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UMI®
ADSORPTION STUDIES
ON CLAYS

by

Karl C. ten Brink, B. Sc. in Chem, M. A.

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of
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The Rice Institute
1940
INTRODUCTION
Introduction

The adsorptive process has been studied widely in colloidal chemistry, and its application has been very extensive even though it is not fully understood in many cases. It now seems to be generally accepted that adsorption may be due to any one or a combination of several different mechanisms. The process of adsorption evolves heat and can be classified on this basis as being similar to chemical reaction involving chemical forces or as being similar to condensation involving van der Waals forces. The measurement of this heat may be done directly or by the use of "isosteres"—curves analogous to pressure temperature equilibrium curves for vapors and liquids—and application of the familiar Clausius-Clapeyron equation.

Other general methods of studying adsorption are the isotherms and isobars. The isotherms have found wide application because of the ease of applying this method to adsorption, both from vapors and from solutions. Curves of this type have led to many interesting discoveries in the adsorption studies, and it is this type of curve that will be considered in the present work.

Most of the work that has been done on adsorption from a theoretical point of view has been done on synthetically prepared materials and their adsorption of water vapor. Also, because of their wide application as commercial adsorbants, charcoal, silica, and alumina have been used in most extensive adsorption studies. The natural clays, however,
have been widely used in recent years as adsorbants for the
decolorization of oils of all types. For the most part this
work has been primarily concerned with the testing and evalua-
tion of natural clays for the decolorization of oils and re-
moval of gum forming materials from lubricating oils. Chemi-
cal treatment of clays for the improvement of this property
is found widely in the patent literature.

Very recently clays have found further use in the
petroleum refining industry as catalysts in the catalytic
cracking process for the preparation of high test gasolines.
This catalytic activity of clays is also closely allied with
their adsorptive qualities. Due to these facts, it is evi-
dent that a study of the adsorptive properties of clays of
different types might be of help in the preparation of more
efficient materials for both decolorization and catalytic
cracking.

As has been pointed out, the process of adsorption
may be divided into two classes. In the process of chemical
adsorption, the binding forces between the molecules of the
adsorbant and the adsorbate are comparable to the forces
within the molecules and hence the process is in general ir-
reversible. On the other hand, in the case of physical or
van der Waal adsorption, the forces are comparable to the
forces between molecules in a liquid or homopolar solid.
This process is reversible. Calculations indicate that the
van der Waal forces are such that surface condensation does
not take place to an appreciable extent except at values
near saturation vapor pressure. However, appreciable adsorption of materials not likely to form surface compounds has been found even at very low percentages of saturation pressure and another explanation has been forthcoming. It is well known that the vapor pressure above a liquid in a capillary is less than the normal vapor pressure above a plane liquid surface. The quantitative statement of this fact is the Kelvin equation:

\[ \log_\varepsilon \frac{p'}{p} = \frac{2\gamma V}{RTr} \]

where \( p \) and \( p' \) are the normal and capillary vapor pressures, \( \gamma \) is the surface tension, \( V \) is the volume of liquid, \( r \) is the radius of the capillary. If one assumes that the surface of the adsorbant consists of many very fine capillaries, it is clear that the "saturation vapor pressure" may take on a series of values depending on those capillary sizes. This would explain, then, the van der Waal adsorption to the very low pressures. This explanation is not suitable, however, as a general explanation of physical adsorption because calculations from the above equation reveal that the postulated pores must often be of molecular sizes, in many cases less than that of the adsorbed molecules. Also, simple relationships of this type cannot be expected to hold for calculations down as low as atomic dimensions. In any event, the explanation may still be useful in a qualitative sense. Other factors such as the specific nature of the adsorbant with relation to the adsorbate must also be taken into account with the extreme case being that of chemical adsorption. The adsorption of hydrocarbon vapors
by clay seems to be a reversible process by most of the experimental evidence and might be termed physical adsorption, but the action of clays as cracking catalysts might indicate that the process involves the more intense molecular forces.

