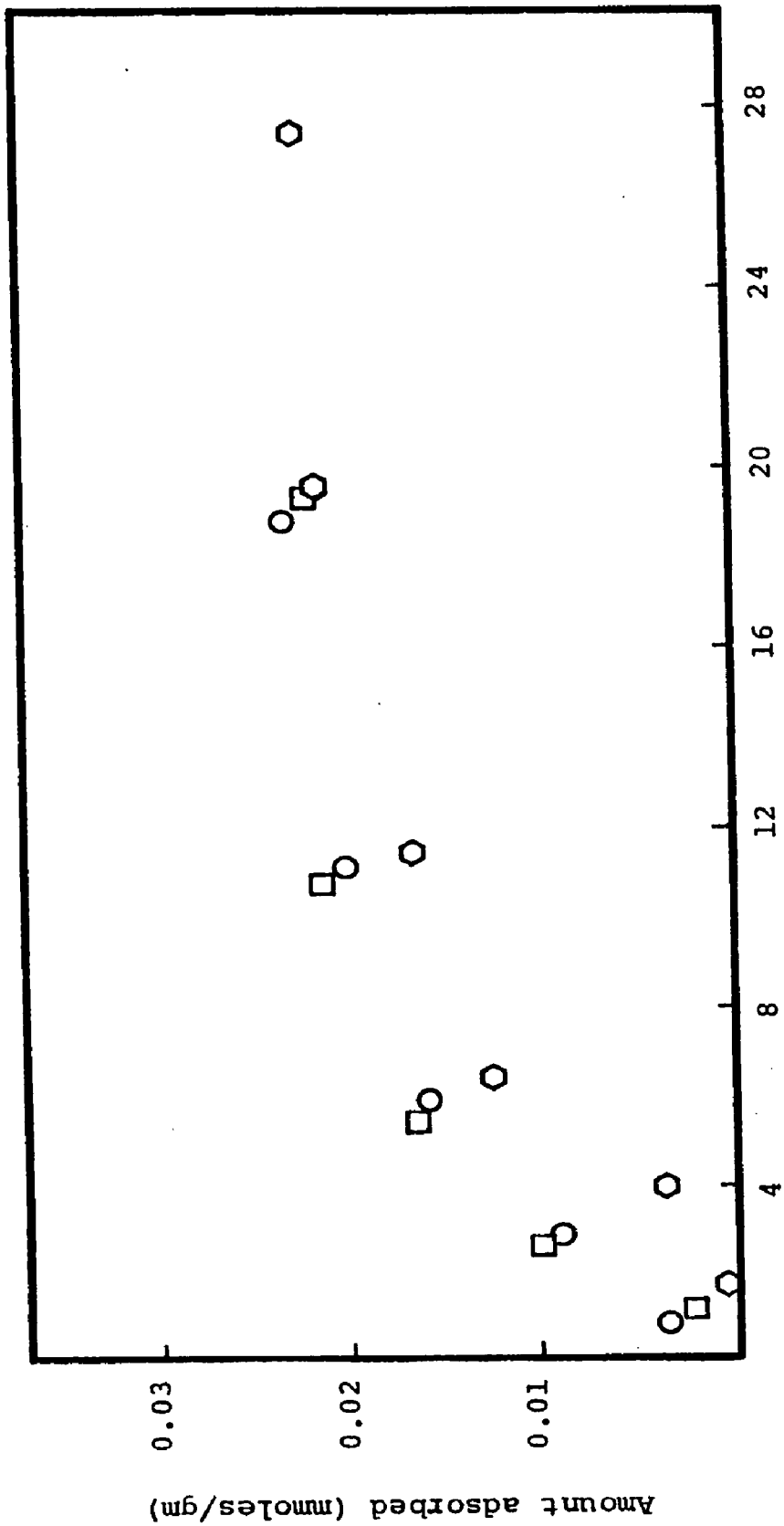

Figure 24. The adsorption of alcohols of varying chain lengths from 4% acetone in hexane on calcium fluoride.

Key: ⬡ hexyl alcohol
□ lauryl alcohol
○ cetyl alcohol

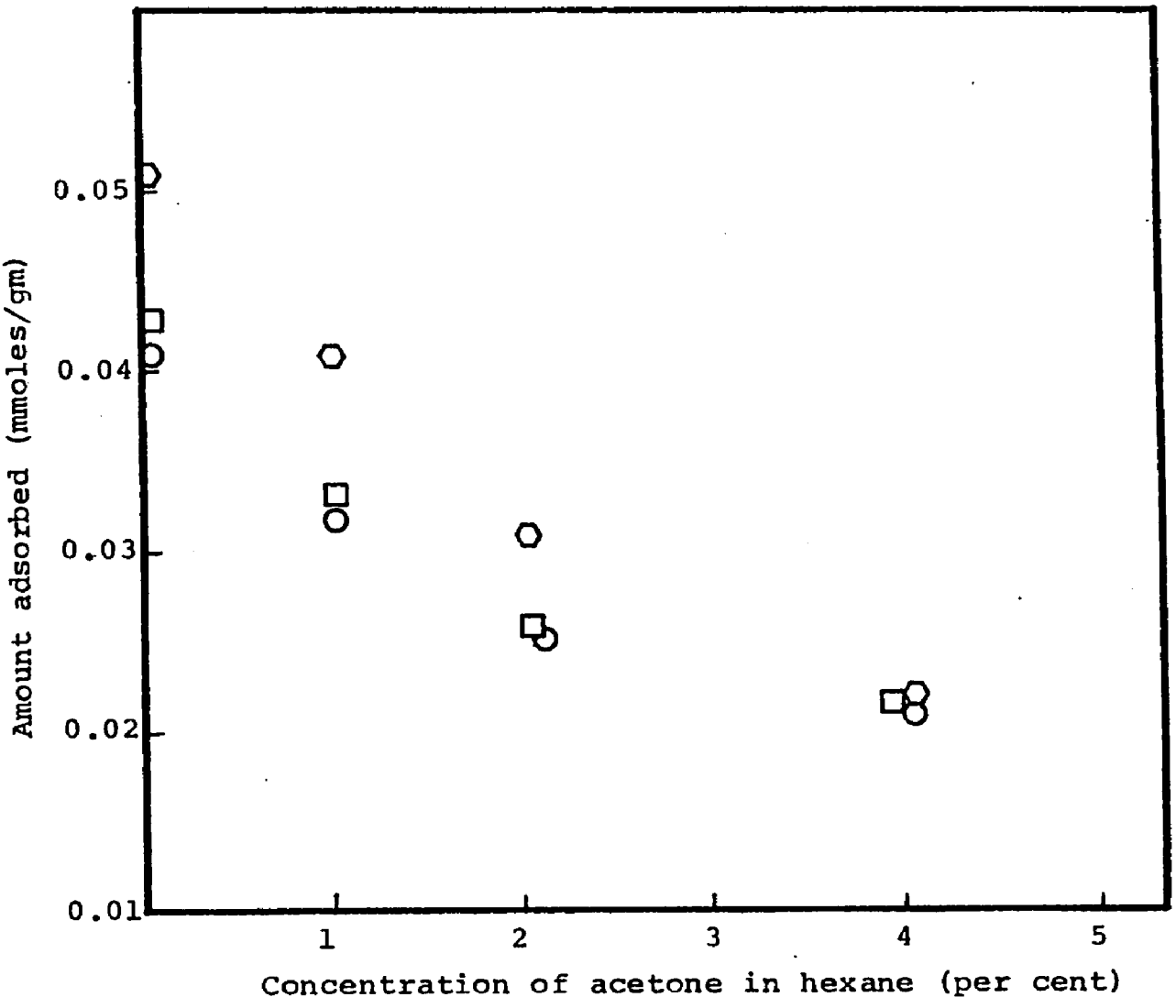

Figure 25. The limiting adsorption values of hexyl, lauryl and cetyl alcohols on calcium fluoride from acetone-hexane solvent mixtures.

Key: ⬡ hexyl alcohol
□ lauryl alcohol
○ cetyl alcohol

centration. It can be seen that the acetone causes not only an overall decrease in the adsorption, but also a reduction in the chain length effect. Indeed, the limiting adsorption values for all three compounds become the same at an acetone concentration of 4 per cent. The initial slopes, also, converge when acetone is added. A point of interest here is that at 4 per cent acetone, the hexanol exhibits deviation from the typical Langmuir shaped isotherms, taking on a pronounced S-shape. The lauryl alcohol also appears to have a very slight S-shape.

Discussion

Prefatory remarks

It would be appropriate to make a few general remarks concerning the shape of the isotherms, and the significance of the adsorption limit, or plateau, and the initial slopes. The experimental adsorption isotherms are roughly Langmuirian in shape, and the data can be approximately fitted by the Langmuir equation:

$$A = \frac{A_{max}\, kC}{1 + kC} \qquad (1)$$

where A is the amount of solute adsorbed, A_{max} is the maximum capacity of the adsorbent at monolayer coverage, k is an adsorption constant related to the energy of adsorption and C is the equilibrium concentration of the solute in the bulk. It is recognized that the Langmuir

equation is derived on the basis of several assumptions, such as uniformity of adsorption sites and no interaction between the adsorbed species, which generally do not represent the real situation. However, it is useful as a reference system for adsorption on polar surfaces from non-aqueous, non-polar solvents, whereby the relative mechanistic adsorption behavior of various compounds may be compared. And, because it is based on real physical considerations, any deviations from it may be recognized and discussed in terms of the non-ideal behavior of the adsorbate.

There are other theoretical and empirical equations available to describe single component adsorption equilibria. The Freundlich equation has also been widely used to represent equilibrium data.

$$A = k_F \, C_e^{1/n} \qquad (2)$$

Here, k_F and n are constants, which are an indication of adsorption capacity and adsorption intensity, respectively. This is an empirical equation, and there does not seem to be any very significant theoretical basis for it.

Other workers have noted that the Langmuir and Freundlich equations do not adequately describe, or fit, all the equilibrium adsorption data over a wide concentration range. In studies of single and multicomponent adsorption rates in aqueous systems, Mathews and Weber[97] proposed an empirical equation, designated the three parameter equa-

tion, which was reported to have a better fit to the experimental data.

$$q_e = \frac{a\ C_e}{1 + b\ C_e^{\beta}} \qquad (3)$$

C_e and q_e are the equilibrium concentrations in the fluid phase, and solid phase, respectively; and a, b and β are isotherm constants. This equation reduces to the Freundlich isotherm at high concentrations, and to the Langmuir isotherm when $\beta = 1$.

The fact that the Langmuir equation was found to be roughly applicable over the concentration ranges investigated here, suggests that the energy of adsorption is high compared to the energy of lateral interaction between the chains of adsorbed molecules. Further, it is an indication that the molecules are adsorbed in a monolayer on the surface. However, when speaking of monolayer coverage, a distinction should be made between complete coverage of the surface, and coverage limited by the number and spacing of the adsorption sites (both of which could be monolayer coverage) and the orientation of the molecules. Because of these factors, the plateau value need not necessarily correspond to complete and total monolayer coverage of the surface, even though the equation fits the isotherm.

The slope at the origin, which is related to one of the constants in the equation, is an indication of the net strength of adsorption, or the affinity that the solute

has for the surface. Thus, by comparing the initial slopes, as well as the plateaus, of different compounds, or the same compound under different conditions, one may compare the strength and extent of the adsorption.

Polar group effect

Adsorption, in general, is determined by several factors, including the strength of interaction between the solute and the surface (X_A), strength of interaction between the solvent and the surface (X_C), the interaction between the solute and solvent (E_{AC},E_{BC}) and the availability of adsorption sites on the surface. When the polar group is varied, the strength of interaction of the molecule with the surface varies. In addition to this, depending on the types of adsorption sites on the surface, the adsorption of molecules with different polar groups would vary due to different types of interactions with the sites.

These effects are seen when the adsorption isotherms of dodecylamine, dodecyl alcohol and dodecanoic acid in hexane onto hydroxyapatite are compared (Figure 3). The acid shows the greatest extent of adsorption 0.32, millimoles/gram, with the amine and the alcohol reaching the same plateau, 0.17 millimoles/gram. This is an indication that there are at least two, and probably three, types of adsorption sites on the hydroxyapatite, and that there are sites available to the acid for adsorption that neither the amine nor the alcohol may be adsorbed onto.

The acid and the amine also have a much stronger net affinity for the surface than does the alcohol, as indicated by the initial slopes. That is, they have a higher interaction energy between the polar group and the surface sites. The limiting adsorption value for the lauric acid, 0.32 millimoles/gram, corresponds to a cross-sectional area of 36 $\mathring{A}^2$. Even though the generally accepted value for carboxylic acids is 20.5 $\mathring{A}^2$, based on condensed film studies, the 36.0 $\mathring{A}^2$ value may represent close to complete monolayer coverage. This is because the surface area of the powder as determined by the B.E.T. method, 70 meters^2/gram, is not all accessible to the acid molecules, because of their size. So the actual surface area available for adsorption is less.

Because the amine and the alcohol have the same limiting value for adsorption, 0.17 millimoles/gram, they are apparently being adsorbed onto the same site, or sites, but each has a considerably different affinity for the surface.

The situation becomes more revealing when the experiments are performed using acetone as the solvent, rather than hexane (Figure 4). The acid adsorption is reduced to 0.19 millimoles/gram, a drop in the adsorption of 0.13 millimoles/gram compared to that in the hexane. The amine, also, shows a comparable decrease in its adsorption of 0.13 millimoles/gram when acetone is used as the solvent rather than hexane. The acetone, then, is in each case

eliminating a particular site (or sites) available for adsorption, which appears to be the same for the acid and the amine. It does this by competing for the site itself, being more polar than hexane, and in this way, preventing access of the site to the amine and the acid. The initial slope of the amine in the acetone system is also significantly less, indicating that the amine has a lower net affinity for the remaining available site.

The dodecyl alcohol, which had a plateau value in hexane of 0.17 millimoles/gram, showed no adsorption at all when acetone was used as the solvent. This is in contrast to the amine, which did exhibit adsorption in acetone. So, even though both compounds seem to be adsorbed onto the same adsorption sites in hexane, they are affected differently when acetone is used as the solvent. A possible interpretation for this could be that the adsorption value of 0.17 millimoles/gram (the adsorption in hexane) actually represents two sites, rather than one. When acetone is used as the solvent, it is capable of effectively poisoning both of these sites in the case of the alcohol, but only has a noticeable effect on one site in the case of the amine, reducing the adsorption to 0.05 millimoles/gram. This value, then, represents functionally one adsorption site, a site for which the amine has sufficiently high affinity not to be displaced from it by acetone. The alcohol, however, is not adsorbed onto this remaining site in the presence of acetone, because of its

lower affinity for this site and, maybe more importantly, because the hydrogen bonding between the alcohol and acetone also acts to prevent adsorption of the alcohol. The combination of these two factors produces an effect which is great enough to prevent adsorption of the alcohol on the second site.

On the hydroxyapatite, then, there are at least three types of adsorption sites, which were delineated by using hexane and acetone as the solvents, as well as compounds with different polar groups.

When calcium fluoride was used as the adsorbing surface, with hexane as the solvent (Figure 5), all three compounds tested, dodecylamine, dodecyl alcohol and dodecanoic acid, reached the same limiting adsorption value (within experimental error), 0.043 millimoles/gram. This value corresponds to a cross-sectional area per molecule of 81 $\mathring{A}^2$. The initial slopes, however, were different, the acid having the steepest slope and the alcohol the lowest, indicating that the acid has the greatest affinity for the solid surface. The curves are all monotonic, indicating one adsorption site. When acetone was used as the solvent instead of hexane, none of the three compounds exhibited any adsorption onto the surface, the acetone effectively eliminating the adsorption site by actively competing for it. The fact that all three types of compounds reached the same plateau, and that acetone completely inhibited the adsorption of all three, is a good indica-

tion that they are all being adsorbed onto the same site. And this site on the calcium fluoride appears to be the same as one of the sites on the hydroxyapatite. It is a site that shows an affinity for all three types of polar compounds, in the same rank order, and a site that is poisonable by the addition of acetone. It is the site that all three compounds have in common on the hydroxyapatite, and the single site of adsorption on the calcium fluoride. The site on hydroxyapatite which is not poisoned by the addition of acetone does not exist on the calcium fluoride.

Since there is only one kind of site available for adsorption on the calcium fluoride, it is possible to use the Langmuir equation to calculate the adsorption constants of the amine, acid and alcohol. The results of this calculation give rise to the following constants: The k for the dodecylamine is 4.1 liters/millimole, the k for the dodecanoic acid is 5.0 liters/millimole and the k for the dodecyl alcohol has a value of 2.1 liters/millimole.

The fact that the initial slopes are different indicates that the compounds have different interaction energies with the surface (X_A). The theoretical model of Bladon et al.[93] predicts that as the X_A increases, the plateau, as well as the initial slope, becomes greater in value. This would mean that the acid adsorption isotherm would have the highest plateau, and the alcohol should show the lowest limiting adsorption value. However, this

is not the case seen experimentally, where all three types of compounds reach the same limiting adsorption. Even though this appears to be a contradiction to the theoretical model, it may be explained in those terms. Calculations performed by Bladon[98] have shown that beyond a certain value of the interaction energy between the polar head group and the surface, or the X_A (8 to 10 kcal/mole), for compounds of the same chain length, any further increase in the interaction energy does not result in a corresponding increase in the plateau value. There still may be, however, differences in the initial slopes. This maximum adsorption value depends on the chain length, and decreases as the chain length increases. It is possible, according to the calculations, to reach this maximum limiting adsorption at only 50% coverage, if the chain length is long enough. (In the model, this chain length corresponded to a hexamer.) Thus, as long as the X_A is greater than approximately 8 kcal/mole, one may observe that compounds with different values of the interaction energy can all exhibit about the same limiting adsorption values.

Or, a possible alternate explanation for this observed result of all three compounds having the same plateau may be that the adsorption site density is so sparse that there is only modest interaction between the adsorbed molecules. This would mean that an increase in the X_A, and the resultant increase in the proportion of vertical to flat configurations, would have little effect on the adsorption plateau values.

Since acetone was able to displace the amine, acid and alcohol from the adsorption site by competing for it, the site is one which is able to react with the carbonyl oxygen atom of the acetone. Several authors[99,100] have shown that acetone interacts, or forms complexes, with calcium on the montmorillonite surface. This interaction was thought to be a cation-dipole type, where a bond is formed by the unshared electron pair of the oxygen atom of the acetone and the vacant orbital of the calcium atom. Slater and Kitchener[101] studied the adsorption of polymers onto fluorite, and suggested that the mechanism of the adsorption by the calcium fluoride was one of a dipole interaction of non-ionic groups with the electrostatic field of the crystal lattice. Since the oxygen and nitrogen atoms of the adsorbing molecules are electronegative, they would be attracted to the calcium atoms on the surface. This, then, suggests that the adsorption site for the three compounds, the same site that the acetone competes for, is the calcium atom on the surface.

One of the assumptions of the Bladon theory is that the surface is flat, energetically homogeneous, there is uniformity of adsorption sites and the sites are the same size as the adsorbing polar group of the molecule. If this were the case, then the extent of adsorption would be determined by the cross-sectional area of the polar group of the adsorbing molecule. This, however, is not the actual situation. Even though the compounds are all

adsorbed onto one type of site, it is possible that there is another chemically different type of site on the surface, and therefore adjacent sites are not of the same kind, as the theory assumes. And since the adsorption involves interaction between the polar head group and a particular site on the surface, the spacing, or the calculated area occupied by each molecule on the surface, would not depend on the size of the adsorbate molecule but on the spacing between the adsorption sites, and their accessibility. Thus, the calculated effective area per molecule of 81 $\mathring{A}^2$ is greater than that which corresponds to the close-packed area. This could be due to wide spacing of the sites, but most likely the sites are spaced fairly closely together, and an adsorbed molecule on one site partly overlaps, or blocks, with its head group or with its chain a neighboring site. The next molecule is therefore adsorbed onto the third site, which may be further from the first site than corresponds to the closest distance of approach of the molecule. Alternatively, it may be possible that the adsorbates are only being adsorbed onto a portion of the total surface. Calcium fluoride has been reported to normally occur with the (100) crystal face, though it fractures along the (111) plane.[102] Consequently, two crystallographic homottatic surfaces would be expected to occur, and these surfaces may behave as two energetically unique surfaces toward certain adsorbates. However, the equilibrium faces of the (111) plane contain only nega-

tively charged ions,[103] fluoride, and would therefore not act as potential adsorption sites for the adsorbates used here. Thus, adsorption may be occurring on only one portion of the total surface of the calcium fluoride. This would also explain why the effective cross-sectional area per molecule was so large; in effect, the area of the solid sample on which adsorption could occur was less than that determined by nitrogen adsorption.

Calculations based on an inspection of an atomic model of the calcium fluoride unit cell and the unit cell dimensions reveal that calcium atoms at the surface of the (100) plane occupy an area of 14.8 $\mathring{A}^2$. Assuming that adsorption occurs only on this plane, for reasons stated above, it is clear then, that each adsorbing molecule would overlap onto and block adjacent adsorption sites, preventing the kind of close-packed manner of adsorption on the surface which would be necessary to give the maximum possible coverage.

The other possibility, as mentioned earlier, is that of non-accessibility of some of the active sites, because of pores or cracks in the surface shielding some of the sites, which would otherwise act as binding sites for the molecules.

The above results are in contrast to those obtained by Hall, Lovell and Finkelstein,[104] who investigated the effect of pre-adsorbed oleate on the adsorption of water vapor on calcium fluoride. Their results led the authors

to conclude that the oleate ions were adsorbed as a uniform, close-packed monolayer covering most of the surface, the effective cross-sectional area of an adsorbed oleate ion being similar to the value for a condensed film on a liquid surface. This does not seem like a likely possibility, however, primarily because the adsorption studies were performed in aqueous solutions, and there would therefore be water molecules also on the surface, precluding a close-packed monolayer of oleate. The actual situation probably was one of multilayer adsorption on the portion of the surface that was available for adsorption.

Solvent effect

From available evidence[62,67,73] it can be seen qualitatively that the solvent from which adsorption occurs can be very important in determining the adsorption characteristics. Clearly, the interaction of the solvent with the solid surface is important, and along with this must be considered the interaction of the solvent with the adsorbing molecule itself, both with the polar head group and the hydrophobic chain. The relative importance and influence of each of these interactions would depend on the specific solvents used, the nature of the surface and the type of solute molecules.

Considering first the surface effect, the existence of competition in physical adsorption between two different components depends most frequently on the differences

in the strengths of interaction between the solid surface and the adsorbates. In general, the observed phenomenon can be understood qualitatively in terms of the varying degrees of polarity shown by the surface and the adsorbates. When acetone, a polar solvent, is added to the hexane solution, it competes with the solute for the adsorption sites on the polar inorganic surface. This competition decreases the maximum adsorption of the solute molecules. How much an effect this competition has on the adsorption depends on the relative strengths of interaction of the acetone and the solute with the surface.

The second factor which must be considered here is the interaction of the solvent with the adsorbing molecule itself. This interaction may be a specific one with the polar head group of the molecule, such as hydrogen bonding between acetone and carboxylic acids. If this hydrogen bond was strong enough to overcome the favorable interaction between the polar head group and the solid surface, it would result in a decrease in the adsorption of the solute, since the polar head group would no longer be able to interact with the polar surface. In the absence of effects such as these, a given solute is as a rule more strongly adsorbed from poor solvents than good solvents. That is, the more soluble a solute is, the lower will be the adsorption. If the addition of the polar solvent increases the solubility of the solute, the adsorption will be decreased, and decreasing the solute solubility in

the bulk by adding a different solvent will tend to increase its adsorption.

The experimental results (Figures 6 through 13) bear this out. The addition of acetone, a polar solvent, to hexane in each case, the amine, acid and alcohol, resulted in a decrease in the adsorption. This decrease in the adsorption was a result of both acetone competition for the adsorption sites and the acetone hydrogen bonding in the bulk with the polar head group of the molecule.

Since both of these factors are involved simultaneously, it is difficult to say how much of an effect each one has by itself. It would therefore be beneficial to separate the two effects. In this way, each one could be evaluated separately, and their relative importance could be assessed.

Before the competitive adsorption effect of the acetone at the surface could be determined, the bulk effects, or the hydrogen bonding had to be evaluated independently. A great number of studies have been done on the determination of hydrogen bonding equilibria in solution by means of infrared absorption spectra.[105-108] In studies performed with hydroxylated materials, it was found that there was a shift in the absorption frequency of the O-H stretching mode and its harmonics to lower frequencies, when hydrogen bonding occurred. The most prominent of these spectral changes occurs in the region of absorption near 3500 cm^{-1}.[109] In very dilute solutions, in the

absence of acetone, a narrow band at 3610 cm^{-1}, due to free O-H groups not participating in hydrogen bonds dominates the lower frequency absorption. As the concentration increases, or when acetone is added, a broad band centered near 3300 cm^{-1} to 3500 cm^{-1}, due to hydrogen bonded O-H groups, appears and becomes the more intense feature. Thus, two absorption bands may be present, one due to the free O-H and one due to the associated O-H. These changes are indicative and informative of the hydrogen bonding equilibria. In addition to the shift of the band, there is a characteristic increase in the integrated absorption, or intensity, of the stretching frequency upon hydrogen bond formation.

Since the concentration of each species, the free and the associated alcohol, is proportional to the absorbance at the respective frequencies,[107] the areas under the curves may be used to calculate the association constant in the following way.

For the equilibrium

$$R\text{-}OH + R{=}O \rightleftharpoons R\text{-}OH \cdot O{=}R,$$

$$K_a = \frac{[R\text{-}OH \cdot O{=}R]}{[R\text{-}OH]\,[R{=}O]} \qquad (4)$$

Let

C = the initial concentration of R-OH

X = the initial concentration of R=O

α = the fraction of total alcohol that is unassociated.

The area of the peak due to free O-H is proportional to [R-OH] and the area of the peak due to bound O-H is proportional to [R-OH·O=R].

Then

$$\alpha = \frac{\text{area}_{ROH}}{\text{area}_{ROH} + \text{area}_{ROH \cdot O=R}} \tag{5}$$

$$[R\text{-}OH] = \alpha C \tag{6}$$

$$[R{=}O] = X - (1-\alpha)C \tag{7}$$

$$[R\text{-}OH \cdot O{=}R] = (1-\alpha)C \tag{8}$$

and

$$K_a = \frac{(1-\alpha)C}{(\alpha C)[X-(1-\alpha)C]} = \frac{(1-\alpha)}{\alpha[X-(1-\alpha)C]} \tag{9}$$

Using this method of correlating the areas under the hydroxyl absorption peaks to the concentration of the free and associated alcohol, the association equilibrium constant could be determined.

All measurements were made with a Perkin-Elmer 337 Grating Infrared Spectrophotometer and 0.1 cm cells. The solvent used was hexane. Quantitative data were obtained from a series of solutions of varying concentrations of lauryl alcohol in the presence of various amounts of added acetone. Spectra were also obtained for just the alcohol in hexane, and, because the acetone also has some absorption near the associated hydroxyl band, a series of solutions of just acetone in hexane was also run to evaluate

this contribution.

Thus, using Equation 9, the equilibrium constant for hydrogen bonding between the lauryl alcohol and acetone was calculated over a range of concentrations. The results are presented in Table IV.

Table IV

Value of the Equilibrium Constant, K_a (liters/millimole), for Hydrogen Bonding Between Lauryl Alcohol and Acetone

Concentration of Alcohol (M)	Concentration of Acetone (%)		
	1.0	1.5	3.0
0.025	0.027	- -	0.023
0.050	- -	0.025	0.030
0.10	- -	0.028	0.032
0.20	- -	- -	0.033

These values yielded an average value of K_a = 0.029 1/mmole.

This value of K_a then, can be used to adjust the measured equilibrium concentration which includes both free and hydrogen bonded lauryl alcohol, to give the concentration of just the free alcohol, since this is the only species which adsorbs.

For the equilibrium given before,

$$R\text{-}OH + R{=}O \rightleftharpoons R\text{-}OH \cdot O{=}R$$

let

C_L = the concentration of the free lauryl alcohol

C_A = the concentration of acetone

C_{LA} = the concentration of the lauryl alcohol-acetone complex

C_{Ltot} = the total concentration of lauryl alcohol

Then

$$K_a = \frac{C_{LA}}{C_L \; C_A}$$

$$C_L = \frac{1}{K_a} \cdot \frac{C_{LA}}{C_A} \tag{10}$$

$$C_{Ltot} = C_L + C_{LA} \tag{11}$$

where C_{Ltot} is the concentration of lauryl alcohol determined in the assay procedure.

$$C_L = C_{Ltot} \cdot \frac{C_L}{C_L + C_{LA}} \tag{12}$$

$$C_L = C_{Ltot} \cdot \frac{C_L}{C_L + K_a \; C_L \; C_A} \tag{13}$$

Factoring out the C_L term from the right side of the equation gives:

$$C_L = \frac{C_{Ltot}}{1 + K_a \; C_A} \tag{14}$$

Because C_A was much greater than C_L under the experimental conditions employed, the equilibrium concentration of the acetone was taken to be the initial added concentration.

It is now possible to plot new adsorption isotherms using these adjusted values of the equilibrium concentra-

tions of the alcohol, to reflect the concentrations of the free, unassociated molecules.

Once the bulk solvent effect has been evaluated and factored out, and new isotherms have been plotted, it is possible to look at the surface effect of acetone, which is one of competitive adsorption.

Figure 26 shows the adjusted experimental adsorption data for lauryl alcohol onto calcium fluoride in varying concentrations of acetone. The solid curves in this figure are theoretically calculated on the basis of Equation 28 based on the derivation which follows. From this experimental data, it is possible to obtain a value for the adsorption constant of acetone, also from Equation 28.

If competitive adsorption is assumed, and adsorption model may be developed to take into account the simultaneous adsorption of both species, the alcohol and the acetone. (An analogous derivation applies in the case of the acid and the amine.)

Let

θ = fraction of surface occupied by all adsorbates

θ_L = fraction of surface occupied by lauryl alcohol

θ_A = fraction of surface occupied by acetone

Then

$$\theta = \theta_L + \theta_A \tag{15}$$

and

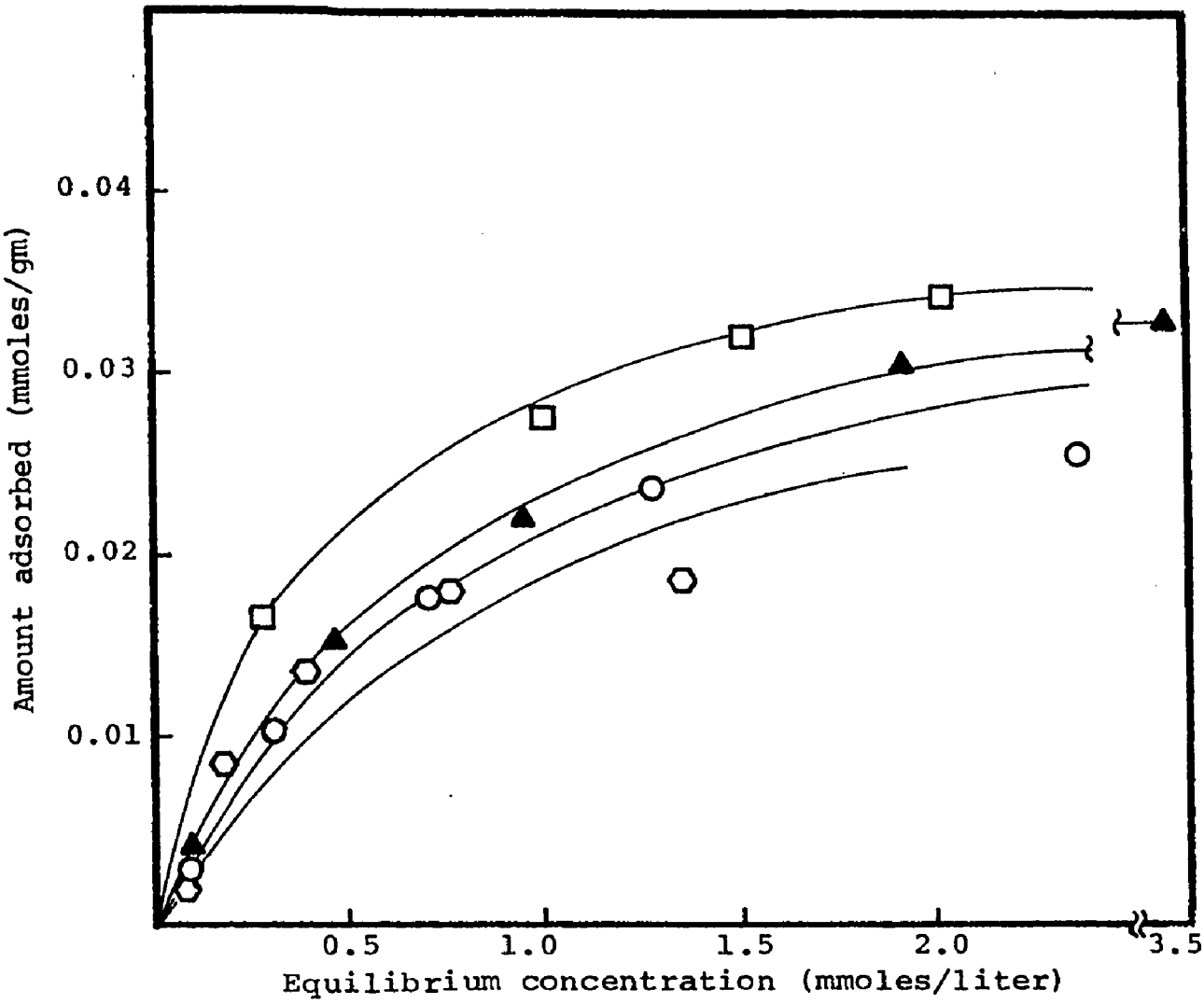

Figure 26. Effect of acetone on the adsorption of lauryl alcohol from acetone-hexane mixtures on calcium fluoride. The equilibrium concentrations of the alcohol are those of the non-hydrogen bonded species. The curves are theoretically calculated on the basis of the Langmuirian competitive adsorption model.

Key: Concentration of acetone in hexane

□ none ○ 2%

▲ 1% ⬡ 4%

$1 - \theta$ = fraction of surface unoccupied.

A kinetic approach allows for independent rates of adsorption and desorption for the lauryl alcohol and acetone. At equilibrium, the rates of adsorption and desorption are set equal in the case of both the alcohol and the acetone.

The rates of adsorption of alcohol and acetone are proportional to the total unoccupied sites and to their respective solution concentrations.

$$- \frac{dC_L}{dt} = k_1 C_L (1-\theta) \tag{16}$$

and

$$- \frac{dC_A}{dt} = k_2 C_A (1-\theta) \tag{17}$$

The terms k_1 and k_2 are the adsorption rate constants for the lauryl alcohol and acetone, respectively.

The rate of desorption is proportional to the fraction of the surface covered by a given adsorbate.

$$\frac{dC_L}{dt} = k_1' \theta_L \tag{18}$$

$$\frac{dC_A}{dt} = k_2' \theta_A \tag{19}$$

The terms k_1' and k_2' represent the desorption rate constants.

At equilibrium the rates of adsorption and desorption are equal for each species.

$$k_1 C_L(1-\theta_L-\theta_A) = k_1'\theta_L \tag{20}$$

and

$$k_2 C_A(1-\theta_L-\theta_A) = k_2'\theta_A \tag{21}$$

Solving Equation 21 for θ_A gives

$$\theta_A = \frac{k_2 C_A(1-\theta_L)}{k_2' + k_2 C_A} \tag{22}$$

Substituting the expression for θ_A into Equation 20 and solving for θ_L gives

$$\theta_L = \frac{C_L k_1 k_2'}{k_1' k_2' + k_1' k_2 C_A + k_1 k_2' C_L} \tag{23}$$

Dividing both the numerator and denominator of Equation 23 by $k_1'k_2'$ gives θ_L as a function of the lauryl alcohol and acetone concentrations, and the two constants.

$$\frac{k_1}{k_1'} = k_L \qquad \text{the adsorption constant of lauryl alcohol} \tag{24}$$

$$\frac{k_2}{k_2'} = k_A \qquad \text{the adsorption constant of acetone} \tag{25}$$

Both of these constants are equilibrium constants obtained from the ratios of the forward and reverse rate constants.

$$\theta_L = \frac{k_L C_L}{1 + k_A C_A + k_L C_L} \tag{26}$$

Since

$$\theta_L = \frac{A_L}{A_{Lmax}} \tag{27}$$

where A_L is the amount of lauryl alcohol adsorbed per gram of adsorbent material, and A_{Lmax} is the maximum amount capable of being adsorbed per gram of adsorbent,

$$A_L = \frac{A_{Lmax}\, k_L C_L}{1 + k_A C_A + k_L C_L} \tag{28}$$

As stated previously, the value for k_L, the adsorption constant for lauryl alcohol, was obtained from the experimental data of the adsorption of the alcohol onto calcium fluoride from hexane, evaluated in terms of the Langmuir equation to give the best estimate of this parameter.

Both C_A and C_L represent equilibrium bulk concentrations. Since under the experimental conditions employed C_A was much larger than C_L, the equilibrium concentration of the added acetone was assumed to be the initial added concentration.

The experimental data in Figure 26 was evaluated on the basis of Equation 28 to determine the best possible value for the adsorption constant for the acetone. The curves in Figure 26 show the calculated values representing the Langmuir, two-component competitive adsorption model, utilizing the best possible values of k_L and k_A. The fit that is obtained between the theory and the experimental

data is quite good, except at 4 per cent acetone, where some deviation occurs.

It was not possible to use the technique employed for the alcohols (the IR spectra) to determine the K_a for the association between lauric acid and acetone, because of the very broad, intense peak in the acid IR spectrum due to dimerized molecules, even at low concentrations. There was essentially no measurable peak, even at the lowest concentration tested, 0.025 M, which could be assigned to free, non-bonded hydroxyl groups.

Instead, K_a for the hydrogen bonding between the acid and acetone was calculated on the basis of Equation 29, whose derivation follows, and the experimental data.

In a derivation similar to that presented in Equations 10 through 14, an expression may be obtained for the concentration of the free, non-hydrogen bonded lauric acid.

$$C_L = \frac{C_{Ltot}}{1 + K_a C_A}$$

where C_L is the concentration of the lauric acid and K_a is the value of the association constant between the acid and acetone.

By inverting Equation 28 and substituting the above expression for C_L into this equation, one obtains

$$\frac{1}{A_L} = \frac{(1 + k_A C_A)(1 + K_a C_A)}{A_{Lmax} k_L C_{Ltot}} + \frac{1}{A_{Lmax}} \qquad (29)$$

The experimental data for the adsorption of lauric acid onto calcium fluoride in varying concentrations of acetone, shown in Figure 12, was evaluated on the basis of Equation 29 to establish the best values for the parameters k_A and K_a. This was done by simultaneous solution of Equation 29 over a range of acetone and lauric acid concentrations.

Using this calculated value of the K_a the bulk equilibrium concentration of the lauric acid was corrected to that of the free, non-hydrogen bonded acid. The results are presented in Figure 27. The solid curves in this figure are the theoretically calculated isotherms, using Equation 28, and the best value of the parameter k_A, as determined from Equation 29.

This analysis has neglected the formation of dimers of the lauric acid, both in the hexane and in the acetone-hexane mixtures. The value for the association constant for the dimerization of lauric acid in heptane has been reported to be 7000 M^{-1} [109]. On the basis of this value, one finds that at a total concentration of the acid of 0.2 mM, 50% of the acid is dimerized. If the equilibrium concentration were adjusted to that of the non-hydrogen bonded species, there would be a slight shift of the initial portion of the isotherm to lower equilibrium concentrations.

However, the extent of this shift would not be sufficient to appreciably change the value of k_L obtained from the data, and thus the value of k_A. This is particularly true because the analysis was primarily performed using lauric acid concentrations in the range <0.4 mM, and the dimerization would not have a significant effect on the results obtained. In addition, the extent of the dimerization of the acid in the presence of acetone, to which it is hydrogen-bonded, is greatly reduced. Thus, the conclusions of the analysis are still valid.

The agreement between the experimental adsorption data and the theoretically calculated Langmuirian curves is quite good at the lower equilibrium concentrations of the acid, but as the concentration increases, the experimental points appear to reach a plateau, whereas the calculated curves are still increasing.

The data for the adsorption of the dodecylamine in the presence of selected amounts of added acetone (Figure 10) was treated in a manner analogous to that of the lauric acid. That is, the experimental data was simultaneously evaluated on the basis of Equation 29 to obtain the best value for k_A and K_a, the equilibrium constant for the association between the amine and acetone. The bulk

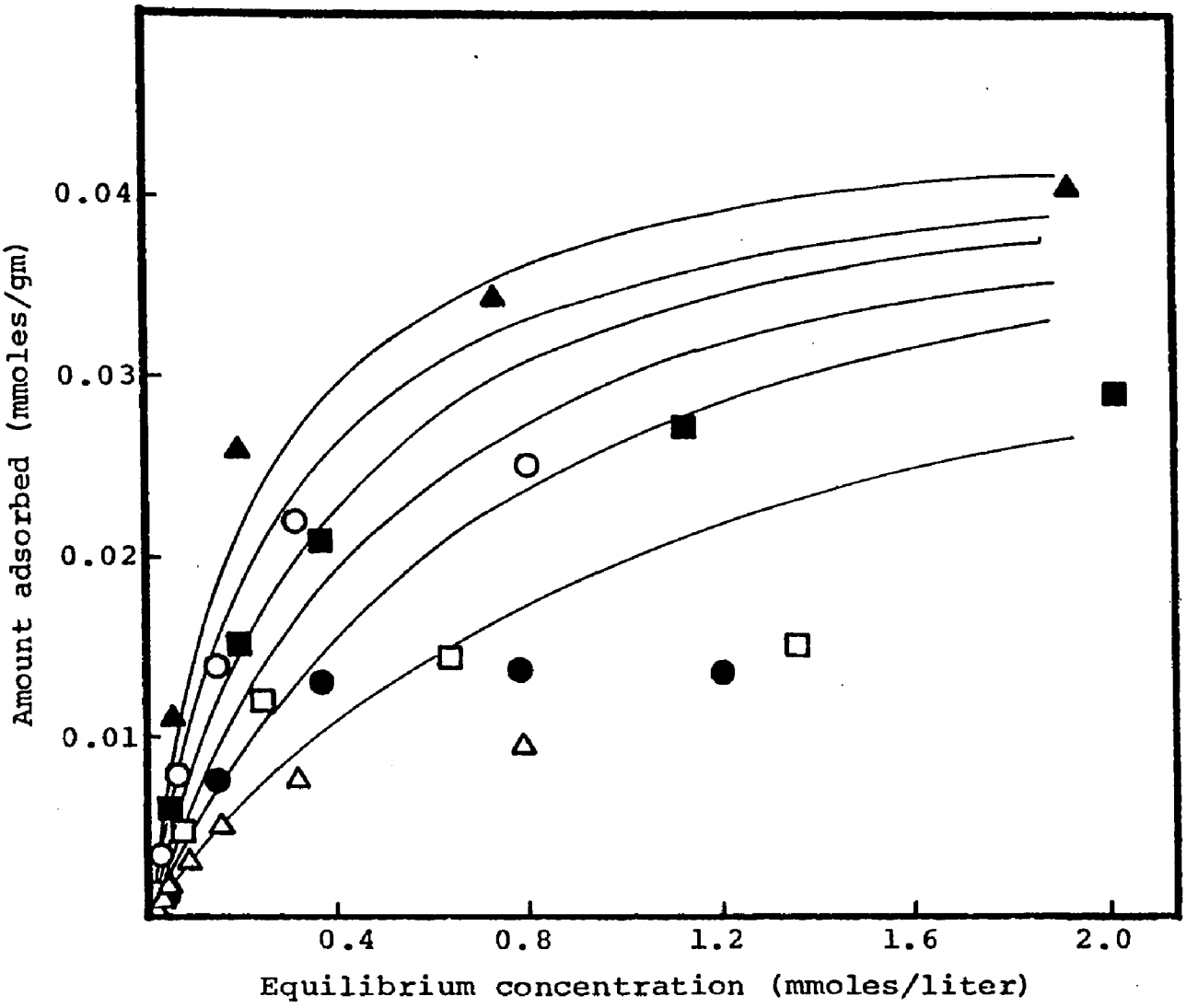

Figure 27. Effect of acetone on the adsorption of lauric acid from acetone-hexane mixtures on calcium fluoride. The equilibrium concentrations of the acid are those of the non-hydrogen bonded species. The curves are theoretically calculated on the basis of the Langmuirian competitive adsorption model.