It is a general practice to express adsorption as the weight of material adsorbed, \( I \), per unit weight of adsorbing material, \( \kappa \), and the adsorption isotherms for vapors may be written \( \frac{x}{m} = f(p) \). Quantitative relationships for the function \( f(p) \) have been formulated such as the Freundlich equation \( \frac{x}{m} = \kappa \rho^n \) where \( \kappa \) and \( n \) are empirical constants. On the assumption of monomolecular surface layers, Langmuir (23) derived the expression \( \frac{x}{m} = \frac{a b \rho}{1 + a \rho} \). The constants are again empirical and neither equation can account for many of the more complicated adsorption isotherms which show the effect of varying capillary sizes and various types of "active centers".

The formation of the optimum size pores or the creation of the correct active centers seems to be the problem involved in the activation of clays for decolorization and catalysis. The general treatment of clays is a process of acid boiling in which alumina, iron, and most of the bases are leached out. The explanation of the activation by this treatment is that by leaching out \( \text{Al}_2\text{O}_3 \) and iron, pores are made in the clay structure. Also, removal of the bases and their replacement by hydrogen gives \(-\text{OH}\) groups on adjacent \( \text{Si} \) atoms which on splitting out water give strains in the silica structure, thus creating active centers.

Much work appears in the patent literature on the
activation of clays as adsorbents. By far the most widely used and seemingly most effective means of activation has been the process of acid boiling. There are several patents which consist of the simple boiling of clays in HCl or H₂SO₄ of varying concentrations and for various lengths of time, (3) (4) (5) (7) (17) (18) (23) (30). These patents indicate that the optimum concentration and length of treatment is largely dependent on the type of clay and the nature of the adsorption work for which the clay is to be used. In general, however, acid concentrations of 5 to 20% and treating times of three to eight hours are used. Tietig (32) used a more vigorous acid treatment. His method involves the burning of H₂ and Cl₂ in the presence of water vapor over the clay.

Nutting (27) (28) points out that many clays are partially leached in nature by the action of naturally occurring acids. When an attempt is made to activate these clays by acid boiling, an excess leaching takes place which seems to destroy the porosity of the clay or make pores so large that they are not very active in adsorption. This is also recognized by Eckart (10). The previous addition of strongly adsorbed cations such as Al³⁺⁺, Fe³⁺⁺, or Mg⁺⁺ seems to plug the naturally formed pores and slows down leaching at these spots during acid boiling, giving a resultant adsorbant which has been uniformly etched and which is greatly improved. This process has also been revealed in the patent literature (35).

It has been pointed out in one work (3) that the adsorption properties of clays is dependent on (A) the amount of silicates capable of being converted by activation to hy-
drated silica in the gel form, and (2) the hydrated silica content of the natural clay. It is further stated that almost every case of activation of clays is the same because it takes advantage of these facts. Examples of activation by means other than acid boiling seem to bear this out.

Felizat (13) activates clay for adsorption work by treating it with an alkali metal silicate and then adding enough acid to neutralize the silicate, forming a clay with silica closely associated with it. A modification of this procedure in which the clay and silicate mixture is boiled during the addition of acid has also been revealed (32). Other methods of clay activation seem to be merely the purification of naturally active clays by various methods. Endell and Ost (11) activate clay by adding CO₂ to a slurry and then electrodialysing to remove the electrolytes adsorbed. Simple electrodialysis or electrofiltration has also been used (39).

From the scant work reported in the literature on the activation of clays by dehydration, it appears that this procedure is sometimes effective and sometimes not, depending on the clay. Alexanian (1), Carlsohn (8), and Kauffman (19) claim clay activation by dehydration, and Zublin (38) claims to further activate acid treated clay by treatment with superheated steam in order to drive off all water without removing the water of hydration. On the other hand, Eckart reports that there is no relation between decolorizing action of a clay and its loss of water on heating.

**Summary of Objectives**

The object of the present work has been to study
the adsorption of hydrocarbon vapors on various types of clays, and to learn from this adsorption study the relative importance of various factors, both chemical and physical, which determine the adsorptive phenomena.