Key: Concentration of acetone in hexane

▲ none ■ 1% ● 3%

○ 0.5% □ 2% △ 5%

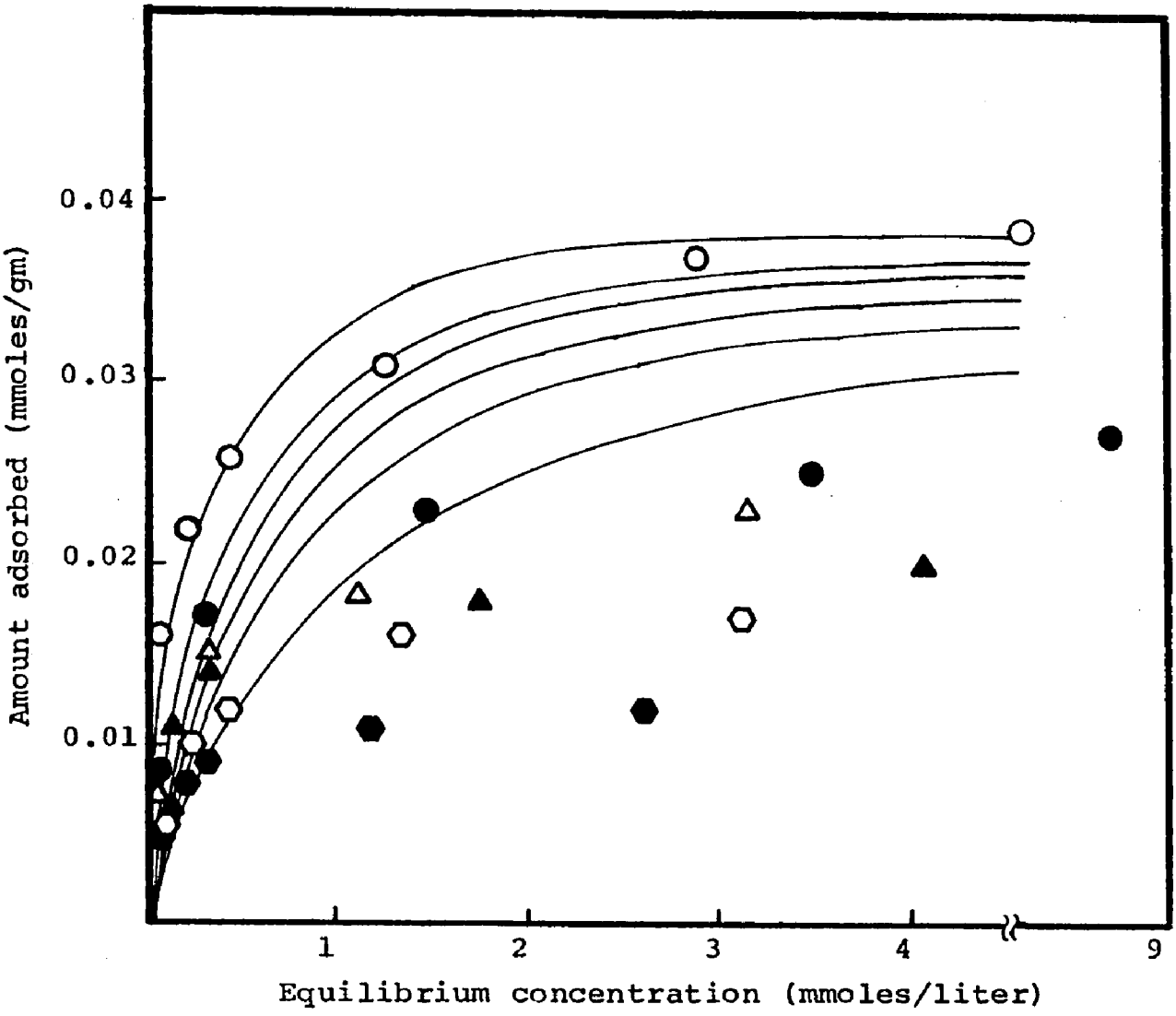

Figure 28. Effect of acetone on the adsorption of dodecylamine from acetone-hexane mixtures on calcium fluoride. The equilibrium concentrations of the amine are those of the non-hydrogen bonded species. The solid curves are theoretically calculated on the basis of the Langmuirian competitive adsorption model.

Key: Concentration of acetone in hexane

○ none △ 0.5% ⬡ 2.0%

● 0.25% ▲ 1.0% ⬢ 4.0%

equilibrium concentration of the amine was then adjusted with the use of K_a to reflect that of the free amine, and the isotherms were replotted. The results are seen in Figure 28. Here, again, the solid curves are theoretically calculated from Equation 28, representing the two-component, competitive adsorption model.

It should be noted that here also, as in the case of the alcohol and the acid, there is good fit between the theory and the experimental data at low concentrations, but that deviation occurs at higher concentrations of the amine.

A summary of the quantitative results obtained from the analysis of the solvent effect, both in the bulk and at the surface, is presented in Table V. As stated previously, the values for the adsorption constants of the alcohol, acid and amine on calcium fluoride were determined on the basis of the Langmuir equation and the experimental data for the adsorption of these compounds from hexane.

Table V

Summary of the Results of the Solvent Effect on the Adsorption on Calcium Fluoride

Adsorbate	k (l/mmole)	k_A (l/mmole)	K_a (l/mmole)
Dodecylalcohol	2.12	0.006	0.029
Dodecanoic Acid	5.04	0.007	0.053
Dodecylamine	4.12	0.007	0.012

The fact that the independently determined values for the adsorption constant of acetone are so close in their value, and that this single Langmuirian constant explains most of the data within experimental uncertainty is a strong indication that only one site is involved here, and that acetone is competing for this same site in each case. This is a valid assumption, since the experimental data at the low concentrations was generally found to agree well with the Langmuirian model; and the adsorption constant evaluated here is that related to the initial slope of the curve. This is further evidence for the fact that all three compounds, alcohols, acids and amines, are adsorbed onto the same site on the surface of the calcium fluoride.

The deviation from the Langmuir model, in the form of levelling off of the isotherms rather than increasing, is found consistently in all three compounds used. This deviation may be expected, when one considers all the assumptions of the Langmuir model, especially the postulation that there is no interaction between the adsorbate molecules. Indeed, the fact that the experimental data fits the Langmuirian competitive adsorption model at all is almost surprising, but the fit is seen to be quite good at the low concentrations. However, this can be understood when the physical situation is considered. At low coverages, because there are acetone molecules adsorbed onto the surface, there would be restriction of the possible configurations assumed by the adsorbed solute molecules. This

would result in the orientation of these molecules being primarily vertical. This factor, in combination with the fact that the density of the solute molecules would be low, would mean that there would be no interaction between the adsorbed molecules, and that the isotherm should be Langmuirian in shape in this low concentration region.

It was thought that the observed deviations could be explained in terms of the Bladon model as being a result of the entropy effect. That is, the observed plateaus, as interpreted in terms of the theoretical model, are not real plateaus, but "apparent" plateaus, in the sense that there is incomplete occupation of the surface sites by the polar head group. The greater is the interaction energy between the surface and the polar head group, the greater is the proportion of vertical configurations, and the lower is the entropy effect. This would result in the "apparent" plateau being higher. The fact that there were increasing amounts of acetone on the surface could mean that the effective interaction energy of the adsorbates with the surface would be lowered, resulting in lower plateaus. However, recent calculations by Bladon[98] dealing with this very question have produced results which are qualitatively similar to those of the Langmuir model. That is, as increasing amounts of a competing solvent are added, the initial slopes are lowered, but the isotherms exhibit a gradual, continual increase, and do not level off at lower adsorption values. Thus, the experimental results are not

in agreement with the model predictions, and cannot be explained on that basis.

The observed deviations are most likely the result of the formation of some higher order complexes between the acetone and the solute. When this occurs in the bulk, it would result in decreased adsorption due to a lower net affinity for the surface. (This could be analogous to the situation in aqueous solvents, where, when the critical micelle concentration is reached, the isotherms approach a limiting value.) Or, if this interaction between the acetone and the solute occurred at the surface, it could result in the acetone molecules permanently blocking potential adsorption sites for the solute. This would result in less total surface area available to the solute for adsorption than there is in the presence of hexane only, and the isotherms would reach their plateaus at lower adsorption values.

In studies on the competitive interactions in adsorption from dilute aqueous bi-solute systems, Weber[110] found the Langmuir competitive adsorption model to satisfactorily describe the inhibitory effect that each solute had on the extent of equilibrium adsorption of the second solute. The competitive systems which were studied were 2-dodecyl-

benzenesulphonate and phenol, and 2-dodecylbenzenesulphonate and chloronitrobenzene, which were adsorbed onto the same porous granular carbon. Conformity to the Langmuir model was observed in both of these systems. The experimental data was linearized and plotted, and a calculated linear trace was determined on the basis of parameters obtained from single solute adsorption data. In each case, there was good correlation between predicted and experimental data, and it was concluded that the model was applicable over a wide range of experimental concentrations.

Chain length effect

When the effect of varying the length of the hydrophobic chain, while keeping the polar head group constant, was studied, it was found that the greatest general effect was seen in the homologous series of the alcohols (Figure 21). The effect was less pronounced in the case of the n-alkyl amines (excluding the data for the butylamine which was believed to be due to another effect) and essentially non-existent for the homologous series of n-alkanoic acids tested. Because the calcium fluoride surface is better defined than that of the hydroxyapatite, having only one adsorption site, the discussion will be limited to the adsorption isotherms obtained on the calcium fluoride powder.

As was seen in the literature review, many other

investigators have observed and studied this chain length effect, and have presented many different theories and explanations for its existence.

In the case of the n-alkanols, it is clear that not only does the quantity of alcohol adsorbed decrease with increasing length of the alkyl chain, but the strength of adsorption, as indicated by the initial slope of the isotherms, also decreases. Both of these experimentally observed effects are consistent with interpretations provided by the Bladon theoretical model.[93]

The theoretical calculations have shown that, at very low concentrations as infinite dilution is approached, while the thermal energy portions of the chemical potentials of the dimer and tetramer molecules, whose configurations have an 'A' segment touching the surface, are the same, the chemical potentials are not the same. The difference is exactly the difference between the entropy per molecule of any two such configurations of dimers and tetramers. This is assuming there are no segment to segment interactions.

Calculations were performed to find the ratio of the fraction of dimer configuration with the 'A' segment touching the surface to the fraction of tetramer configurations with the 'A' segment touching the surface, and this ratio was found to be 1.413. That is, the dimer has a larger percentage of all possible configurations with the head group touching the surface. The tetramer, then, loses

a greater percentage of all its possible configurations, or degrees of freedom, by being adsorbed onto the surface with its head group touching the surface. It is entropically less favorable for the longer chain length molecule to be adsorbed. As a result, the dimer and tetramer adsorption isotherms do not coincide at very dilute concentrations, the dimer showing a greater initial slope than the tetramer. This predicted relationship is seen experimentally, where the shorter chain length alcohol shows a greater adsorption at the low concentrations. This theoretically predicted relationship continues to play a role in the adsorption, until the surface coverage becomes great enough so the molecules begin to "see" each other, where a different factor begins to control the adsorption.

Experimentally, a chain length effect is also observed at higher coverages, or in the plateau region. This, too, is predicted and may be explained on the basis of entropy considerations. Because of entropic considerations, there is always some fraction of the total kinds of configurations on the surface which are flat, even at high coverages. That is, they have the whole chain, or a portion of it, lying at the liquid-solid interface. So, as the chain length gets longer, there are obviously more of these flat configurations possible, since there are more segments present. As a result, when the surface becomes populated enough for the molecules to be in close proximity to one another, or "see" one another, these non-vertical configura-

tions begin to have an important effect on the total amount adsorbed. That is, these types of configurations can cause other molecules to feel interference or restriction of movement from molecules on adjacent sites, or even be prevented from being adsorbed by coverage or complete blockage of a site by the chain segment or segments of a molecule already on the surface. The chances of this occurring are greater as the chain length gets longer, and thus, the longer chain length molecules will be adsorbed less, on a molecular basis. Simply stated, one mole of the shorter chain length compound occupies less surface area with all its configurations than does one mole of a longer chain length compound.

The relative difference between the limiting adsorption values is seen to decrease with an increase in the chain length. That is, the difference in the plateaus between the hexyl alcohol and lauryl alcohol is greater than that between the lauryl alcohol and cetyl alcohol. This effect is also in agreement with the results of the Bladon model.[98] Calculations have shown that the difference between the adsorption plateaus of the monomer and dimer is the greatest, with the limiting adsorption values beginning to converge as the chain length is increased by one segment in each case; for example, the difference between the trimer and tetramer is less than that between the dimer and trimer.

From the above discussion, it is evident that for this configurational, or entropic, effect to occur, the adsorbing sites must be close enough together for the adsorbed molecules to be aware of one another. If the sites are so far apart that the molecules will not feel the interference of the adjacent molecules, this chain length effect will not be present.

It can be said with reasonable certainty that the experimentally observed chain length effect is an entropy effect, since the other factors which can influence the adsorption do not come into play here. Since the polar anchoring group is the same for each molecule, the strength of interaction with the surface, X_A, will be the same in each case, so this is not a contributing factor. Further, the variation is not due to varying adsorption of solvent, since this would require the number of solvent molecules adsorbed on the surface to be a function of the alkyl chain length of the solute. Finally, the solvent interaction with the adsorbing molecule is the same in each case, since neither the solvent varies nor do the types of segments in the chain or the polar head group. So the E_{BC} and E_{AC} terms stay constant throughout.

From the data in Figure 20 it is clear that there is no comparable general chain length effect observed in the homologous series of amines tested. It is also true, as previously discussed, that the amines have a significantly greater strength of interaction with the adsorption sites.

This was demonstrated by the greater initial slope of the adsorption isotherm of the amine as compared to that of the alcohol. The model predicts that as the interaction energy of the polar head group with the surface increases, the ratio of the number of vertical configurations to the number of flat configurations also increases, and quite rapidly. That is, as the strength of interaction with the surface gets larger, more and more configurations take on the vertical orientation, since this allows for a greater number of the more favorable contacts between the polar group and the surface to occur. As a result, there are fewer of the flat configurations and there is less interference in the adsorption and less restriction of movement between the molecules, which were the reasons for the observed chain length effect. If most of the molecules are oriented vertically, the adsorption of different chain length molecules should be nearly the same.

However, it is apparent that butylamine exhibits an unusually high adsorption in hexane, both on calcium fluoride and hydroxyapatite. The adsorption is much greater than that of hexylamine and the other longer-chain amines, approaching a plateau of 0.08 millimoles/gram, onto calcium fluoride. This value is almost double the plateau value for the other three amines, hexylamine, octylamine and dodecylamine. It corresponds to a cross-sectional area for the amine of 43 $\mathring{A}^2$. These results are not consistent

with the above discussion of the chain length effect in the amines. Calculations were performed by Bladon,[98] with reasonable selection of parameters, to see if the theoretical model could explain this experimental data. This critical investigation showed that the data was not consistent with the predictions of the model, and that the observed effect was due to factors not considered in the model, since it could not be explained in those terms.

One possible explanation considered was an accessibility factor, where there might be pores in the surface which are not accessible to the longer chain length molecules. This would result in almost the same kind of selectivity, or preferential adsorption, which exists when there is more than one kind of adsorption site, or different types of adsorbing molecules. However, this would mean that the same kinds and sizes of pores would exist on both surfaces, the calcium fluoride and the hydroxyapatite, since they both showed the same unreasonably high adsorption of the butylamine. This is unlikely. So, the effect should be attributed to something other than a pore effect. When the results are considered, it appears as if the butylamine were being adsorbed onto an additional site, which is unavailable to the hexylamine and the longer chain length molecules. The site density on the surface may be such that when a molecule of a certain length is adsorbed onto one site, it may shield, or block, adjacent sites,

due to its orientation. This would occur assuming that configurational restrictions of the molecule would require the initial portion of the chain of the molecule to be at an angle to the surface when the amine head group is adsorbed. This spacing of the sites appears to be just such that this blocking occurs with hexylamine and the longer chain length molecules, restricting their accessibility to the adjacent sites. As was stated before, the calculated area per calcium atom on the surface of calcium fluoride is 14.8$\mathring{A}^2$, and that on the surface of hydroxyapatite has been reported to be 19.5 $\mathring{A}^2$.[111] Since calcium atoms are the proposed adsorption sites, this shielding mechanism seems quite likely. The butylamine molecules, however, may be just short enough so that they do not completely block the adjacent sites, and other butylamine molecules may be able to have access to these sites.

The higher butylamine adsorption, then, appears to be a result of accessibility to sites which are restricted to longer chain length molecules because of a steric effect. These effects would result in a great enhancement of the predicted chain length effect.

When adsorption isotherms were obtained for the same homologous series of amines on hydroxyapatite, with acetone as the solvent (Figure 18), not only was the adsorption reduced, from 0.17 to 0.05 millimoles/gram, but the butylamine no longer showed the relatively much higher adsorption that it did in hexane. The overall reduction is due

to competition for certain adsorption sites by the acetone, as was discussed earlier, but the lack of a chain length effect must be the result of a combination of factors. The acetone, being a smaller molecule, may be able to have access to the sites on which only the butylamine is adsorbed, and when it is added to the solution, effectively competes for these sites in addition to the sites on which the longer chain length molecules are adsorbed, since they are the same kind of site. In effect, the acetone poisons the sites which were responsible for the observed difference between the adsorption of the butylamine and the longer molecules, thus eliminating the accessibility effect. In addition, the steric effect would not have any influence in this case, since all the amine molecules would be surrounded by acetone molecules on the surface, and would be far enough apart that there would be no interference between neighboring amine molecules. And finally, it may be that the amines have a very high affinity for the remaining adsorption site, from which the acetone does not displace them. As discussed previously, a high interaction energy with the surface results in more of the vertical configurations, and in this way reduces the chain length effect.

The fact that the butylamine showed the same kind of unusually high adsorption on both calcium fluoride and hydroxyapatite is further indication there is a similar type of adsorption site on both surfaces. Indeed, when

the adsorption of butylamine on hydroxyapatite in acetone is subtracted from its adsorption from hexane, a curve results which is almost identical in its characteristics to the isotherm for the adsorption of the butylamine from hexane on calcium fluoride. This suggests that the site on hydroxyapatite for which the acetone competes is the same as the site on calcium fluoride.

The homologous series of n-alkanoic acids showed no apparent chain length effect, neither on hydroxyapatite from hexane or acetone (Figures 14 and 15), nor on calcium fluoride, from hexane (Figure 16). The acids were previously shown to have the highest strength of interaction, X_A, with the surface by exhibiting the greatest initial slope on the isotherms. This means that the molecules are oriented primarily in a perpendicular configuration on the surface. As a result, there would be very little chain length, or entropy, effect. However, it is clear that even though the configurations may be primarily vertical, the molecules are not close-packed. According to the theoretical model, an entropy effect should be seen at low coverages, even if there is none in the plateau region. However, this is assuming that the adsorbed molecules are able to assume all possible configurations on the surface. In the case of the acids, this might not be possible, since it is likely that there is directionality in the adsorption. That is, due to the nature of anchoring of the adsorbing polar group, there may be restrictions in the

total configurations possible. If this were the case, the entropy effect would be diminished, or completely eliminated, both at low coverages and at the plateau level.

Other workers have, however, noticed a chain length effect on the adsorption of a homologous series on n-fatty acids from non-polar solvents. Allen and Patel,[89] in adsorption studies of n-fatty acids on iron oxide, found that the number of molecules adsorbed decreased, rapidly at first and then more slowly, as the carbon chain length increased. Holmes and McKelvey[77] showed that longer chain acids adsorbed in decreasing amounts from a toluene solution onto silica gel. Similar results were obtained by Vetrova et al.,[72] Zeliznyi et al.,[73] and Armistead et al.,[59] who found a pronounced chain length effect on the adsorption of fatty acids on silica.

Most of these studies were done using silica as the adsorbent. It has been shown[112] from heat of wetting measurements that calcium fluoride has an electrostatic field strength about twice as great as that of silica. Indeed, the calcium fluoride was close to titania (TiO_2) in polarity; this means that the electrostatic interaction with an adsorbate would be strong.

Heats of adsorption for fatty acids onto titania from heptane[89] have been shown to be considerably greater than those for fatty acid adsorption on silica from carbon tetrachloride.[71] And since calcium fluoride was similar to titania in its surface polarity, the same relationship

would hold. Thus, the energy of interaction between the carboxyl group and the calcium fluoride surface is greater than that between the acid and the silica surface, which is thought to take place through hydrogen bonding.[68] According to the model, the stronger the interaction between the polar head group and the surface, the greater will be the proportion of vertical configurations. And, as a result, there will be a reduction in the chain length effect. On silica, where the interaction with the surface is weaker, more non-vertical configurations exist on the surface, and a chain length effect may be observed.

Kipling and Wright,[58] in adsorption studies with stearic acid, also concluded that the orientation adopted at the interface is a function of the energy of interaction with the surface. They suggested that a perpendicular orientation is assumed on polar surfaces, such as titania, but on less polar surfaces, such as silica, the acid was adsorbed parallel to the surface. Although the latter view was later shown to be not entirely correct,[59] this, too, explains why a chain length effect is seen in fatty acid adsorption onto silica.

The results presented in this section are in general agreement with those obtained by many other workers. Most of the earlier investigators who observed a similar chain length effect simply described it as a reversal of Traube's rule, and attributed the decrease in adsorption with longer chain length to the fact that these molecules were less

polar, and hence were more strongly attracted by the organic solvent and less strongly adsorbed.[77] A somewhat similar explanation was proposed by Hackerman and Roebuck,[64] who suggested that the greater adsorption of the shorter chain length molecules of a homologous series was a result of their greater reactivity. The lower the molecular weight, the greater the percentage of functional polar group per molecule. In a qualitative sense, the observed chain length effect in non-polar solvents is a reversal of Traube's rule, but the interpretation is quite different from that of Traube's rule, which is based on the surface activity of the compounds.

Crisp[68] suggested that this effect was not due to differences in the energies of adsorption, as had been previously thought, since he found these to be independent of chain length. But since differences in the adsorption of members of a homologous series had been observed, he correctly interpreted this effect as being due to a difference in the available surface area for the different chain length molecules. That is, the higher members of a homologous series were stated to have a greater apparent molecular size. This view is basically in agreement with the interpretations presented in this paper, although the author made no attempt to explain in greater detail these differences in the molecular area with differences in chain length, or the nature of the influence on the adsorption.

More recently, a number of different theories have been put forth to explain the chain length effect, but they all have as their basis the orientation of the molecules at the interface. Rupprecht[62] visualized the arrangement of the molecules in the adsorption phase in only two possible ways--the molecules lying flat on the surface, or the molecules in a perpendicular orientation. In his adsorption studies the apparent molecular areas of the adsorbed molecules increased up to a chain length of C_{10}, but showed no increase beyond that. He postulated that the shorter-chain molecules were in the flat-lying configuration, and that the longer species preferred a perpendicular orientation. This appears to be a fairly unrealistic interpretation of the results, and was a result of restricting the consideration of possible configurations to only the parallel and the perpendicular. The results may be explained on the basis of the configurational entropic considerations of the adsorption, as discussed previously. The reason that the effect of lengthening the carbon chain appears to have a greater effect on the adsorption of the shorter chain molecules, is that as the molecule gets larger, the relative difference in the chain length gets smaller. That is, increasing the chain length of a short molecule by two carbon atoms has a much greater relative effect on its adsorption than the same increase would have on a C_{16} compound, for example. As a result, the adsorption of the longer chain molecules is affected much less by a further

increase in the chain length.

Other investigators[70-72,88] have interpreted the chain length effect as being a result of the orientation of the adsorbed molecules at the interface such that their alkyl chains lie at a definite angle to the surface. This was the mechanism suggested by Ganichenko et al.[88] when they concluded that in their system the decrease in the adsorption with an increase in chain length could not be due to the porous structure of the sample, or to competition from the solvent. They postulated that the orientation of the adsorbed molecules changes with the growth of the length of the hydrocarbon chain, the molecules apparently being positioned at a certain angle to the surface. In this way, according to the authors, the longer chain molecules, situated obliquely to the surface, can effectively shield a portion of the adsorption sites. Vetrova et al.[71] concluded that as the chain length increases, the dispersion interaction of the hydrocarbon radicals with each other and with the surface of the adsorbent increases, the molecules assume a more inclined position, and the fraction of surface area available for adsorption decreases.

This view of the angled orientation of the adsorbed molecules was put forth because the data could not be explained by assuming either the parallel or the perpendicular orientation. An alternative interpretation, and possibly a more realistic one, is put forth by the model presented here, where many different configurations are

possible for each molecule, the number of each one being determined by such factors as the energy of interaction between the polar head group segments and the surface, that between the solvent and the surface and that between the solvent and various segments of the molecule.

The results of these workers, then, can be interpreted in terms of the model as being due to the numbers of flat, or partially flat, configurations on the surface, causing a reduction in the total amount adsorbed with an increase in the chain length. On this same basis, the model can explain the influence of such factors as the nature of the solvent or the nature of the surface on the adsorption by seeing how these things affect the kinds of configurations on the surface. This interpretation seems to be more reasonable than explaining these influences in terms of the effect that the solvent and nature of the surface have on the angle of inclination of the alkyl chain to the surface, as Mathews and Colwill[70] did.

The model may also explain the results obtained by Armistead, Tyler and Hockey,[59] who observed a chain length effect in the adsorption of n-fatty acids on silica from hexane. They were only able to conclude that the limiting adsorption could not be attributed to either the close packing of the hydrocarbon molecules oriented with their chains parallel to the plane of the adsorbent surface, or to the saturation of a fixed number of adsorption sites on the surface. Since silica is not a highly polar surface,

there would be a significant number of non-vertical configurations at the interface, causing a reduction in the molar adsorption as the chain length increased.

In a more recent study, Mills and Hockey[91] found a dependence on the chain length in the adsorption isotherms of methyl esters of fatty acids on silica, both in the initial slopes and in the limiting adsorption values. They deduced that the entropy contribution to the free energy term for the adsorption had to be negative, and suggested that this would be the case if the hydrocarbon chains of the solute underwent a change in solvation on adsorption. These solvated chains would then form an "ordered" layer at the solid surface, the structural coherence of which would result in lower adsorption. In addition, the authors found that the heat of adsorption was independent of chain length,[113] indicating that there was little enthalpy contribution to the free energy of adsorption. This supported the argument that the variation in adsorption with chain length was the result of an entropy effect. Their conclusion , however, that the change in entropy on adsorption is negative due to solvation, or "ordering" of the hydrocarbon chains neglects the fact that there is loss of entropy of the adsorbed molecules due to the decrease in the number of total possible configurations on adsorption.

The views and interpretations of the chain length effect observed in the adsorption of organic compounds from non-polar solvents have been many and varied, but a good theory has been lacking. This interpretation may provide a new basis for understanding this widely-studied phenomenon.

Chain length effect in mixed solvents

The adsorption isotherms obtained when the acetone competitive adsorption was studied showed some deviation from the theoretically calculated curves, representing the Langmuir, two-component, competitive adsorption model. Whereas the theoretical curves all tended toward the original plateau (the adsorption value in hexane only), the experimental isotherms levelled off at values less than the original plateau. The greater was the acetone concentration, the lower were the adsorption values at which the plateaus were reached.

It was thought that perhaps this deviation was a result of an entropy effect, occurring because of the presence of acetone on the surface. That is, perhaps the effective interaction energy was reduced because of the

population of the surface by acetone, and as a result, the entropy effect was greater.

To assess this possibility, the chain length effect was studied in various concentrations of acetone in hexane solvents. The results are seen in Figures 22, 23 and 24. It is apparent that the entropy effect is not enhanced, as would have been the case if the above possibility did occur, but, is reduced. It is reduced to the point where, at 4 per cent acetone, there is no longer any difference in the plateau values of the three compounds. It should also be noted that the isotherm for the hexyl alcohol has taken on a pronounced S-shape, which is characteristic in cases where the solvent competes very strongly for the surface. The lauryl alcohol, also, appeared to be starting to exhibit an S-shaped isotherm.

Since the entropy effect was reduced by adding increasing amounts of acetone, a more active solvent than hexane, the conclusion would have to be that it did so by occupying many of the binding sites itself, and in this way spreading apart the alcohol adsorption sites so far that there was no more interaction between the chains. The acetone also has an effect on the total possible configurations of the alcohol. By being adsorbed onto sites adjacent to the alcohol molecules, the acetone restricts their motion and orientation, and in this way reduces the total possible configurations to only those where only the polar head group is touching the surface. That is, the flat

configurations would be eliminated, since it would be more unfavorable to have a 'B' segment on the surface rather than an acetone molecule, which is polar. The shorter chain length molecule would be hurt more in this case, since it would lose a greater portion of all its configurations. When the ratio of the number of configurations with only the 'A' segment touching the surface to the total possible configurations on the surface for a dimer molecule is compared to the same ratio for a tetramer, the values are almost the same: 0.25 and 0.21, respectively. According to the model, this means that the plateau values of the two compounds will also be the same. So, the reduction in the entropy effect, as manifested by the convergence of the adsorption isotherms, both in the plateau region and the initial slopes, is a result of a reduction in the number of possible configurations and the creation of single, isolated adsorption sites, with no other sites immediately adjacent.

Because the concentration of acetone at 4 per cent is very much greater than that of the alcohol, the surface would be covered with acetone molecules and the initial adsorption of the alcohol would be very low, as is seen in the case of the hexyl alcohol. As the concentration of the alcohol on the surface increases, lateral interaction between the hydrocarbon chains promote further adsorption, and an inflection in the curve results. Because the dodecyl alcohol and cetyl alcohol have longer chains, this lateral

interaction is more pronounced, and the cooperative adsorption is greater and occurs at lower equilibrium concentrations. As a result, the fairly flat initial portion of the curve is not seen, as it is in the case of the hexyl alcohol.

Calculations based on the theoretical model predict that the use of a competitive solvent will lower the adsorption of the compounds, but that the longer chain compound will be affected to a greater degree than the shorter chain length compounds. This results in an enhancement of the entropy effect, both in the initial slopes and the plateau region, with the curves being spread apart, not a reduction, which is the case seen experimentally. This may be because there are factors which the model does not consider, such as the sparseness of the adsorption sites of the alcohols, when the acetone is also present on the surface. The model has considered the configurations of the molecules on the surface and calculations have shown that the ratio of vertical to flat configurations increases greatly when a competing solvent is added to the bulk solution.

Similar trends in the adsorption behavior of a homologous series were observed by Zeliznyi and coworkers.[73] They studied the characteristics of adsorption of a series of n-fatty acids on silica gel from n-heptane, and compared these results to the corresponding data obtained with carbon tetrachloride and benzene as the solvents. They found that the carbon tetrachloride and benzene resulted

in an overall reduction in the limiting adsorption of the members of the homologous series. In addition, there was a levelling off of the differences in the adsorption of the individual members of the homologous series in benzene. That is, there was less chain length effect on the adsorption in the more active solvent, benzene. They interpreted these results in terms of the effect that the benzene has on the adsorption of the various members of the series. According to the authors, the solvent affects the adsorption in two ways: if it is active, it can interact with acids, forming complexes of varying degrees of stability, and the solvent can compete for the adsorption sites on the surface. Both of these influences would lead to a lowered adsorption of the solute. Benzene, being an active solvent, is able to effectively reduce the adsorption, by competing for the surface sites, of not only the longer chain homologues (which were stated to form less stable bonds with the hydroxyl groups of the silica gel), but the short-chain acids as well. In addition, the adsorption of the shorter molecules is reduced even further, due to their interaction with the benzene in the bulk. This ability to form complexes reportedly decreased with the growth of the acid's molecular weight. Thus, through the action of these two influences, the adsorption of the shorter-chain acids was reduced to a greater extent than that of the longer-chain homologues, and the adsorption isotherms of the various members of the homologous series

come closer together.

In the above interpretation, the configuration of the molecules on the surface was not even considered. Armistead, Tyler and Hockey[59] also found that, with the exception of the C_6 and C_8 acids, there was no chain length effect on the adsorption of n-fatty acids on silica from benzene solutions. This was in contrast to the results obtained with n-hexane solutions, where a chain length effect was observed. The authors determined that the limiting adsorption in benzene corresponded to a surface coverage of 0.49 molecules per 100 $\mathring{A}^2$ of surface, which was much less than the surface concentrations of the adsorption sites. Further, from heat of immersion measurements,[85] they concluded that the fatty acids were adsorbed at the silica/solution interface in an orientation such that the alkyl chain is not interacting with the surface. These two observations are in complete agreement with the interpretation presented in this paper: that is, the acid molecules are adsorbed in a vertical orientation onto sites that have been spread apart, due to adsorption of solvent molecules. The result of this, then, is that no chain length effect is observed under these conditions.

ADSORPTION STUDIES IN AQUEOUS SYSTEMS

The importance of the adsorption process in the various mechanisms of protection of tooth enamel has been recognized for a number of years, but a basic mechanistic understanding of this process is lacking. An understanding of the adsorption process and the factors which affect it would be beneficial in determining the optimum conditions for the maximum possible protection of the surface. And, in a broader sense, it is hoped that a basic investigation such as this would contribute to a general understanding of processes involved in adsorption from aqueous solution.

This portion of the work, then, represents a general investigation, or survey, of the adsorption behavior of polar organic compounds onto an inorganic surface from aqueous solutions. It is a study of the effect of various factors on the adsorption, and its intent is to determine such things as the species of the adsorbing substance, the nature of the adsorption sites, the nature of the interaction and the orientation of the adsorbate molecules at the surface.

EXPERIMENTAL

Materials

Hydroxyapatite (HAP): $Ca_{10}(PO_4)_6(OH)_2$

Most of the experiments were performed using Victor

hydroxyapatite, which was described in the previous section. In addition, several experiments were performed with a hydroxyapatite sample prepared by Dr. A. Molokhia,[1] which has a surface area of 70 m^2/gm and a calcium to phosphate ratio of 1.64.[114] This sample is reported to have fewer carbonate impurities and better crystallinity than Victor hydroxyapatite. When this sample is referred to, it will be referred to as AM-HAP.

Amines

The amines used included dodecylamine,[2] dodecylmonomethylamine,[3] dodecyldimethylamine,[4] decylamine[5] and octylamine.[2]

The hydrochloride salts of the solid amines were prepared by dissolving the amines in a small amount of hot n-propanol, and adding concentrated hydrochloric acid to the solution dropwise, in an amount just slightly in excess of an equimolar amount, to insure that all of the amine has reacted. The solution was cooled at room temperature, and then placed in an ice bath. The resulting crystals were collected, the filtrate cooled again and a second batch of crystals collected. The material was

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[1] College of Pharmacy, University of Michigan, Ann Arbor.
[2] Aldrich Chemical Co., Inc., Milwaukee, Wis.
[3] K and K Laboratories, Plainview, N.Y.
[4] Pfaltz and Bauer, Inc., Flushing, N.Y.
[5] Eastman Organic Chemicals, Rochester, N.Y.

recrystallized three times in n-propanol.

The hydrochloride salts of octylamine and decylamine, which are liquids at room temperature, were prepared by mixing equimolar amounts of the amines and concentrated hydrochloric acid (with the acid in slight excess). The acid was added dropwise while the mixture was stirred continuously with a magnetic stirrer. The resulting solid was dried at room temperature and then recrystallized three times in n-propanol.

Acids

The sodium salts of the fatty acids, octanoic,[1] decanoic[2] and dodecanoic (lauric)[1] were prepared by mixing equimolar amounts of the acid and sodium hydroxide (1N), with a slight excess of the base to insure complete neutralization of the acid. In the case of the decanoic and lauric acids, they had to be melted first since they are solids at room temperature. The base was added very slowly, while stirring continuously with a magnetic stirrer. The resulting solid was recrystallized in ethanol, and purity was checked by means of thin layer chromatography.

The purity of the radioactive compounds used, sodium octanoate,[3] sodium decanoate[3] and sodium laurate,[3] was determined by means of a radiochromatogram, scanned on the Packard Radiochromatogram Scanner.

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[1] Eastman Organic Chemicals, Rochester, N.Y.

[2] Matheson, Coleman and Bell, Norwood, Ohio.

[3] ICN Isotope and Nuclear Division, Irvine, Calif.

Buffers.

All of the amine experiments were done using acetate buffers, which were prepared by combining the calculated quantities of accurately weighed sodium acetate crystals and 1N acetic acid. The experiments performed with the fatty acids were done with 0.05M Tris buffers [tris(hydroxymethyl)aminoethane] where appropriate quantities of Tris and Tris hydrochloride were combined to give the desired pH.

Procedure

In the case of the amines, 10 ml of a known concentration of adsorbate solution were added to 100 mg of hydroxyapatite powder in 100-ml volumetric flasks. The only exception to this occurred in the slurry density experiments, where the amount of hydroxyapatite was varied from 50 mg to 1 Gm.

Because the assay of the fatty acids was a radioactive one, the solution added to the hydroxyapatite powder was a mixture of radioactive and non-radioactive materials. In each case, a constant amount of appropriately diluted radioactive material was added to each sample solution before it was added to the powder. Ten milliliters of this solution was then removed and added to the powder in the volumetric flask.

The flasks were shaken by means of a wrist-action

shaker in a constant temperature water bath maintained at 30°C for 20 hours. The rate of shaking was maintained constant in all experiments. At equilibrium, the flasks were removed and the contents were centrifuged in polyethylene tubes. An aliquot of the supernatant was then removed for assay.

Because there was the possibility of precipitation of the calcium salts of the fatty acids occurring during the equilibration period, due to any dissolved hydroxyapatite, in each case a portion of the experimental buffer solution used was presaturated with hydroxyapatite for a solubility check of the acid. The presaturation was done by shaking the buffer with an amount of powder equivalent to that used in the adsorption samples, for the same length of time and under the same conditions. After centrifugation, the supernatant buffer was removed and was used to make a solution of the highest concentration of acid used in that particular experiment. This was done routinely to make sure that there was no precipitation.

Assay method

The assay method for the amines involves complexation of the amine with picric acid. The concentration of this picrate complex is determined spectrophotometrically. Five milliliters of the surfactant solution are shaken in a separatory funnel with two successive portions of 15 ml

of a solution of 0.2% picric acid in methylene chloride. (The methylene chloride was purified by distillation prior to use.) The two 15 ml portions are drawn off and of these 30 ml, 5 ml are pipetted into a 25 ml volumetric flask. The solution is brought to the 25 ml mark by addition of methylene chloride. The absorbance of these solutions is determined spectrophotometrically at a wavelength of 410 nm.[1] The Beer-Lambert relationship is obeyed up to a concentration of 2.5 millimolar. A set of standards is determined each time, carrying each known solution through the same assay procedure. The concentrations of the unknown solutions are then determined, using this standard curve.

Picric acid is used as the reagent here for assaying the amines because it has a strong absorption spectrum and a single strong anionic functional group that has been shown to react quickly and quantitatively with the base. It is a very sensitive method, and allows the determination of small amounts of amines more accurately than a titration method.

In the assay procedure, the amine-picrate salt is separated from any excess unreacted picric acid by the extraction with methylene chloride. As long as the pH used is high enough (pH>3) to insure that the picric acid will exist as an anion and not be extracted into the organic phase, a negligible amount of picric acid will be extracted.

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[1] Hitachi Perkin-Elmer UV-VIS Spectrophotometer, Model 139, Hitachi Ltd., Japan.

The assay for the fatty acids was a radioactive one, as stated above, where the counts in each sample were directly related to the concentration. Initial counts were determined by withdrawing a 1 ml sample from each of the solutions used in the experiment (before addition to the powder), and placing it in 10 ml of scintillation cocktail in a scintillation vial. The cocktail was prepared by making 500 ml of a solution of 50 Gm of naphthalene and 2.5 Gm PPO (2,5-diphenyloxazole) in p-dioxane. Final counts were obtained similarly, where a 1 ml aliquot was taken from the supernatant solution after the samples were centrifuged. The samples were counted in the Beckman Liquid Scintillation System.

Also, to make sure that the final counts would not be affected by any dissolved material due to the hydroxyapatite, or any products formed as a result of the dissolution, a few select samples of solutions of the fatty acid in the presaturated buffer were also counted in each experiment. These counts were then compared to counts obtained from samples of the acid in buffer which was not presaturated.

The final concentration was then determined by directly relating the initial counts, initial concentration and final counts. The amount adsorbed was taken as the difference between the initial and final concentrations in the solution.

Adsorption of amines on hydroxyapatite

Preliminary studies were done to assess the effect of the nature of the polar group on adsorption. The primary, secondary and tertiary amines, dodecylamine hydrochloride, dodecylmonomethylamine hydrochloride, and dodecyldimethylamine hydrochloride, were used for this purpose. The effect is demonstrated in Figure 29. The tertiary amine exhibited no adsorption at all, and therefore does not appear. It can be seen that the primary amine is adsorbed to a much greater extent than the secondary amine. This may be due to the fact that the bulkier head group of the dodecylmonomethylamine does not allow as close packing at the interface as occurs with the dodecylamine, thereby reducing the amount adsorbed. This is assuming that they are both oriented the same way on the surface.

It should also be noted that the isotherms are S-shaped, which is in contrast to the Langmuir type of adsorption, where the initial part of the curve is fairly linear, without any inflection until the plateau is reached. There have been several explanations of the conditions which may result in an S-shaped isotherm. A curve such as this results if the solvent is strongly adsorbed, if there is multilayer adsorption or if the adsorbate is monofunctional--that is, if the adsorbing molecule has a single point of strong attachment.[115]

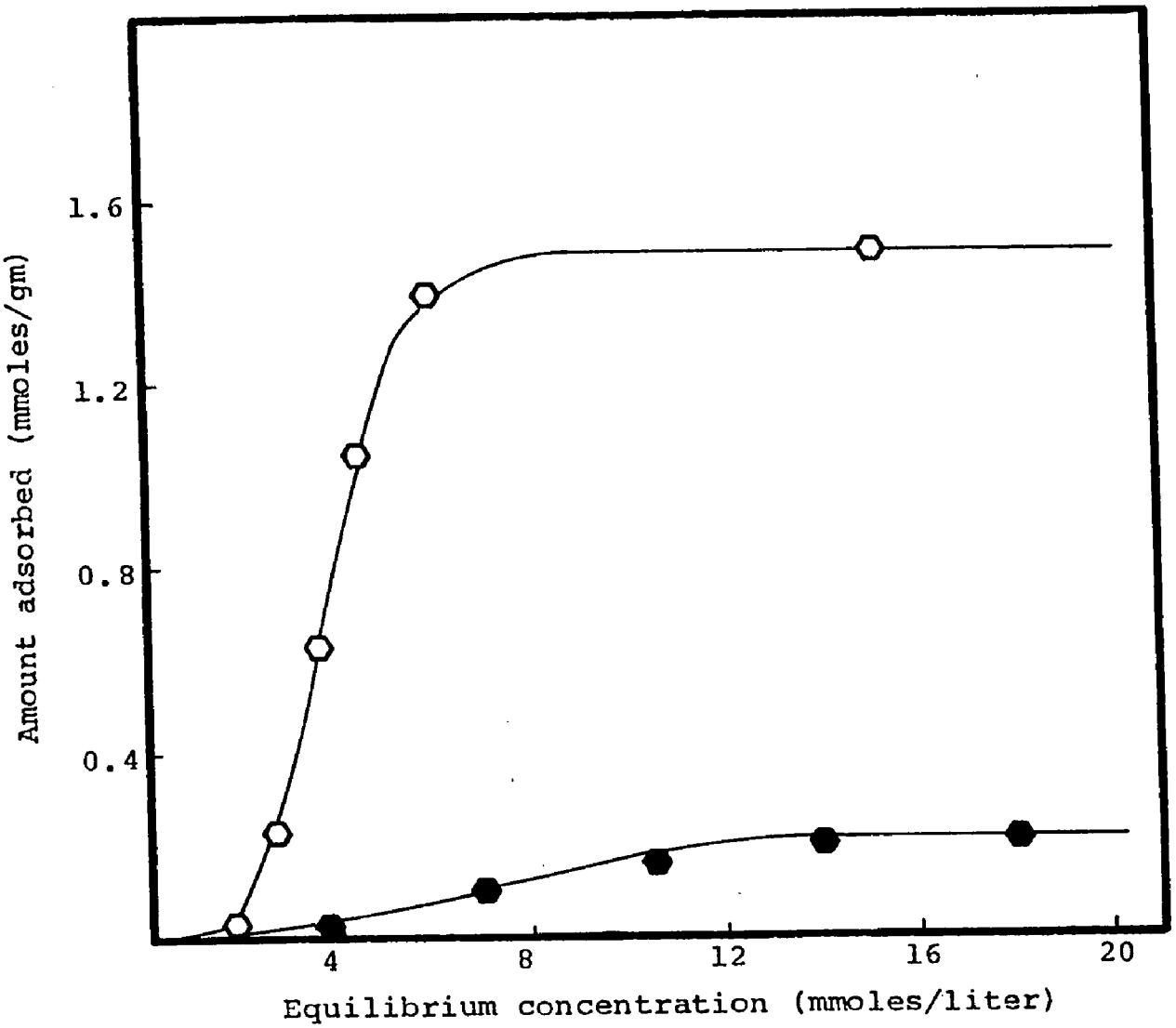

Figure 29. Adsorption of dodecylamine hydrochloride and dodecylmonomethylamine hydrochloride onto Victor hydroxyapatite at pH 4.5.

Key: ⬡ dodecylamine hydrochloride

● dodecylmonomethylamine hydrochloride.

According to Greenwood et al.,[116] the point of inflection in an S-shaped curve occurs at about one-half of the critical micelle concentration (cmc), and may indicate a change in orientation of the adsorbed molecules, from parallel to perpendicular with respect to the surface. Wakamatsu and Fuerstenau[117] explained the S-shaped adsorption isotherms as consisting of three regions: region one characterized by a fairly flat portion of the curve, in which the surfactant ions adsorb individually through coulombic attraction for the surface; region two, which results from the onset of association of the hydrocarbon chains of the surfactant ions, causing the sharp rise in the isotherm; and region three, in which the charge in the Stern plane exceeds the surface charge with resulting electrostatic repulsion acting to inhibit adsorption. It has been stated[118] that the forces responsible for this association at the surface are the same as those operating in the bulk which cause micelle formation. At a certain critical concentration at the solid-liquid interface, the adsorbed molecules begin to associate into two-dimensional patches, or aggregates, of ions, called "hemi-micelles."[118,119] The bulk concentration corresponding to the onset of these lateral interactions between the hydrocarbon chains of adjacent molecules adsorbed on the surface is called the hemi-micelle concentration, and is approximately 1/100 of the cmc. The lateral interactions are Van der Waal's in nature, and it is the operation of this Van der Waal's

interaction energy that is the fundamental postulate of the hemi-micelle theory.

Healy[120,121] discussed this lateral Van der Waal's interaction in terms of being a specific adsorption potential contribution to the adsorption free energy of a surfactant. The formation of these hemi-micelles would result in a considerable overall lowering of the free energy of the system, causing a strong modification in the adsorption process. This is seen in the form of a sharp increase in the isotherm. He envisioned the electrostatic interactions as localizing the molecules on the surface, so that a significant hydrophobic energy term might act.

According to Tamamushi and Tamaki,[122] the S-shaped curve is a result of electrostatic adsorption of one layer, followed by the build-up of a multilayer, due to Van der Waal's attraction.

The S-shaped curve may be the result of a cooperative adsorption mechanism, where, once sufficient molecules adsorb onto the surface, strong lateral hydrocarbon interactions promote further adsorption, and an inflection in the curve results. This condition would be most likely to occur if the molecules were adsorbed so that they were in a perpendicular orientation. A vertical orientation of surfactant molecules was suggested by Dick et al.,[123] because they found a significant increase in the area per adsorbed molecule at the hemi-micelle concentration as the branching on the molecule was increased. This would

not be the case if the molecules were in a horizontal orientation.

Since the adsorption of dodecylamine onto hydroxyapatite was much stronger than that of the secondary amine, it was decided that subsequent experiments would be done with the primary amine.