The initial work was designed to learn the relative magnitude and flexibility of adsorption due to the following factors:

1. The atomic structure of the mineral grain.
2. The degree of dispersion of the clay grains, and the relative importance of the external surfaces.
3. The relative importance of the spacing of secondary aggregates, i.e., spaces between the clay grains.
4. The effect of exchangeable ions within the clay grains.
5. The effect of intra particle spaces, or channels of near molecular sizes in the primary grain structure.
EXPERIMENTAL PART
Experimental Procedure

Adsorption measurements have been made in many different ways, and the inherent errors and limitations of the several methods have been discussed by Mc Bain (24). Mc Bain's improved method of adsorption study is conveniently applied to isotherm work, but in order to gain accuracy in measurements, the quartz fibers must be made very delicate and hence the size of samples must be very small. Chambers and King (9) realizing the difficulties of using small samples and desiring greater accuracy have designed a new adsorption balance in which the quartz spring is substituted by a float (similar to a hydrometer) suspended in mercury. With this equipment, the accuracy of the Mc Bain balance is tripled using samples as large as six grams.

In the present work it was desired that samples of four to six grams be used so that the amount of adsorption would be measurable. However, accuracy as great as 1 part in 20,000 was not considered necessary so that the King method was not used. The apparatus used is shown diagrammatically in figure (1). It is similar in principle to the Mc Bain-Tanner balance (24). The balance part was made from a Westphal balance. The zero point was obtained by passing a current through the solenoid which acts on the small permanent magnet. The electromagnet is calibrated against a standard weight before and after each run in order to determine the voltage per gram. Since fairly high voltages are used in some cases, the electromagnet is tapped for a few turns and the voltage measured for these turns with a
potentiometer. It was found that the weight calibration varies very little over a period of time and the variation with weight is practically negligible. However, the calibrations were always made over the same weight range as that used in the actual experiment.

The procedure for an isotherm run is as follows: a conveniently large sample is placed in the sample bucket and wet with the liquid whose vapors are to be absorbed (or desorbed). With five to ten cubic centimeters of the liquid in the system, it is evacuated and the liquid is allowed to evaporate. This washes the system free of air and leaves only the vapors. The tube containing the sample is lowered into a constant temperature bath and is allowed to come to equilibrium, the time required usually being one to four hours. In running a desorption isotherm the pressure is lowered in steps and the corresponding weight is observed from the potentiometer as outlined above. In order to follow the adsorption of the vapors, the system is evacuated as much as possible and small amounts of liquid are admitted from the vacuum side of the apparatus, the pressure rising in steps. After the isotherm has been run, the absolute amount of material adsorbed must be determined. This is done by evacuating the system as much as possible and at the same time heating the sample in an oil bath to 150–170°C. The voltage reading taken at this time is assumed to be the reading for the sample with no adsorption, since it is taken only after the sample has ceased losing weight. Hence, the weight of material adsorbed at any given pressure will be represented by the dif-
ference between the voltage reading at that pressure and the last mentioned voltage reading. The method can best be demonstrated by a table of data for a typical desorption isotherm.
(See Table 1.)

Treatment of Clay and Desorbing Isotherms:

In most of the following experiments, benzene vapors at \(30^\circ\) C were used. Benzene was chosen because it is probably the most tenaciously adsorbed of the low molecular weight unsaturated compounds whose molecular dimensions are accurately known. All the clay samples were in the form of pellets. These were formed by making a thick paste, extruding this paste through a small tube and drying the resultant cylinders of clay.

Wyoming Bentonite was chosen as a typical base saturated montmorillonite type clay. The high \(pH^+\) value of the natural clay indicates that it has not received much acid leaching in nature so it might be a good example of an unleached bentonite. The sample used in this experiment had been swelled in water for several months, and then electrodialysed to remove all the exchangeable bases and any naturally occurring salts which might be adsorbed. This material was dried at \(110^\circ\) C. The desorption isotherm is shown in figure (2). As will be noted, the curve is very flat until the pressure becomes less than 10% of the saturated vapor pressure (118 mm Hg at \(30^\circ\) C) at which point there is a sharp break to the zero value. This curve is typical of the Freundlich or Langmuir adsorption curve, and might indicate that there are relatively few pores present for capillary condensation or intensely active spots which might be responsible
for a curve with breaks in it.