Figure 30 shows the effect of varying the concentration of sodium chloride on the adsorption. A marked reduction in the maximum amount adsorbed, as well as a distinct displacement of the curves to lower equilibrium surfactant concentrations can be seen. However, there is no further effect at sodium chloride concentrations above 0.1 M. A limiting value of the adsorption is reached at 0.5 millimoles/gram, and the plateau is reached at an equilibrium concentration of about 2 mM. This value corresponds to the cmc of dodecylamine hydrochloride in 0.2 M sodium chloride solutions as reported by Roseman.[124]

The displacement of the curve to lower equilibrium concentrations with increased electrolyte concentration has also been observed by other investigators.[122,124] It may be correlated to the result of the effect of the added electrolyte upon the cmc of the surfactant. The addition of the negatively charged chloride counterions to a solution of the positively charged surfactant tends to screen out the positive charge on the polar group by effectively reducing the size of the electrical field. This makes it possible for the surfactant molecules to

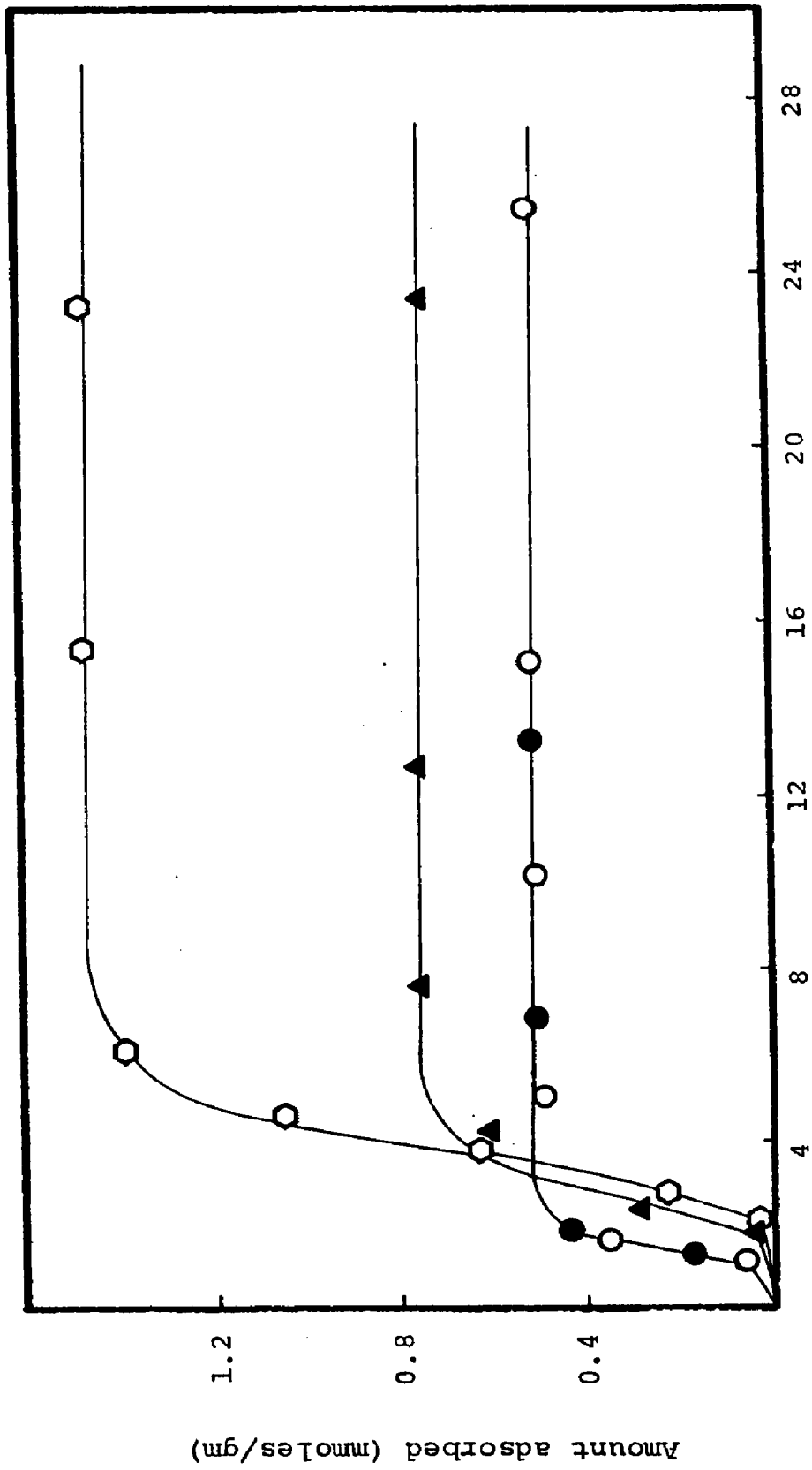

Figure 30. Effect of added electrolyte on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 4.5.

Key: Sodium chloride concentration

⬡ none ○ 0.1 M

▲ 0.05 M ● 0.2 M

come closer together and form micelles at lower concentrations. The size and aggregation number of micelles have also been reported to increase with added electrolyte.[125] The important factor to note here, as pointed out by Corrin and Harkins,[126] is that only ions of opposite charge from that of the micelle are able to produce an effect on the cmc. This decrease in the cmc with added electrolyte would result in region two of the adsorption isotherm, as postulated by Wakamatsu and Fuerstenau, occurring at lower equilibrium concentrations of the surfactant.

The fact that the isotherm reaches its limiting value at the cmc suggests that the cmc determines where the adsorption saturation is reached. Others have also noted this correlation.[116,122,124,127] However, the plateau value of 0.5 millimoles/gram could also correspond to complete coverage of the surface. Whether this coverage is a monomolecular layer or bimolecular is difficult to say with certainty. Roseman[124] postulated that a limiting adsorption value of 0.54 millimoles/gram on hydroxyapatite represented monomolecular coverage, assuming the cross-sectional area per adsorbed molecule to be 20.5 $\mathring{A}^2$. However, in this case, a bimolecular layer seems more probable, for several reasons. First of all, the value of 20.5 $\mathring{A}^2$ is that obtained from condensed film studies,[56] which is not analogous to the situation here. There are very likely some solvent molecules adsorbed on the surface, and there may be some repulsion between the charged polar

groups of the amine molecules. Both of these factors would tend to prevent close packing of the surfactant molecules. Also, since the solvent is aqueous, it may be more energetically favorable to have bilayer adsorption, so that the polar groups of the second layer are oriented toward the solvent. Somasundaran and Fuerstenau[119] also postulated a similar arrangement, which would occur in region three of the isotherm. They suggested that after the net charge on the solid surface becomes zero (due to the adsorption of surfactant molecules), the surfactant ions that associate with those already adsorbed might adsorb with the polar head group away from the surface. This would, according to the authors, reduce the repulsion between the ionic heads. Bilayer coverage would also help to explain the S-shaped curve, as stated before. Initially, there is only monolayer adsorption, but as soon as enough molecules are on the surface, others begin to orient themselves in a second layer, causing a steep rise in the isotherm.

The value of maximum adsorption in the pH 4.5 buffer, without added sodium chloride was unusually high, and did not correspond to that obtained by previous workers,[124] the only difference in the experiments being the slurry densities. Therefore, a study of the effect of slurry density was carried out and the results are presented in Figure 31. Again, a limiting plateau value of 0.5 millimoles/gram is reached when 500 mg of hydroxyapatite is

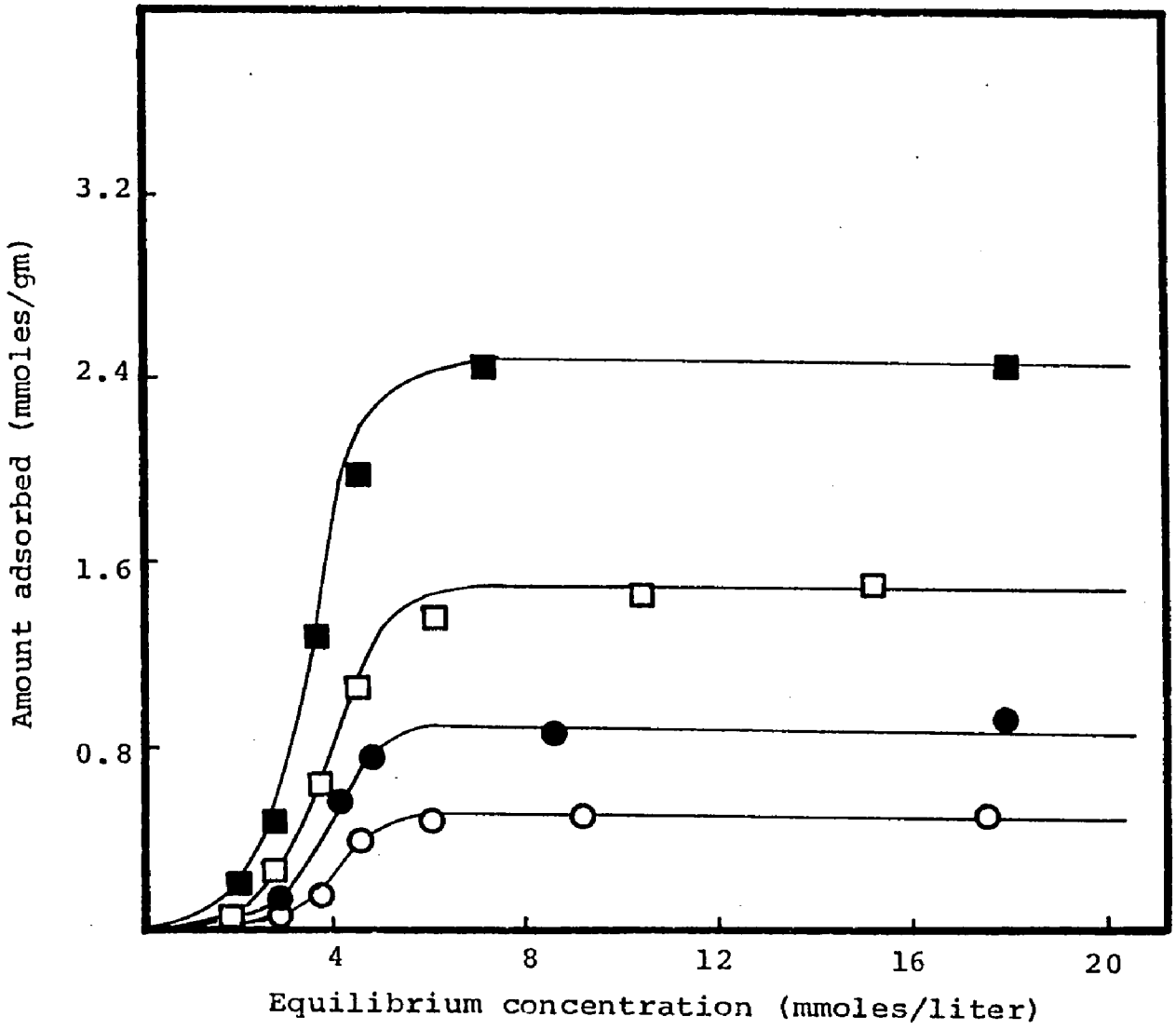

Figure 31. Effect of slurry density on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 4.5.

Key: Amount of hydroxyapatite used

■ 50 mg □ 100 mg

● 250 mg ○ 500 mg

used in the experiment. The use of 1000 mg did not produce any further change in the adsorption isotherm. There is no displacement of the curves here, indicating that the cmc is not changing.

It was thought that the very large differences in the amount adsorbed due to slurry density variations could be due to differences in the dissolution of the HAP. At low pH, there is dissolution of HAP, which may change the surface area and surface structure. And since dissolution varies with slurry density, the conditions of adsorption may have been different in each case. To investigate this possibility, the HAP was pre-dissolved by shaking 1 gm with 100 ml of 0.5 M acetate buffer, pH 4.5, for 48 hours. This resulted in 22% of the HAP dissolving, as determined by phosphate assay of the supernatant. However, when the predissolved, and now less soluble, material, was used in varying slurry densities, the same results were obtained. This also eliminated the possibility of any kind of surface impurities affecting the adsorption. Table VI summarizes this slurry density data.

An interesting point which is seen here, is that this slurry density effect was not nearly as pronounced with AM-HAP as with the Victor HAP.

A probable explanation for this slurry density effect at pH 4.5 is that there is precipitation of the amine, due to an interaction with the phosphate ion in solution. (This interaction and resultant formation of an insoluble

Table VI

Effect of Slurry Density on the Adsorption of Dodecylamine Hydrochloride onto Hydroxyapatite

Buffer: 0.05 M Acetate, pH 4.5

Amount of HAP	Amount adsorbed (millimoles/gm) Victor HAP	Victor HAP (predissol.)	AM-HAP
50 mg	2.50	2.42	1.02
100 mg	1.50	1.60	0.65
250 mg	0.86		
500 mg	0.50	0.60	0.57

compound was observed when an attempt was made to prepare a solution of dodecylamine hydrochloride in phosphate buffer.) If the amount of this precipitation was about the same in each case, the resultant error in calculating the amount adsorbed in the 50 mg case would be greater than in the 100 mg case, etc. These errors, then would result in the observed differences in the isotherms.

To see if there would be a slurry density effect in the presence of added electrolyte, experiments were done in 0.05 M acetate buffer, with 0.05 M, 0.10 M and 0.20 M sodium chloride. It was expected that the effect would not be as great, since the electrolyte itself acts to decrease the adsorption plateau at pH 4.5. The results are shown in Table VII. It is evident that the electrolyte effect becomes the predominant one, above a concentration

of sodium chloride of 0.1 M.

Table VII

Effect of Slurry Density on the Adsorption of Dodecylamine Hydrochloride onto Hydroxyapatite in 0.05 M acetate buffer, pH 4.5, with added electrolyte

	Amount adsorbed (millimoles/gm)		
Amount HAP	0.05 M NaCl	0.10 M NaCl	0.20 M NaCl
50 mg	1.06	0.54	0.49
100 mg	0.76	0.52	0.51
250 mg	0.51	0.51	
500 mg	0.50	0.51	0.51

Since there was a possibility that the acetate ion of the buffer may have an effect on the adsorption, the effects of varying concentrations of acetate were investigated. The results are shown in Figure 32. In each case, the pH of the buffer was 4.5. It appears clear that there is some sort of interaction with the acetate ion, resulting in an increase in the amount of surfactant adsorbed, up to an acetate concentration of 0.05 M. Beyond this, an increase in the acetate concentration results in a decrease in the adsorption plateau, as well as a displacement of the curves to lower equilibrium concentrations. This is probably due to the increasing ionic strength.

To make sure that this effect was not the result of

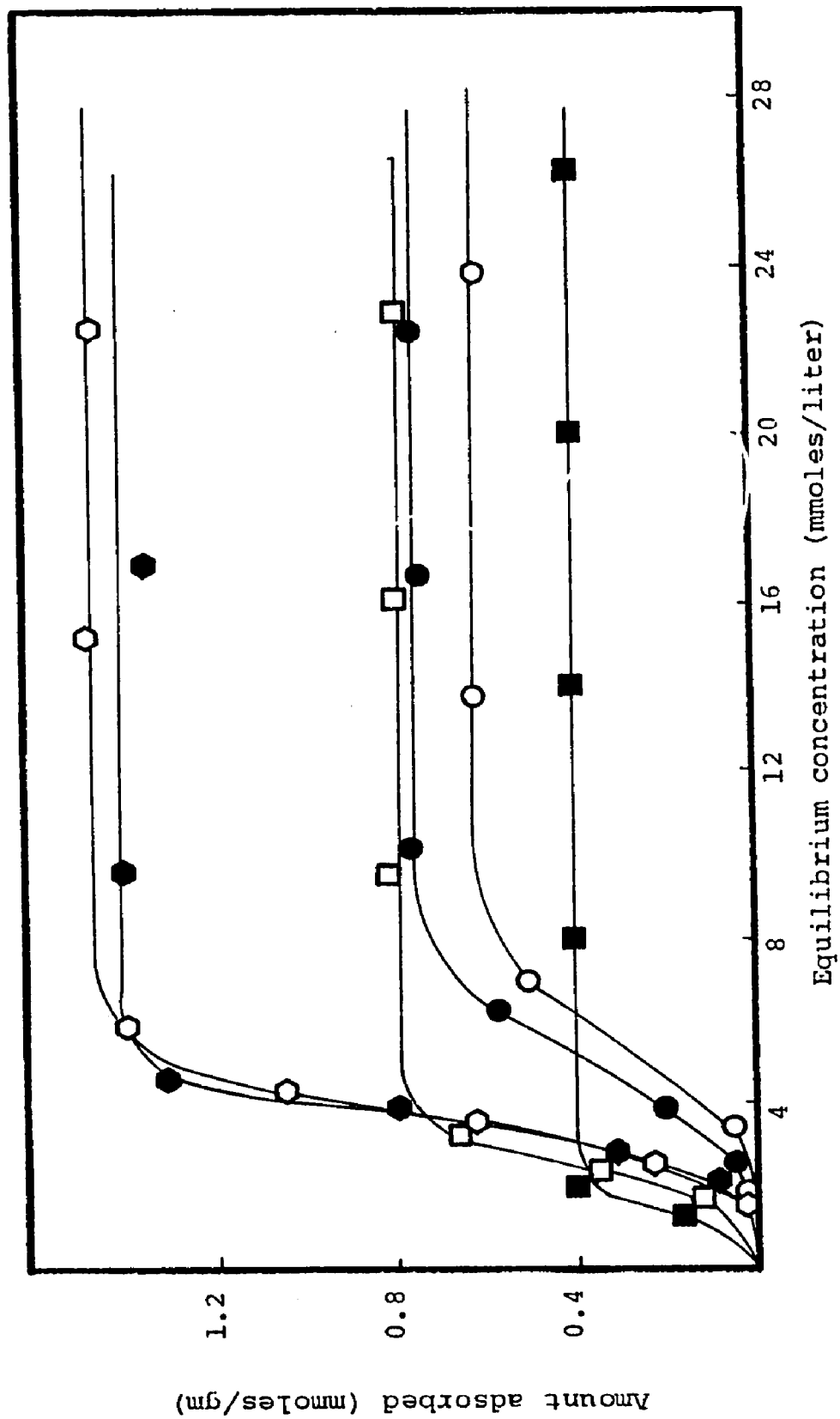

Figure 32. Effect of acetate concentration on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 4.5.
Key: Concentration of acetate

some sort of surface impurity, the experiments were repeated using the predissolved Victor HAP. They were also done using AM-HAP, for comparison. The results are presented in Table VIII. Again, it should be noted that the observed acetate concentration effect on the adsorption onto Victor HAP is missing when AM-HAP is used.

Table VIII

Effect of Acetate Concentration on the Adsorption of Dodecylamine Hydrochloride onto Hydroxyapatite at pH 4.5

	Amount adsorbed (millimoles/gm)		
Acetate Conc.	Victor HAP	Victor HAP (Predissol.)	AM-HAP
0	0.62	0.69	0.81
0.01 M	0.76		0.67
0.05 M	1.50	1.58	0.58
0.1 M	1.38		0.46
0.2 M	0.80		
0.5 M	0.40	0.38	0.35

Figure 33 demonstrates the effect of varying the pH from 4.5 to 7.0 on the adsorption of dodecylamine hydrochloride. It is evident that above pH 5.5, there is no change in the adsorption. Therefore, the indication is that the protonated form of the amine is the one adsorbing. Since at pH 6 the limiting value of 0.51 millimoles/gm was reached, it was decided that future experiments would be

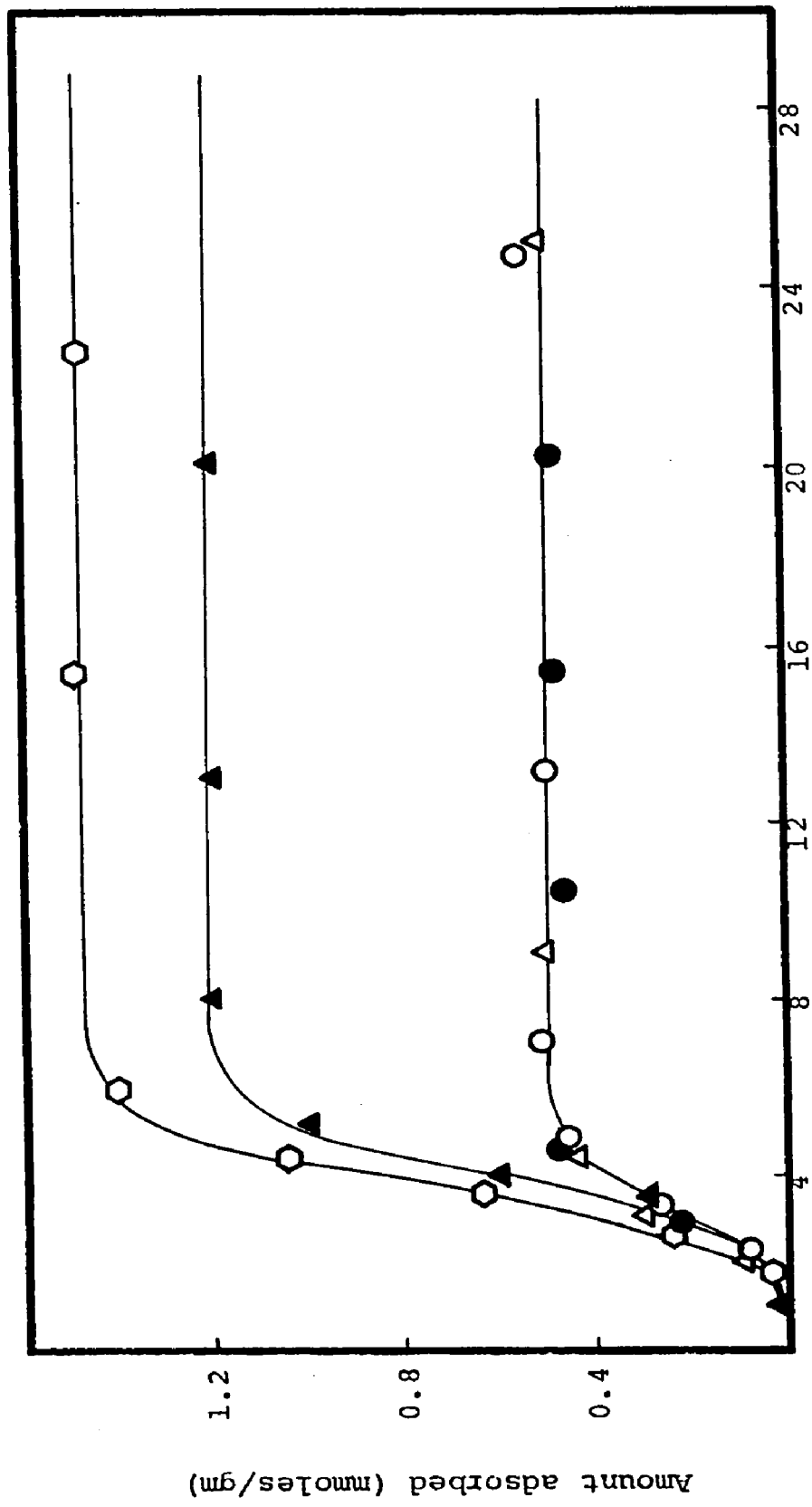

Figure 33. Effect of pH on the adsorption of dodecylamine hydrochloride onto hydroxyapatite.

Key:

○ pH 4.5 ▲ pH 5.0 ○ pH 5.5 ● pH 6.0 △ pH 7.0

done at this pH, to eliminate the other effects already mentioned.

Experiments were done to see if the slurry density had any effect at pH 6 and, as can be seen in Figure 34, there was almost no effect, in contrast to pH 4.5.

Further, the effects of added amounts of sodium chloride at pH 6 were studied (Figure 35). As can be seen, there is no change in the amount adsorbed, but there is displacement of the isotherm, due to the electrolyte effect of reducing the cmc. Thus, by doing the experiments at pH 6, it was more certain that any further effects observed on the adsorption under different conditions would be real and not a result of interfering influences.

The effects of adding 0.001 M calcium and phosphate ions on the adsorption of dodecylamine hydrochloride in the pH 4.5 buffer were investigated, and it was found that phosphate enhanced the adsorption (from 1.5 millimoles/gram to 1.68 millimoles/gram) and the calcium depressed it (from 1.5 millimoles/gram to 1.4 millimoles/gram). However, because the reasons for the various effects at this particular pH were not entirely understood, the same investigation was performed at pH 6. Only the effect of calcium ions is shown, because it was not possible to prepare all the solutions for an experiment with added phosphate ions (as dibasic sodium phosphate). Above concentrations of the amine of 2 mM, through interaction of the amine and phosphate ions, a precipitate resulted. From the dilute

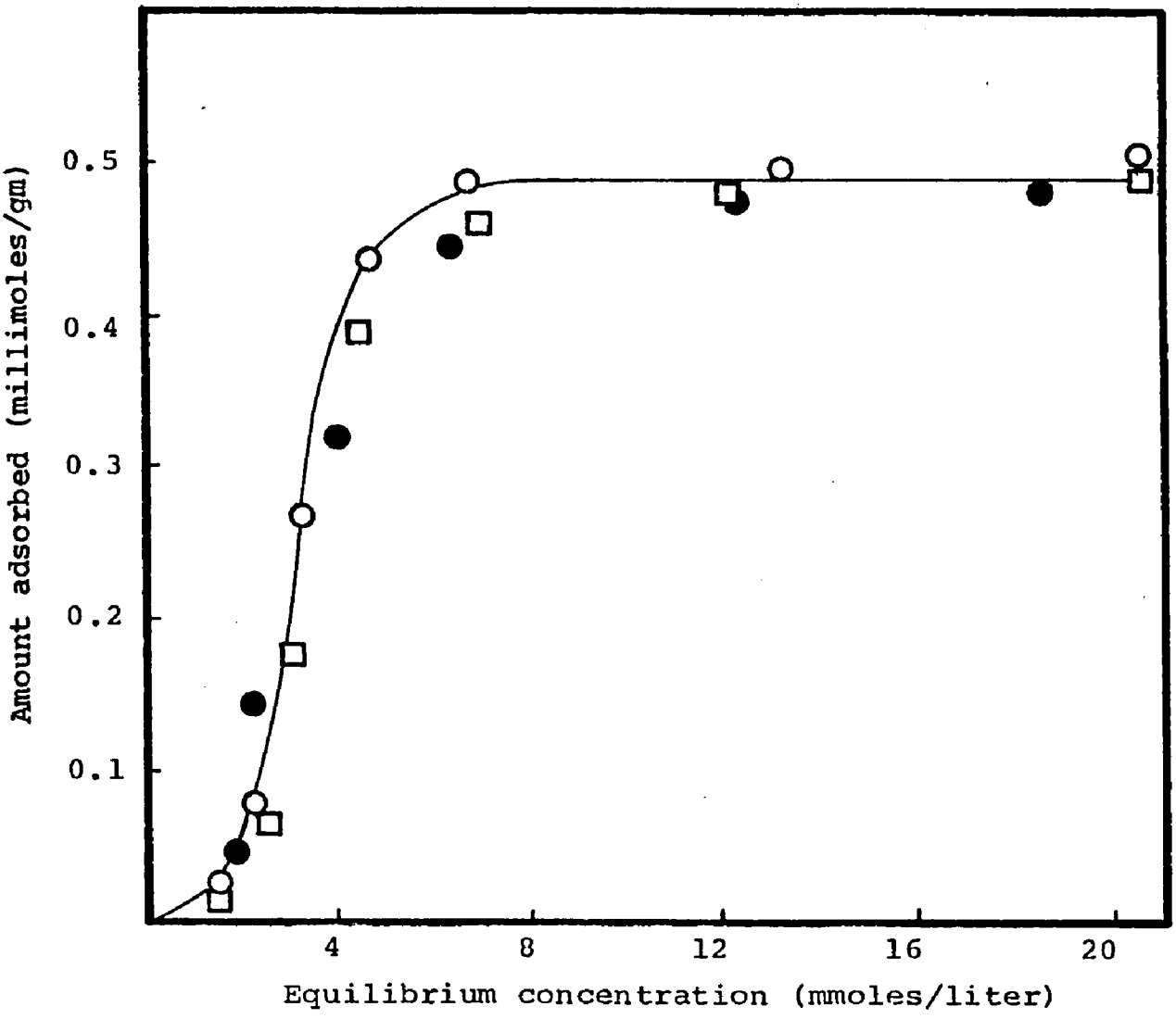

Figure 34. Effect of slurry density on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 6.0.
Key: Amount of hydroxyapatite used
○ 100 mg ● 250 mg □ 500 mg

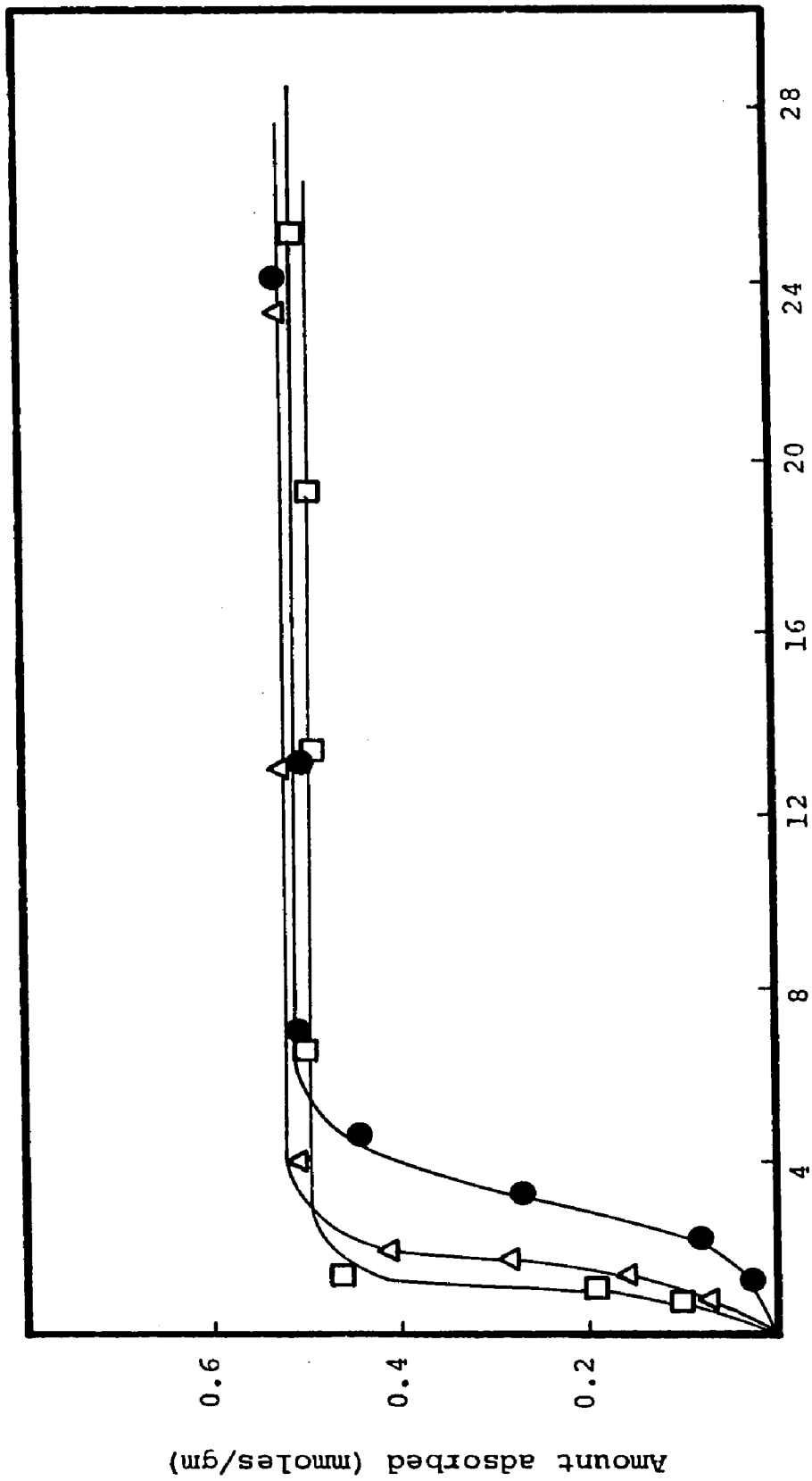

Figure 35. Effect of added electrolyte on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 6.
Key: Concentration of sodium chloride

solutions that could be made, however, the initial portions of the isotherms indicated that there was enhanced affinity in the adsorption with added 0.001 M phosphate present. This effect of added phosphate may be the result of two different mechanisms. Addition of excess phosphate to the solution results in an uptake of the ion by hydroxyapatite,[128] making the overall mineral surface more negative.[129] In this way, it would result in greater attraction between the positively charged amine head group and the more negative surface. Or, more likely, the nature of this effect is a result of the specific adsorption of the phosphate ions onto the surface at specific sites, resulting in a phosphate-rich surface. The fact that the amine adsorption is enhanced suggests that there are now more available binding sites, and that these adsorption sites are the phosphates. The value for the experimentally measured and theoretically calculated area for surface phosphorus ions in hydroxyapatite has been reported to be 32.4 $\mathring{A}^2$.[111] The fact that these are the adsorption sites for the amines further precludes the idea that the limiting adsorption value of 0.5 millimoles/gram represents a monolayer, since this required the amines to occupy only 20.5 $\mathring{A}^2$ on the surface.

Figure 36 demonstrates the effect of adding the common ion calcium (as calcium chloride) on the adsorption of dodecylamine hydrochloride. The experiment was done with 0.2 M sodium chloride also in the solution to swamp out

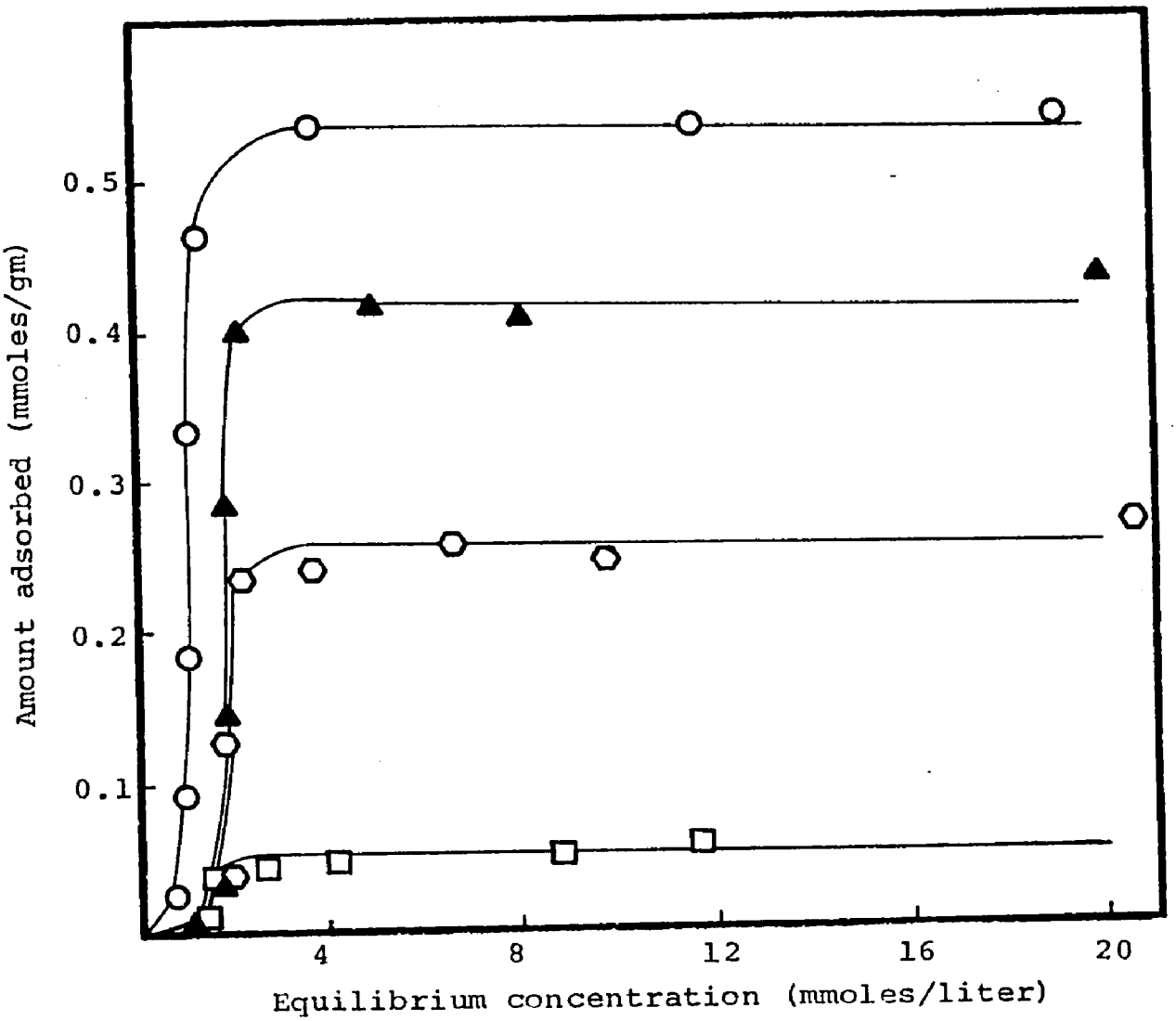

Figure 36. Effect of calcium concentration on the adsorption of dodecylamine hydrochloride onto hydroxyapatite at pH 6, with added 0.2 M sodium chloride as swamping electrolyte.

Key: Concentration of calcium

○ none ⬡ 0.02 M

▲ 0.01 M □ 0.04 M

any electrolyte effects. There is a small initial shift of the curve to higher equilibrium concentrations, indicating an inhibition of adsorption with the addition of 0.01 M calcium, but higher concentrations of calcium cause no further displacement of the isotherm. (Experiments were performed at low concentrations of the amine, and the initial portions of the curves, with added 0.01, 0.02 and 0.04 M calcium, were almost identical.) One can see, however, that there is a marked reduction in the total amount of dodecylamine hydrochloride adsorbed.

The fact that the plateaus are depressed in this manner by added calcium seems to negate simple competitive adsorption for the phosphate site. If competitive adsorption were occurring, at high enough concentrations of the surfactant the same plateau should be reached in each case, but, as can be seen, each isotherm levels off at a lower value, depending on the concentration of the calcium. One might argue here that the isotherms reach the limiting adsorption value when the cmc of the surfactant is reached ($\sim$2 mM), but since there is essentially no difference between the initial portions of the curves with added calcium above 0.01 M, they would all reach the plateau at the same level if the cmc were the determining factor. Figure 37 demonstrates the same effect, but in this case AM-HAP was the adsorbent. The effect of the calcium was not nearly as pronounced in this case, and it may be because of surface structural differences between the two

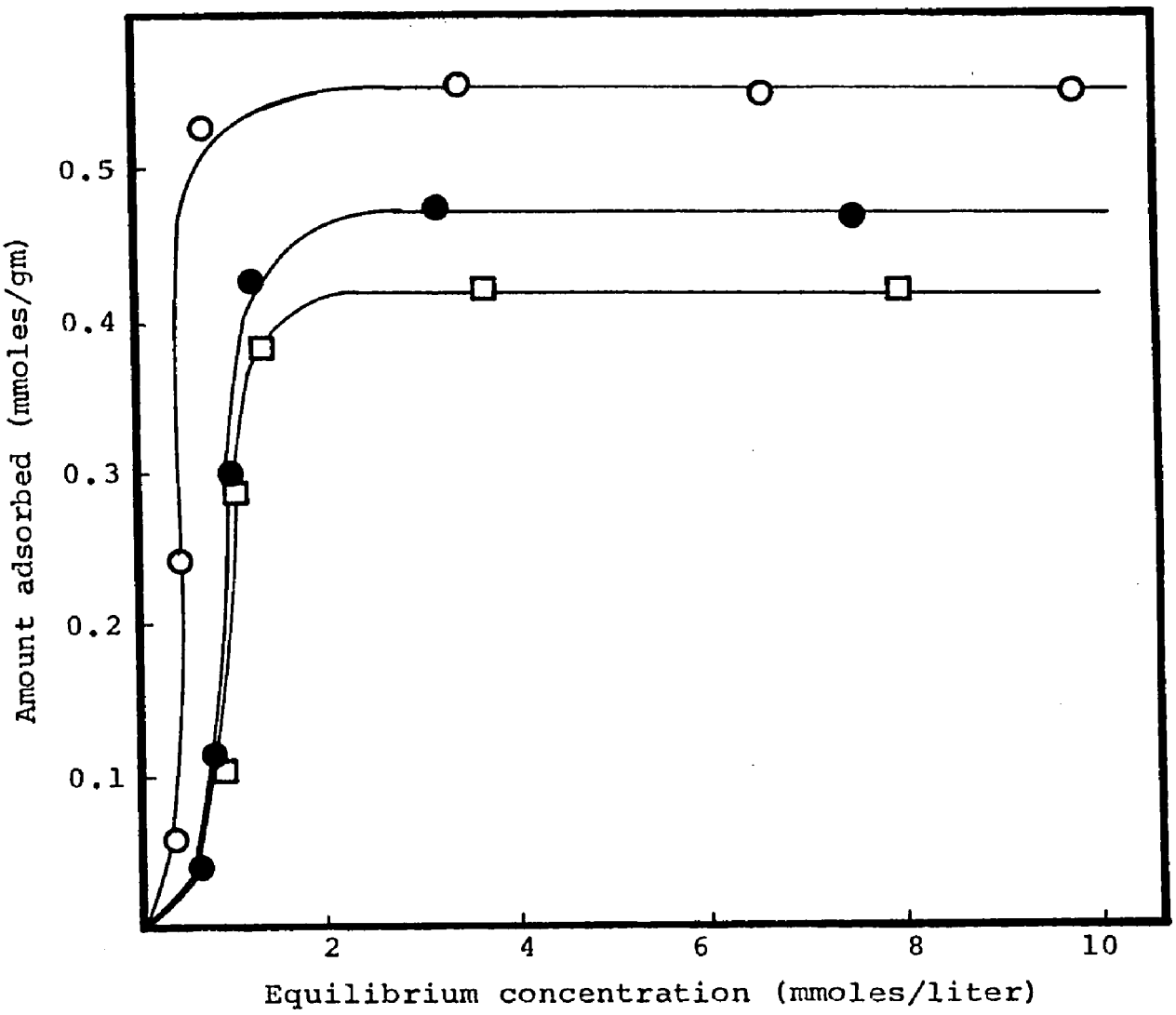

Figure 37. Effect of calcium concentration on the adsorption of dodecylamine hydrochloride onto AM-HAP at pH 6, with added 0.2 M sodium chloride.
Key: Concentration of calcium

○ none ● 0.02 M □ 0.04 M

apatites.

The lowering of the adsorption plateaus could possibly be due to a complex in solution between the amine and the calcium ions, which would result in decreased adsorption. This is presented as a possible explanation because an increased solubility of the amine was noted in solutions with added calcium ions, and this effect would reduce the adsorption of the amine molecule.

The observed effect of added calcium ions may also be due in part to the fact that the calcium confers a positive charge to the surface. Leach[128] and Somasundaran[129] found that added calcium ions produce a positive zeta potential on the surface of hydroxyapatite, and Somasundaran postulated that this effect is brought about by specific adsorption of calcium onto the apatite. This positively-charged surface would then tend to repel the positively-charged surfactant molecules.

The effect of added calcium ions on the adsorption was also determined in 0.05 M acetate buffer, pH 6.0 with no added electrolyte, and in 0.2 M sodium chloride solutions. Similar effects were observed.

The chain length effect is demonstrated in Figure 38. Octylamine hydrochloride was also studied, but even with concentrations of this amine as high as 0.1 M, no adsorption could be detected.

The isotherm for the decylamine hydrochloride is at higher equilibrium concentrations than that for the dodecyl-

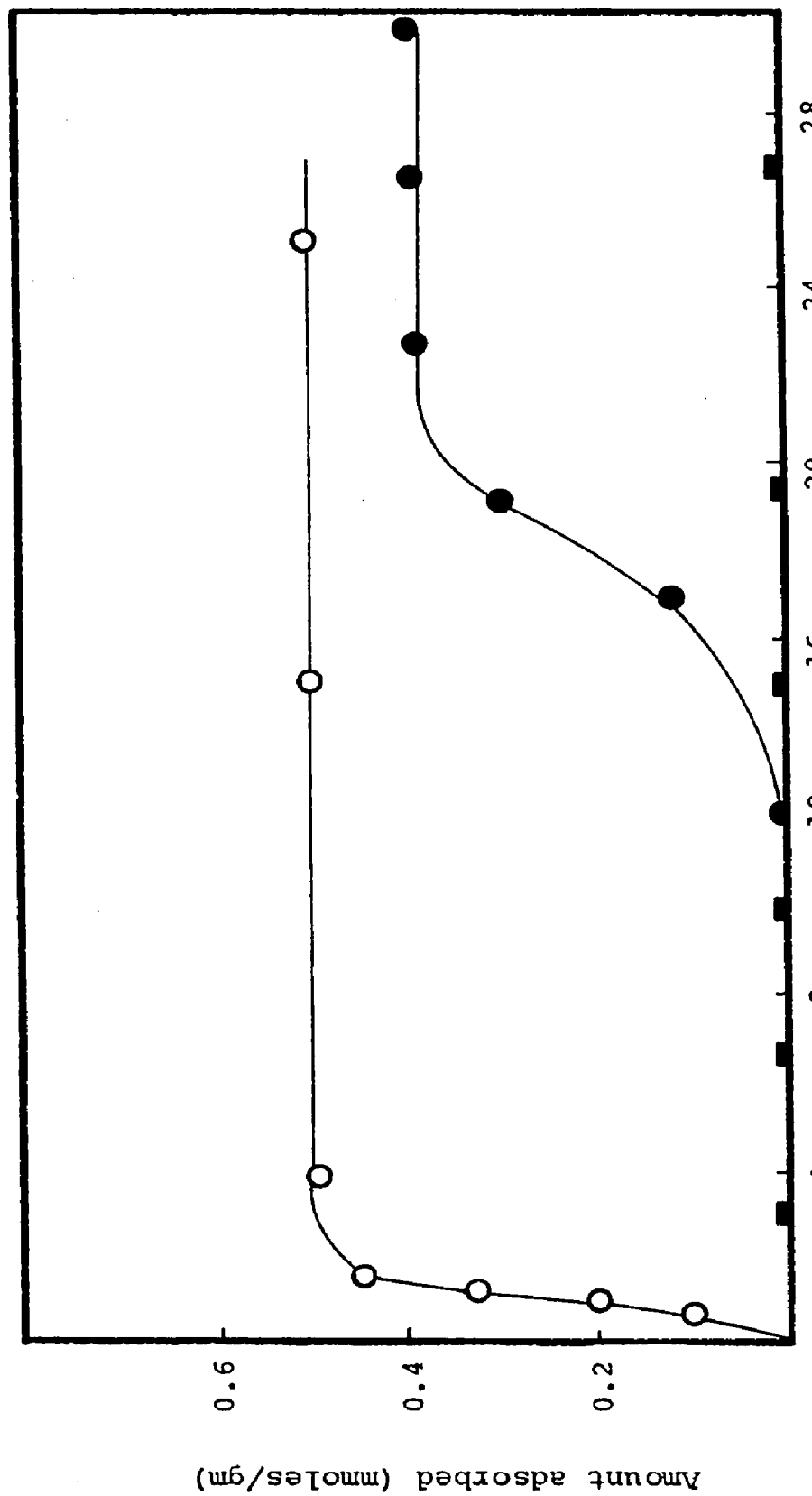

Figure 38. Effect of hydrocarbon chain length on the adsorption of n-alkylamines onto hydroxyapatite at pH 6, with added 0.2 M sodium chloride.