8. Pure washed kaolin was used as an example of another fundamental type of clay structure. Two samples of this material were prepared, one being heated at 110°C to remove adsorbed water and the other being heated at 450°C to remove the "crystal water" (20). The resultant isotherms are also in figure (8). It is seen that the adsorption is very small in this case until the saturation vapor pressure is approached. Both the kaolin samples are practically the same when it is noted that the differences between them are very small and may be due to experimental error. The sharp rise in these curves at the higher vapor pressures is probably due either (1) to the presence of fairly large pores etched in the clay by nature, or (2) to some extensive spacing between the primary grains in the secondary aggregate. This first idea is consistent with the fact that the natural kaolin used has a pH value considerably below seven.

9. A sample of Texas clay used in most of the experiments which follow was found to have quite different adsorptive qualities. The bulk of the natural clay is of the montmorillonite type as shown by X-ray diagrams. The x-ray pattern for the clay as received shows impurities of large primary particle sizes. This is also noted on microscopic examination. In order to study the colloidal fraction and hence, the almost pure montmorillonite part of this clay, a large portion of it was dispersed in NaOH solution and allowed to swell for several days. This suspension was 33 1/2 solids by weight and had a pH of 10.5. Two liters of the suspension
was diluted to five gallons and the coarse material settled out, the supernatant suspension being super-centrifuged. X-ray pictures on the colloidal fraction show the typical montmorillonite pattern. The super-centrifuged material was washed several times with concentrated NH₄OH in order to replace most of the adsorbed materials. It was then dried at 150°C to remove any residual ammonia leaving the pure acid clay. A desorption isotherm was run on this material. The curve is shown in figure (2). This curve is relatively high, and unlike the Wyoming bentonite, it is not typical of the familiar adsorption isotherms. The breaks which occur in this curve appear at a pressure which is consistent with the theory that very small capillaries may be formed within the primary grains by acid leaching of the clay in nature. Also, the acidity of the natural clay is further confirmation of this idea.

The results of these data indicate that the wide difference of particle sizes and the fundamental differences in the clay types are minor factors in the adsorptive phenomena.

As a first check on the foregoing interpretation of the adsorption power of natural clays, purely physical means of spacing the natural clay grains were tried in order to distinguish capillary adsorption in clumps of grains from other adsorptive phenomena.

4. Kistler (21) has pointed out that ordinary hydrosols can be dehydrated without any shrinking if the dehydration takes place above the critical point. In many instances liquids of lower critical constants than water can
be substituted for the water in a gel and release of this liquid also forms an unshrunken "aerogel". Kistler's aerogels have a very low density and consequently must have a very high porosity. Since Kistler worked only with synthetic gels, it was decided that this procedure would be tried with gels formed from natural clays in order to obtain a very porous clay structure. A stiff gel of electrodialysed Wyoming bentonite was prepared containing about 15% solids by weight. Using an ordinary Soxhlet extraction, the water in the gel was replaced by acetone with no shrinking. This acetone gel was placed in a bomb with an excess of liquid acetone and heated well above the critical temperature the pressure rising to 1200 pounds per square inch. At this point the pressure was released and the bentonite aerogel was obtained. This material had about the same volume as the original water gel so that it had fairly large capillaries due to the spacing of the particles in the original gel. The technical difficulties of this method are many and several attempts were made before a successful aerogel was prepared. The estimated density of this material was 0.03 grams per cubic centimeter. The desorption isotherm on the bentonite aerogel is shown in figure (3). From this it can be seen that the large pores that must result from this procedure as well as the extended available area of the primary grains are not effective to cause increased adsorption.

3. The effect of exchangeable ions: As a physical means of cleaning the clay surface, electrodialysis was chosen. The colloidal fraction of the Texas bentonite treated as outlined in Section (3) was electrodialysed until the
electrolyzing current was nil. This material was dried at 110°C and a desorption isotherm was run. As can be seen from the curve in figure (3) the adsorption is considerably greater than that of the undialysed clay although the general shape of the curve is the same, even to the position of the breaks. This is probably due to the fact that dialysis removes the strongly adsorbed ions and leaves only slightly increased available space for the adsorption of benzene.