Key: ○ dodecylamine hydrochloride ■ octylamine hydrochloride
● decylamine hydrochloride

amine hydrochloride, and shows much less affinity for the hydroxyapatite. The limiting adsorption value is also less, indicating less coverage of the surface. These results may be expected for several reasons.

As was stated before, saturation adsorption is generally reached at a concentration of the surfactant which corresponds to its cmc. The cmc values of dodecylamine hydrochloride and decylamine hydrochloride in 0.2 M sodium chloride solutions are 2 mM[124] and 22 mM,[125] respectively. It is clear that these concentrations correspond almost exactly with those, at which the plateau value of the isotherms are reached.

Wakamatsu and Fuerstenau[117] obtained similar results when they studied the adsorption of a series of sodium alkylsulfonates at the alumina-water interface. They interpreted this effect in terms of their hemi-micelle theory. That is, region two of the isotherm, which is characterized by a marked change, or increase, in the slope, is a result of the onset of association of the hydrocarbon chains of the surfactant molecules at the surface. This association, or hemi-micelle formation, gives rise to a specific adsorption potential which causes the adsorption to increase markedly. The hemi-micelle concentration, that is the bulk concentration necessary to induce association in the interface, increases with decreasing chain length. Somasundaran et al.,[118] from determinations of the effect of chain length on the electrokinetic poten-

tial of silica in aqueous solutions of alkylammonium acetates, obtained evidence for hemi-micelle formation, and also concluded that an increase in the alkyl chain length results in a lowering of the hemi-micelle concentration.

The results are in qualitative agreement with those predicted by Traube's rule, which is based on the extent of surface activity of a homologous series of compounds. Because surface activity is related to adsorption at the interface, Traube's rule has been expressed in terms of the increase in strength of adsorption of ascending members of a homologous series. And, when other effects are not present, for a given solvent, the less soluble solutes are generally more strongly adsorbed than the more soluble. The more soluble a substance is, the more favorable are solute-solvent contacts, resulting in a decrease in the extent of adsorption. As the chain length decreases, the molecule becomes more soluble in the aqueous media, and there is less tendency for it to come to the surface. That is, the free energy of adsorption decreases.

From these isotherms, the importance of the length of the hydrocarbon chain in the adsorption mechanism is evident. The electrostatic interaction with the surface, which is responsible for the initial stage of the adsorption process, is apparently not very strong. The important factor, then, in promoting the adsorption process appears to be the lateral chain interactions between the molecules on the surface. As the chain length increases, these

interactions also become greater, leading to enhanced adsorption.

Adsorption of acids on hydroxyapatite

In order to gain further insight into the interactions involved in the adsorption onto hydroxyapatite, compounds with a different polar group, carboxylic acids, were investigated. These studies could be not only physically important, by providing further basic scientific information on the adsorption process, but also clinically interesting. Sodium ricinoleate has been found to be an effective agent in inhibiting plaque formation on the teeth, and basic studies with salts of fatty acids could provide information on the conditions which would give the optimum coverage on the surface.

To help attain this insight, a number of factors were investigated as to their roles in influencing the adsorption process. These were the chain length effect, the electrolyte effect, the common ion effect and the pH effect. The compounds used were sodium laurate, sodium decanoate and sodium octanoate.

Chain length effect

Since the results of the amine adsorption studies showed that the chain length had a marked effect on the

adsorption, it is of interest to investigate the extent of this influence on fatty acid adsorption. Isotherms were determined for the adsorption of the sodium salts of three different fatty acids, octanoic, decanoic and lauric, onto hydroxyapatite from pH 9 Tris buffer (0.05 M). The results are presented in Figure 39.

The nature of the isotherms is similar to that seen in the adsorption studies with the amine salts. That is, the curves are S-shaped, suggesting a cooperative mechanism for the adsorption involving lateral interactions of the hydrocarbon portion of the molecule.

The high level of the saturation adsorption, or plateau, (1.56 millimoles/gram for sodium laurate), is an indication of a multimolecular film on the surface. According to Tamamushi and Tamaki,[122] on polar adsorbents, in aqueous solution, when the first stage of adsorption of the electrostatic type is completed, the second stage of the adsorption due to Van der Waal's forces takes place, and consequently a multilayer is built up on the surface. Hansen, Fu and Bartell,[82] in studies of the adsorption of some organic compounds from aqueous solution, obtained results which led them to conclude that the adsorption was multilayer, with the adsorbed film containing water molecules as well as the organic compound.

Using the value of 70 M^2 per gram for the surface area of Victor hydroxyapatite, a complete monomolecular layer would require the adsorption of 0.54 millimoles per

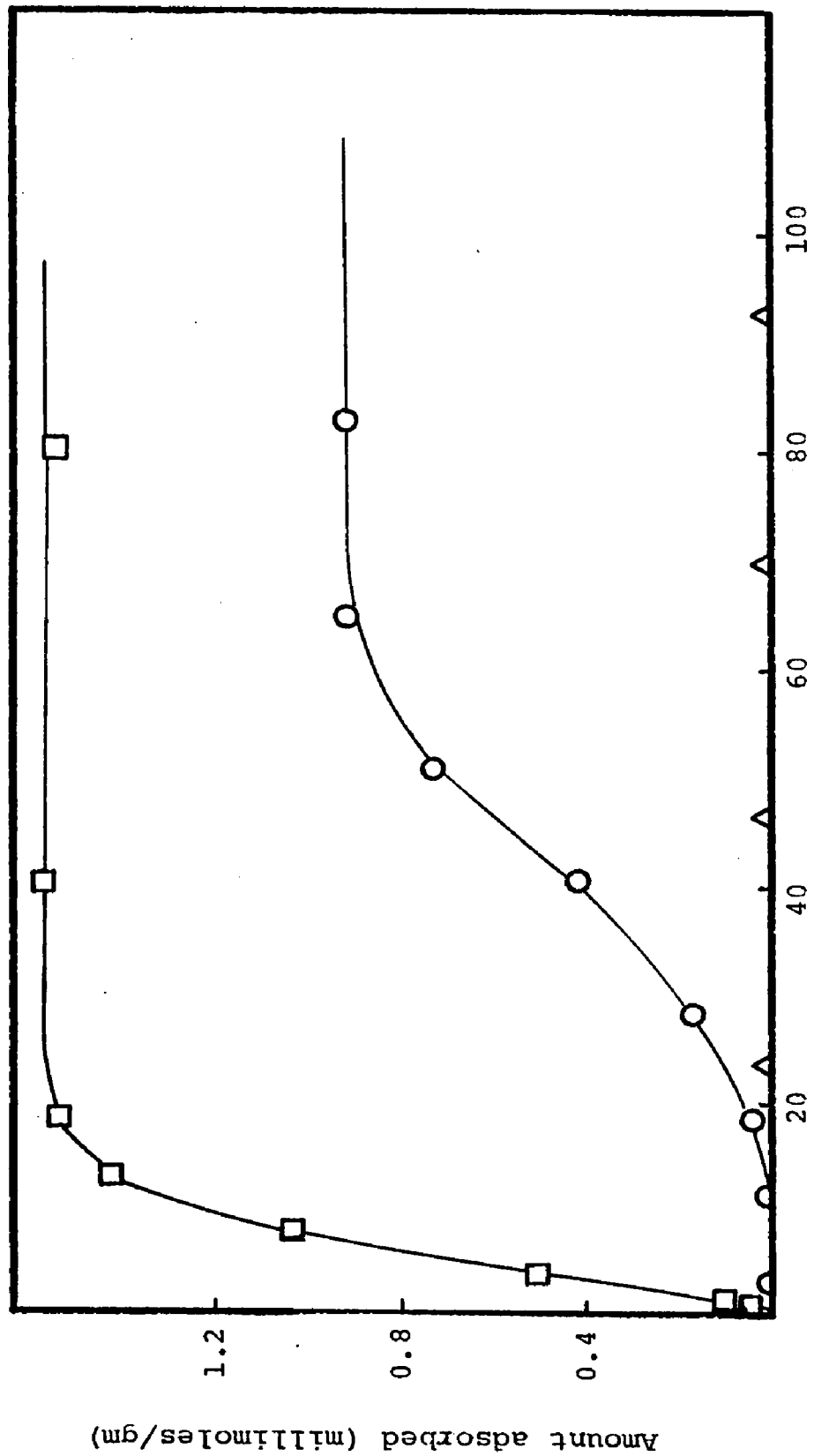

Figure 39. Effect of chain length on the adsorption of sodium salts of n-fatty acids on hydroxyapatite at pH 9.

Key: □ sodium laurate ○ sodium decanoate

△ sodium octanoate

gram. This assumes an area of 20.5 $\mathring{A}^2$ per molecule, which is the recorded value for condensed films of fatty acids. However, the actual monolayer would have a saturation adsorption value less than the 0.54 millimoles/gram for several reasons. The area of 20.5 $\mathring{A}^2$ is an unrealistic one in this case, because it is based on a film of close-packed molecules, which is not likely on the solid surface. The actual area occupied by each molecule would depend on the spacing of the adsorption sites, as well as the orientation of the molecules. Also, the value of 70 M^2/gram was determined by gas adsorption, and the larger fatty acid molecules may not have access to some areas of the surface. This would reduce the effective area available for adsorption. And finally, water itself is strongly adsorbed onto the surface and becomes included in the adsorbed acid film.[82] This, too, reduces the effective area available for the acid adsorption.

As a result of these factors, it is very difficult to determine exactly what value of maximum adsorption a monolayer would have. Consequently, it is not possible to resolve exactly how many adsorbed layers the maximum adsorption value represents. For sodium laurate, the experimental value for the maximum amount adsorbed from the Tris buffer, pH 9, is 1.56 millimoles/gram. This value could reasonably represent a multilayer structure of four to eight layers of adsorbed sodium laurate, with water molecules included in the film. Visual observation of the

solid after centrifugation indicated that the surface was hydrophobic; some of the powder was floating on the surface and did not appear to be wetted in the samples having the higher concentrations of the acid. This would indicate that an odd number of layers of the fatty acid was adsorbed onto the surface.

The high adsorption value may be due to the fact that there are aggregates, or micelles on the surface. Higashiyama and Takinaka,[130] in adsorption studies with aqueous solutions of sodium laurate, found that the chemical species adsorbed were laurate ions forming micelles. Since this occurred at a concentration above the cmc, they concluded that adsorption of the laurate ion micelles takes place at concentrations approaching or greater than the cmc.

The cmc may also explain why the isotherms for the acids do not exhibit as much steepness as did those for the amines. Since saturation adsorption is in each case reached at a concentration corresponding to the cmc, the lower the cmc is the steeper the curve would be. The reported cmc for dodecylamine hydrochloride in water is 13 mM, as opposed to 22 mM for sodium laurate.[126]

It is evident from Figure 39 that there is a pronounced chain length effect on the adsorption behavior. A decrease in the length of the hydrophobic chain results in a decrease in the maximum adsorption value, as well as an increase in the concentration at which the saturation adsorption is reached. The sodium octanoate did not exhibit

any measurable adsorption at this pH (pH 9), up to the maximum concentration tested, 200 millimolar. The cooperative adsorption effect, or the lateral interactions between the hydrocarbon chains, appears to be much weaker in the sodium decanoate than in the sodium laurate, since it has a much more gradual increase in its isotherm than does the sodium laurate. The cmc appears to be the important factor in determining where the saturation adsorption is reached in each case, as stated before, the two values coinciding almost exactly. As a result, the plateau levels would be determined as well. Since the sodium decanoate, being a shorter chain length molecule, has a much higher cmc than sodium laurate [in water, 96 mM as compared to 22 mM for sodium laurate[131]], it reaches its saturation adsorption at a higher equilibrium concentration. So, the chain length effect on the adsorption is actually a result of the chain length effect on the cmc.

The solubility, also, may be an important factor here, as it was in the case of the amine adsorption. It is generally true that as the solubility of a solute increases, the tendency for adsorption decreases. The shorter chain length compounds, being more soluble in the aqueous media, would be more favored to stay in solution rather than come to the surface.

Electrolyte effect

The adsorption isotherms of sodium decanoate onto hydroxyapatite in the presence of 0.05 and 0.1 M sodium chloride are shown in Figure 40. Tris buffer, pH 9, was used. The adsorption isotherm obtained for the solution without sodium chloride is also presented for comparison purposes. From this figure, it is clear that there is displacement of the adsorption isotherm to lower equilibrium concentrations of the sodium decanoate. The maximum amount of the adsorption remains constant for the two concentrations of sodium chloride used. The addition of 0.10 M sodium chloride produced no further shift in the isotherm than was caused by the 0.05 M sodium chloride. It is well known that the cmc of a long-chain electrolyte is lowered by the addition of a salt to the aqueous solution. Thus, since the cmc value coincides almost exactly with the concentration at which the adsorption attains saturation, the addition of sodium chloride shifts the curve to lower equilibrium concentrations.

Common ion effect

Even though the extent of dissolution of hydroxyapatite is low, due to the basic pH used in the experiments, there would still be some calcium and phosphate ions present in solution both during adsorption and at equilibrium. Therefore, the effect of the added common ion,

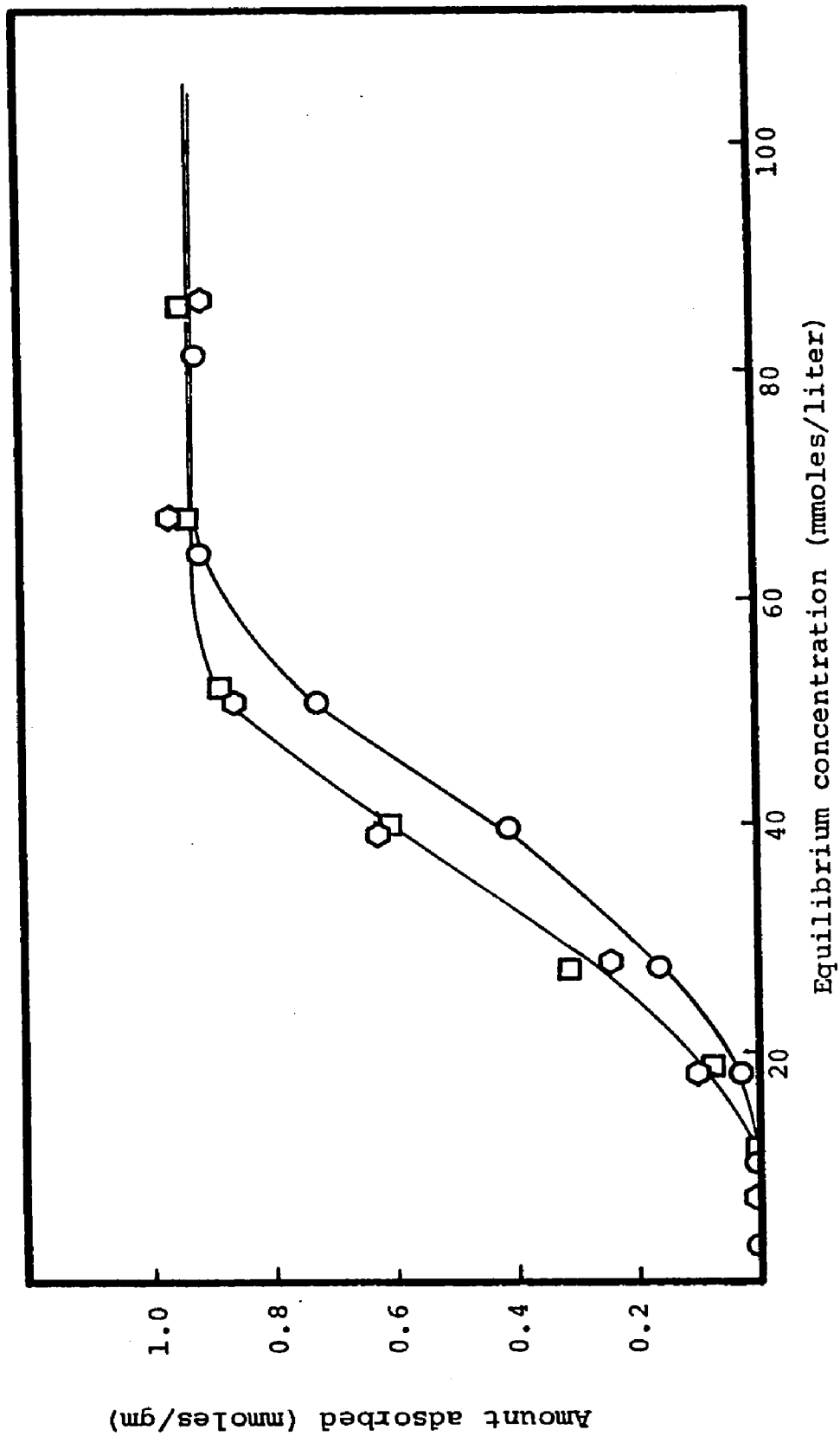

Figure 40. Effect of added electrolyte on the adsorption of sodium decanoate on hydroxyapatite at pH 9.

Key: Sodium chloride concentration

○ none ⬡ 0.05 M □ 0.10 M

phosphate, was investigated to obtain more insight into the acid-surface interaction. It was impossible to examine the effect of added calcium ions, due to the precipitation of the calcium salts of the fatty acids, even at concentrations as low as 0.001 M calcium.

The effects of added extraneous phosphate (as dibasic sodium phosphate) are presented in Figures 41 through 43. In each case sodium laurate was adsorbed on hydroxyapatite in Tris buffer, pH 9, 10 and 11, respectively, in the presence of varying amounts of added phosphate. It is clear that there is an inhibitory effect on the equilibrium adsorption levels of the sodium laurate in each case, with the addition of phosphate ions. Similar effects were observed by Magrill,[52] who found that the adsorption of sodium phytate onto hydroxyapatite was inhibited by the presence of phosphate ions in the solution. McGaughey and Stowell[54] reported that phosphate ions in saliva inhibited the adsorption of salivary proteins by hydroxyapatite. It was shown by Bernardi and Kawasaki[50] that polypeptides are adsorbed onto hydroxyapatite through their carboxyl groups, and postulated that the same groups are responsible for protein interaction with hydroxyapatite. They found that the interaction of the polypeptides with a hydroxyapatite column was reduced when the eluting buffer contained phosphate ions. It was suggested that this interaction occurred between the carboxyl groups of the polypeptides and the calcium sites of the hydroxyapatite sur-

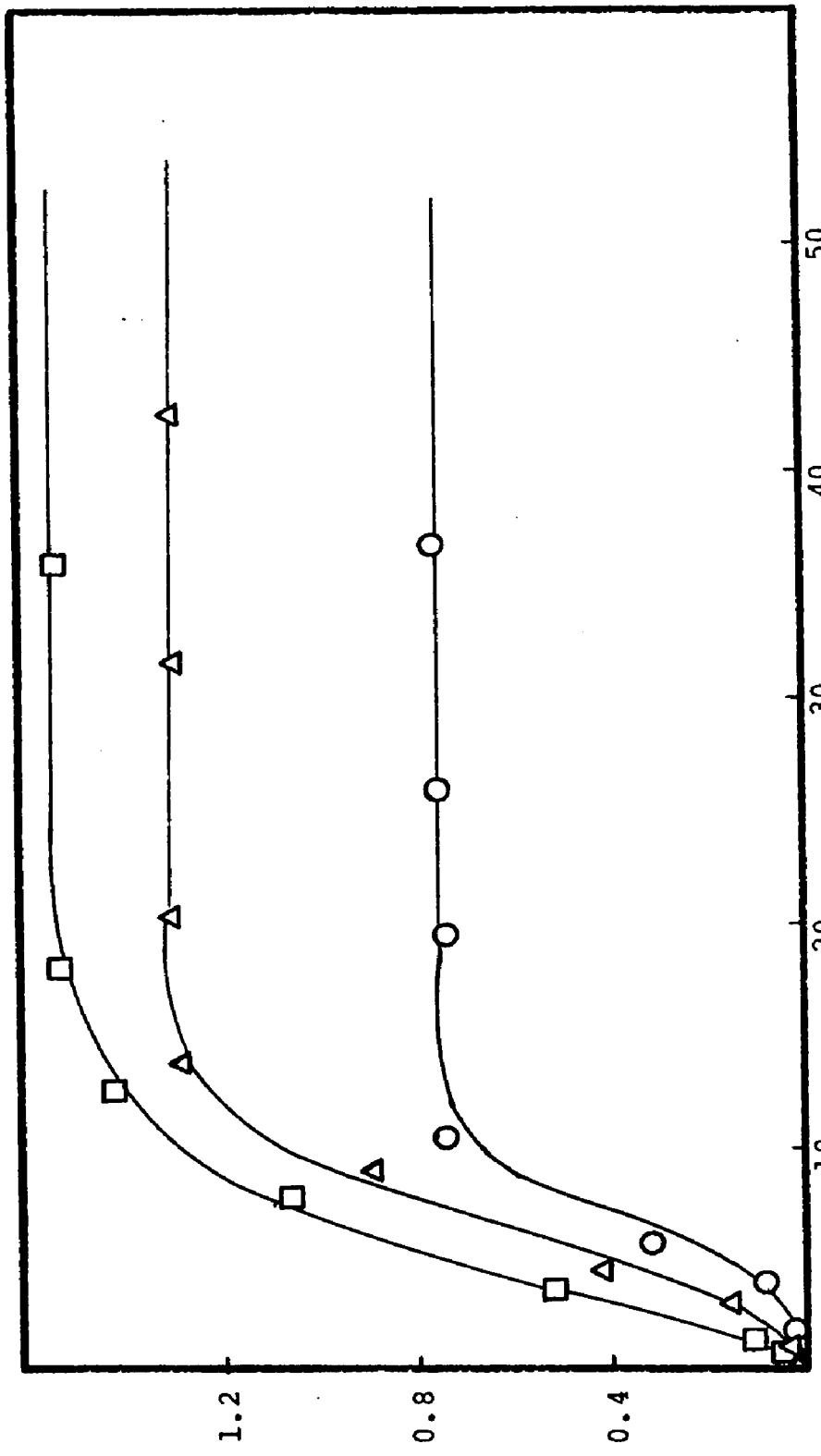

Figure 41. Effect of phosphate concentration on adsorption of sodium laurate on hydroxyapatite at pH 9.

Key: Phosphate concentration

□ none △ 0.01 M ○ 0.10 M

Figure 42. Effect of phosphate concentration on the adsorption of sodium laurate on hydroxyapatite at pH 10.

Key: Phosphate concentration

□ none △ 0.01 M

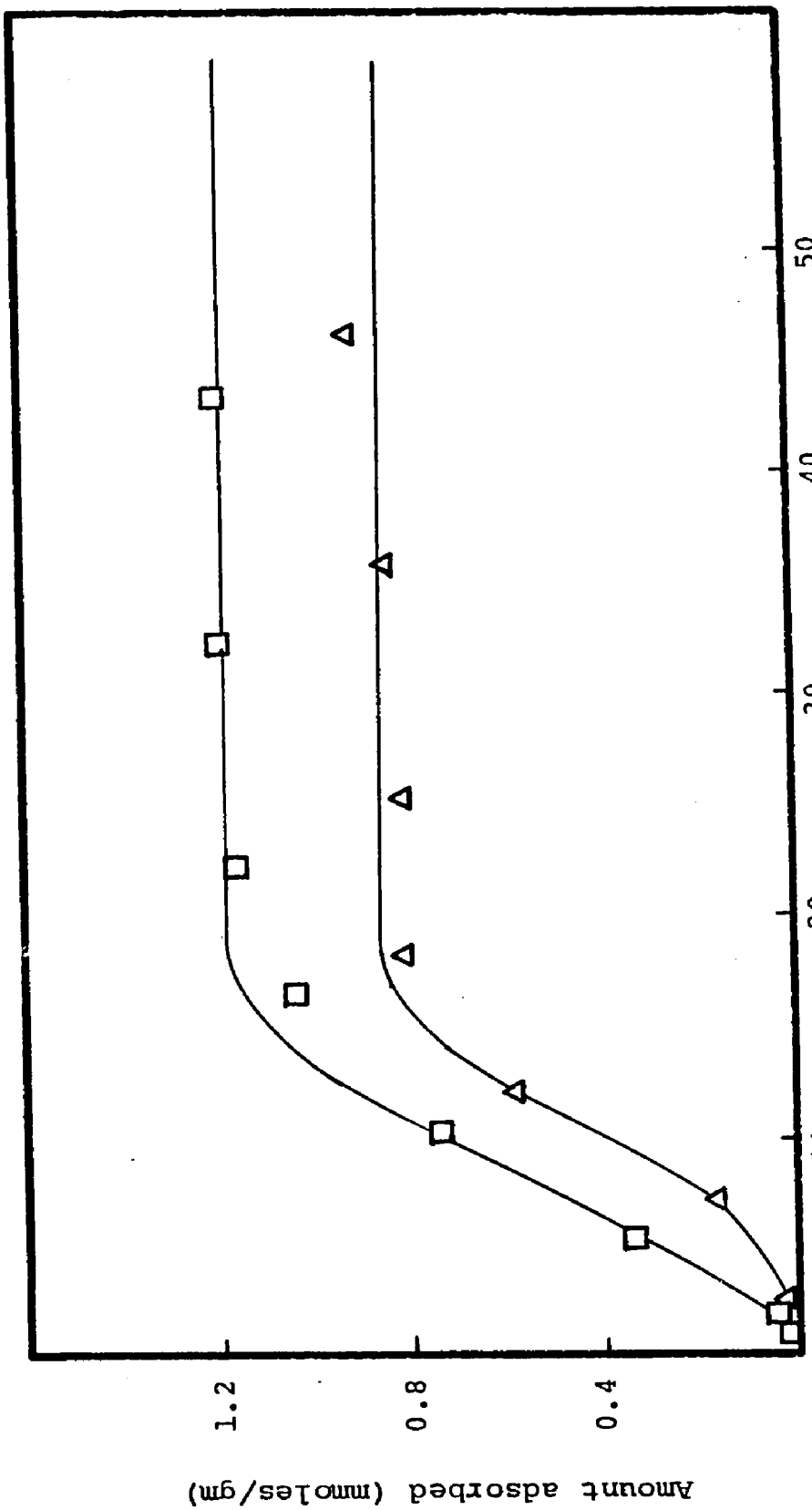

Figure 43. Effect of phosphate concentration on the adsorption of sodium laurate on hydroxyapatite at pH 11.

Key: Phosphate concentration □ none △ 0.01 M

face.

From the experimental data, it seems clear that the general effect associated with phosphate inhibition of sodium laurate adsorption could arise from the physical situation in which sodium laurate and phosphate are competing for the same surface binding sites. These sites are thought to be the calcium atoms on the surface of the hydroxyapatite. The reason that the curves reach a plateau, instead of increasing, as should be the case in true competitive adsorption, may be due to the fact that when the cmc is reached, there is no further increase seen in the adsorption isotherms.

The inhibitory effect on the adsorption may also be due in part to the fact that addition of phosphate ions to solutions in contact with hydroxyapatite makes the entire surface more negative. Somasundaran[129] found that this was true over the entire pH range, not just when the mineral was oppositely charged. This would mean that the negatively charged acid would be less attracted to the surface.

pH effect

Figures 44, 45 and 46 illustrate the effect of varying the pH on the adsorption of sodium laurate, sodium decanoate and sodium octanoate, respectively, onto hydroxyapatite in Tris buffer. It is apparent that the pH has a marked influence on the adsorption. In the case of sodium

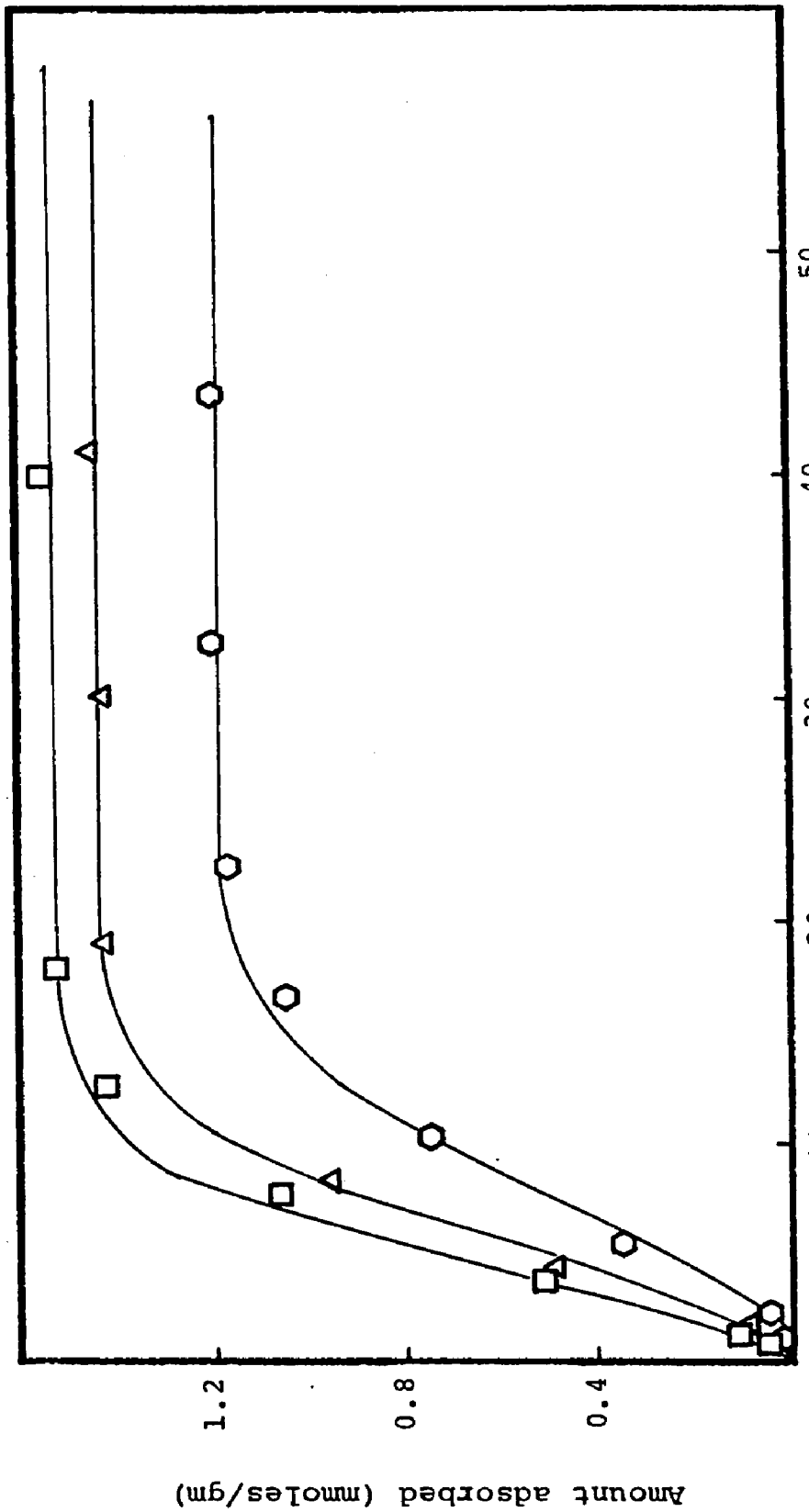

Figure 44. Effect of pH on the adsorption of sodium laurate on hydroxyapatite.

Key: □ pH 9 △ pH 10 ⬡ pH 11

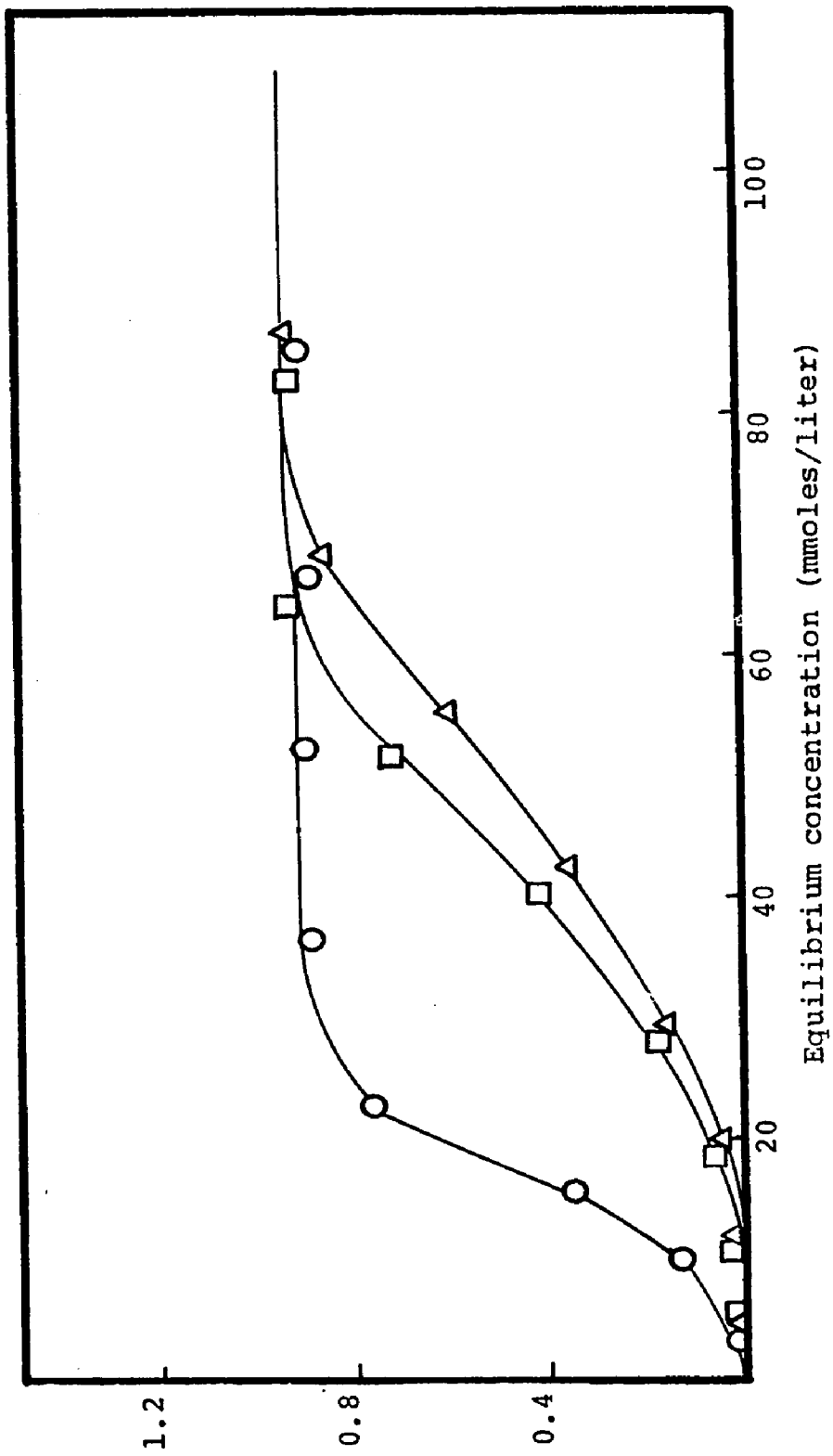

Figure 45. Effect of pH on the adsorption of sodium decanoate on hydroxyapatite.

Key: ○ pH 8 □ pH 9 △ pH 10

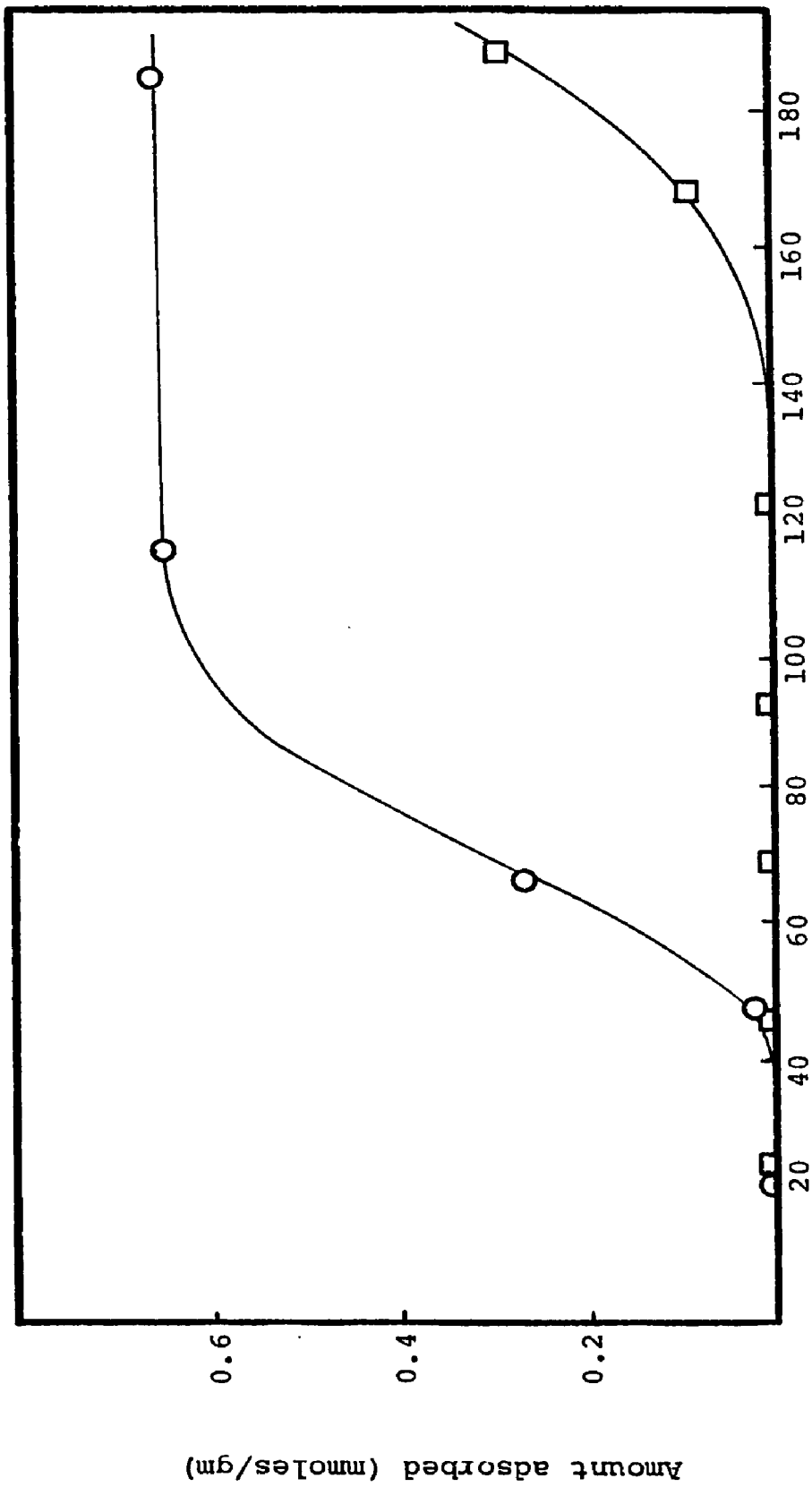

Figure 46. Effect of pH on the adsorption of sodium octanoate on hydroxyapatite.

Key: ○ pH 7.2 □ pH 8.0

laurate, the adsorption was reduced with an increase in the pH. Also, there was an increase in the equilibrium concentration at which saturation adsorption was reached with an increase in the pH. The isotherms of sodium decanoate show no change in the maximum adsorption with a change in the pH, but there is a decided shift, or displacement, of the curves to lower equilibrium concentrations with a decrease in the pH. At pH 8, sodium octanoate is just beginning to show adsorption at an equilibrium concentration of 150 mM, but if the pH is decreased to 7.2, saturation adsorption is reached at a concentration of 100 mM. These kinds of results would not be expected, at first thought, since the ionized, negatively charged, form of the acid is the species adsorbing and at pH's as high as the ones used, the amount of the ionized form should be almost constant, relative to the un-ionized species. The adsorption should therefore not be expected to vary with the pH. The pH effect, then, is evidently due to factors other than its effect on the proportion of ionized to neutral acid. Similar results were obtained by McGaughey and Stowell[54] who found that a decrease in the pH resulted in increased protein adsorption on hydroxyapatite.

One possible explanation for the displacement of the curves to lower equilibrium concentrations with a decrease in the pH could be that the buffer contents are acting to decrease the cmc of the solute as did the sodium chloride. Alcohols, amines and similar compounds containing a polar

group have been shown to produce a considerable lowering of the cmc.[125] However, the displacement of the isotherm for sodium decanoate with a pH change from 9 to 8 in 0.05 M Tris buffer was greater than that produced when 0.10 M sodium chloride was added. So, it is unlikely that this is the complete explanation. A more likely explanation might be that a decrease in the pH of the buffer solution causes some kind of alteration of the adsorption sites on the surface. This was the reasoning proposed by Tamamushi and Tamaki,[122] since they found that there is a pH dependence in the adsorption of both cationic and anionic surfactants on certain polar adsorbents (alumina, silica), but not on others (barium sulfate, calcium fluoride). As was stated earlier, there was no detectable effect of pH on the adsorption of dodecylamine hydrochloride on hydroxyapatite. The fact that such an effect exists in the case of the fatty acids would indicate that the particular site of the adsorption of the acids only is affected. A decrease in the pH of a solution in contact with a hydroxyapatite surface causes a shift in the equilibrium of the following reactions of the surface calcium atoms to the left[129]:

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$$

$$CaOH^+ + OH^- \rightleftharpoons Ca(OH)_2 .$$

This would result in more calcium atoms being available for interaction with the acid, thus enhancing the adsorp-

tion. In addition, as the pH increases, the surface of hydroxyapatite becomes more negative due to the hydrolysis of the phosphate ions on the surface.[129] As a result, the negatively charged acid would have less tendency to come to the surface.

Somasundaran, Healy and Fuerstenau[132] observed that the transition between region one and region two in the adsorption isotherm for dodecylsulfonate on alumina occurred at a lower concentration as the pH was decreased. They attributed these results to the fact that the hemi-micelle concentration decreased with a decrease in the pH, due to an increase in the positive surface potential. This would ensure that the hydrocarbon chain interactions would occur at a lower solution concentration, causing a shift in the isotherm to the left. A similar explanation was proposed by Dick et al.,[123] who obtained analogous results with alkyl benzene sulfonate surfactants. Further, Somasundaran and Fuerstenau[119] concluded that the greater charge on the solid particle (alumina) at lower pH will need a greater adsorption density of sulfonate before the zeta potential is brought to zero. (This was said to occur at the point where the slope of the adsorption isotherm decreases, and the curve begins to level off.) There would therefore be a different adsorption density at the transition between regions two and three at different pH's. This adsorption density would be higher as the pH was decreased.

SUMMARY AND CONCLUSIONS

Comprehensive, systematic studies have been carried out on the adsorption of several polar organic compounds onto inorganic surfaces, both in aqueous and non-aqueous solvents.

The effect of the type of the polar head group on the adsorbing molecule was investigated to elucidate the nature of the polar head group-surface site interactions, and their influence on the strength and extent of adsorption. Three different compounds were studied (an acid, an amine and an alcohol), from both hexane and acetone, onto hydroxyapatite and calcium fluoride. It was seen that the type of polar head group had a significant effect on the adsorption on hydroxyapatite, but not on calcium fluoride, where all three compounds reached the same limiting adsorption value. On the basis of the obtained results, it was possible to distinguish three types of adsorption sites on hydroxyapatite, one of which was believed to be the same as the single, effective site on calcium fluoride.

The addition of acetone to the hexane solvent was found to have a very strong inhibitory effect on the adsorption of all three compounds, on both surfaces. The results were interpreted on the basis of the formation of hydrogen bonds between the acetone and the solutes in the bulk, and the competitive adsorption of the acetone on the same surface binding site. An analysis of the mixed-sol-

vent, calcium fluoride data was performed that enabled the quantitative evaluation of both of the above factors.

Investigations of the effect of the length of the hydrocarbon chain on the adsorption were carried out by using homologous series of acids, amines and alcohols. The results indicated that the greatest general effect is found in the case of the alcohols, with the limiting adsorption decreasing as the chain length is increased. The homologous series of fatty acids exhibited the least chain length dependence in the adsorption behavior. The experimental results were interpreted in terms of the Bladon, Higuchi and Molokhia theoretical model, which explains such effects on the basis of configurational, or entropic, considerations.

Adsorption studies were also carried out in aqueous systems, with n-alkylamines and n-fatty acids being adsorbed onto hydroxyapatite. This portion of the work represented a general survey of the relationship and importance of the various factors able to influence the adsorption process. These included the effect of added electrolyte, pH, common ions and the chain length.

The methodology developed in this work for the investigation of the adsorption could be a valuable tool for examining mechanistic factors in the adsorption process. The use of a combination of several different polar organic compounds in competing and non-competing solvents provides a technique for defining and distinguishing the adsorption

sites on a heterogeneous surface. By carrying out such studies on different surfaces and comparing the adsorption behavior on each, one may arrive at conclusions about the similarity (or dissimilarity) of binding sites on the different surfaces.

A correlation has been established with the theoretical model, and many of the experimental results may be interpreted in terms of the theoretical predictions. The use of the Bladon model has provided a means for achieving greater insight into the mechanistic aspects of the adsorption process. It has provided a framework with which it has been possible to qualitatively explain the effect of a number of different factors on the adsorption, and may be used to predict certain trends in the adsorption of different compounds, in different solvents.

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