8. Both silica and alumina are soluble in strong alkali but their rates of solution are different. This being the case, it can be seen that possibly the clay surface would be etched by strong alkali forming capillaries of either SiO₂ or Al₂O₃. The Texas clay dispersed in water and NaOH at a pH of 10.5 as outlined above was allowed to swell for several days. To this suspension was added NaOH until its total concentration was 10 grams per 100 grams of clay. This mixture was heated and stirred vigorously for a period of 24 hours. At the end of this time, the NaOH was neutralized by the addition of HCl dropwise until a pH of 5.5 was reached. The mixture was placed in a porous pot and electrodialysed for a period of several days, during which time the amount of water decreased. The clay was then redispersed in NH₄OH and dried at 450°C. Another portion was dried at 700°C. The curves for the desorption isotherms on these samples are shown in figure (3). As will be noticed there is no increase at low pressures and only a slight increase in adsorption at higher pressures which indicates that some capillaries of fairly large dimension may have been formed. Another possibility is
that a deposit of \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) gel was formed on the surface on the grains rendering it more active. The fact that heating to 700° C caused a decrease in the adsorption may indicate that capillaries were formed and the heating partially sintered them.

A survey of the literature on the activation of clays as adsorbents indicates that the most effective artificial means discovered so far is acid boiling. The optimum conditions of acid boiling for the Texas clay used in these experiments has been found to be boiling in 10% acid for six hours. The weight of acid is calculated as 50% of the weight of the dry clay. These conditions were determined by decolorization experiments, and have been adopted as standard in this work so that at least one variable factor will be held constant for comparison studies. Figure (4) shows the desorption isotherm for the colloidal fraction of the Texas clay boiled in \( \text{H}_2\text{SO}_4 \) under the above conditions, and washed free of \( \text{SO}_4^2- \). It will be noted that in this case as in all the acid boiled cases the adsorption is very high compared to the natural clays.

The explanation of this high adsorption most consistent with the foregoing experiments is as follows:

The primary clay grain is attacked selectively by the acid with the removal of appreciable amounts of \( \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \). The result is primary particles resembling molecular sponges.

The removal of exchangeable bases, the etching of spaces between primary grains, or the changes in particle sizes have been shown to be of minor importance compared with this development of intra
particle spaces.

9. The colloidal fraction of the Texas clay was boiled in HCl under the standard conditions and washed free of AlCl₃ and FeCl₃ by washing with 10% HCl. On analysis, the wash water showed that 6.50% of the weight of the dry clay was present as Al₂O₃ and 7.61% was present as Fe₂O₃. Since some of the Al₂O₃ may be associated with the Fe₂O₃, the values given may not be entirely correct, but their total is of the correct order of magnitude. This shows that a large portion of the alumina and iron in the clay structure has been removed leaving a large number of SiO₂ capillaries. Even though much of the total iron and alumina present in the clay has been removed, the basic structure has been unchanged as evidenced by the fact that the X-ray pattern is identical with that of the original clay.

Figure (4) shows the isotherm for this sample dried at 120° C. It is considerably lower than the curve for the sulfuric acid boiled case.

9. Due to the fact that the HCl boiled clay gave a lower isotherm than the H₂SO₄ case, it was thought that possibly Cl⁻ was still adsorbed, cutting down on the benzene adsorption. Consequently, this clay was washed free of chlorides, dried at 120° C and a desorption isotherm was run. The curve, shown in figure (4), was higher than the unwashed case but still isn’t as high as the sulfuric boiled clay. Again we have a manifestation of the fact that adsorbed ions do not greatly alter the benzene adsorption.

It is interesting to note however that the specific acid used
for the acid boiling does make a difference.

10. Certain synthetic catalysts have very high adsorption curves in the low pressure regions. These materials are synthetic silica gels with materials such as $\text{Al}_2\text{O}_3$ added. The addition substance probably creates active centers or possibly forms a more compact sponge-like material. To note the effect of addition agents of this type, an HCl boiled clay washed free of $\text{Cl}^-$ was washed with $\text{Zr(NO}_3\text{)}_4$ solution and heated to $540^\circ$ C. Analysis of the wash water showed the dry clay adsorbed 2.75% of its dry weight as $\text{ZrO}_2$. In addition to a possible specific action, the $\text{Zr}^{4+}$ should displace any other adsorbed ions on the clay and render the surface clean. The curve in figure (5) shows that the adsorption in this case was lowered by the $\text{ZrO}_2$—probably because the capillaries or other active spots were blocked by the strongly adsorbed tetravalent ion.

Although the lowering is not great, this experiment seems to indicate that the tetravalent ion has a more intense action than the univalent and bivalent ions discussed in previous experiments. This is the expected phenomenon according to the concepts of colloid chemistry.

11. The method of Nutting (27), of adding the metallic ion to the acid solution before boiling, was used to see if his experiments and conclusions could be explained in the light of the present study. Zirconium Nitrate was added to the acid solution, and analysis of the wash water after the acid boiling showed that 1.4% of the weight of the clay was present as $\text{ZrO}_2$. This clay was washed free of $\text{Cl}^-$ and heated
at 540° C. The desorption isotherm is shown in figure (5). The fact that the curve is high in the pressure range 30-60 mm as compared to the acid boiled clay and then tends to flatten out seems to be evidence in favor of Nutting's theory of the action of the metallic ions (See page 5).

12. Following this same line of reasoning, possibly a strongly attached organic molecule might have the same effect as the strongly adsorbed metallic ions during the acid boiling process. Due to its adsorption on bentonitic clays, methyl red was chosen as the organic material included in the acid solution. This mixture was boiled under the standard conditions, washed free of Cl⁻, and heated at 540° C. The isotherm on this sample is shown in figure (6). It is interesting in that it shows a slight increase in the pressure range 30-60 mm. This is another bit of evidence which points strongly toward the above mentioned theory.

13. Silica has been mentioned as a particularly active adsorbant, and its effect on the adsorptive properties of the Texas clay was studied. In order to deposit SiO₂ on a clay using a minimum amount of electrolyte, the HCl boiled clay was soaked in pure redistilled ethyl silicate. The clay wet with the ethylsilicate was placed in about 80% ethyl alcohol to which a trace of HCl had been added and was boiled for a period of seven hours to insure hydrolysis of the silicate. This was washed and dried at 540° C and the isotherm was run, giving the curve in figure (5). At high pressures the adsorption is high but drops off rapidly at lower pressures. This seems to indicate that the SiO₂ blocks the
smaller pores, but due to its own adsorptive nature causes an increased adsorption at higher pressures.

14. As a further study of the effect of addition agents to acid boiled clay, $\text{Al}_2\text{O}_3$ was precipitated in its presence. A sample of the colloidal fraction of the Texas clay was boiled in $\text{HCl}$ under the standard conditions, and $\text{NH}_4\text{OH}$ in excess was added before filtering. This precipitated both the iron and aluminum in the presence of the silica capillaries of the clay. The substance was washed with $\text{NH}_4\text{OH}$ until free of $\text{Cl}^-$ and dried at $120^\circ\text{C}$. The curve in figure (6) shows that this operation caused a considerable increase in the adsorption by the acid boiled clay over the entire pressure range. This experiment indicated that the original capillaries are not blocked off by the $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$, and these substances cause a specific change in the nature of the surface probably due to the formation of highly active centers.

15. A second sample of the Texas clay boiled in $\text{HCl}$ was filtered free of the $\text{AlCl}_3$ and $\text{FeCl}_3$, and $\text{AlCl}_3$ solution was added to the clay in order to see if the iron increased or decreased the adsorption. Enough $\text{AlCl}_3$ was added so that the amount of $\text{Al}_2\text{O}_3$ would be 5% of the weight of the dry clay. As above, $\text{NH}_4\text{OH}$ was added to this mixture to precipitate the alumina. The clay was then filtered and washed with ammonia until free of $\text{Cl}^-$ and dried at $120^\circ\text{C}$. The desorption isotherm on this material was almost identical with the one described in Section 14 as can be seen from the curve in figure (6). This seems to be proof that the iron present as a precipitate
of Fe₂O₃ does not alter the adsorption a great deal.

16. The first studies of a deposit of SiO₂ on the acid boiled clay showed a decrease in adsorption. As was pointed out, the SiO₂ was formed in contact with the clay and had opportunity to block any highly active areas. In order to study this further by changing the method of formation of the SiO₂, a 10% solution of Na₂SiO₃ was prepared. Carbon dioxide was bubbled into this solution with violent agitation until the solution became turbid without the formation of a gel. This indicates that the SiO₂ particles had grown appreciably. At this point enough of the standard HCl boiled Texas clay was added to the solution so that the total amount of SiO₂ would be about 20% of the weight of the dry clay. The silica gel was observed to be forming after the clay addition but was broken immediately by violent agitation. This mixture was washed several times and then electrodialysed free of all remaining electrolytes. It was dried at 540°C. The desorption isotherm on this material is shown in figure (7), and as can be seen it shows a decided increase over any of the foregoing samples. Evidently the SiO₂ particles were large enough before contacting the clay that they did not block any active areas or capillaries but merely enhanced their activity. The function of the SiO₂ deposited in this manner could be due to (1) a greatly increased number of pores of a certain size, or (2) a deposit on the clay or in its capillaries which has particularly high binding forces.

17. As a further study of the silica and alumina
addition to acid boiled clay, a clear silica gel was prepared by bubbling CO₂ through a 5% solution of Na₂O \cdot 2SiO₂. This clear gel was still basic, indicating unconverted silicate, so HCl was added and allowed to diffuse into it. The gel was then partially washed. A portion of the colloidal fraction of the Texas clay was boiled in HCl under the standard conditions, but was not filtered. To this the Si₃O₇ gel was added in an amount such that 10% of the weight of the clay was Si₃O₇.

After this mixture was made homogenous by violent agitation, ammonia was added to neutralize the HCl and precipitate the Al₂O₃ and Fe₂C₃. It was filtered and washed several times with ammonia and finally with water. This clay was then electrodialysed in order to remove the adsorbed ions, and dried at 540 °C. The desorption isotherm for this material shown in figure (7) is very similar to those described in Sections 14 and 15 and not quite as high in certain regions as the one described in Section 16. These experiments indicate that the state of subdivision of the addition agent is important as well as the material itself.
DESORPTION ISOTHERMS on HCl boiled Texas Clay Colloidal Fraction.
Benzene Vapor at 30° C.

- Clay added to silica sol. Dried at 540° C.
- Clay plus boiling solution added to silica gel. Precipitated and washed with NH₄OH. Dried at 540° C.
Table I

Desorption Isotherm—Benzene Vapor at 30°C.

HCl Boiled Texas Clay—Colloidal Fraction.

Weight Sample (M) = 3.9550 g.

Tare = 0.6 g.

Electromagnet Calibration = 0.645 volts/g.

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INTERPRETATION OF RESULTS
AND
SUMMARY
Interpretation of Results:

As was stated in the introduction, the object of this research was to study factors governing the adsorption of benzene vapor on clays, and by this adsorption to study the effect of chemical and physical treatments on clays. The experiments show that the adsorption of benzene varies widely with the type of clay structure, the kaolinite type adsorbing much less than the montmorillonite type. This might be explained by the fact that in montmorillonite there is much more surface of the silica type available than in the other clays. Also, the degree of dispersion of montmorillonite is greater than that of kaolin and a greater external surface is therefore available. Another interesting result, which is in agreement with previous experimenters, is that clays exhibiting the same structure do not have the same adsorption characteristics. For example, the Wyoming bentonite and Texas bentonite having identical X-ray patterns have different adsorption properties in benzene vapor. As pointed out in the description of the experiments, the geological history of the Texas clay is such that this material has received much natural weathering and leaching, and hence, fine capillaries have been formed by the removal of alumina from the structure. These pores present a large area for adsorption, and also offer the possibility of capillary condensation which was discussed in another part of this paper. The characteristic breaks in the adsorption isotherms point strongly toward this latter idea. The Wyoming bentonite, unleached by nature, gives an isotherm typical of the Freundlich or Langmuir type. This type curve
is explained on the basis of molecular layers on the adsorbent surface. Since this curve has very low values, it is reasonable to assume that this simple explanation based on a uniform surface is not broad enough to explain all the results. By assuming surfaces of different activity, the inflection points could be accounted for on the basis of the Langmuir theory, but the lines which are steep in the region approaching saturation vapor pressure still require an explanation such as capillary condensation.

The cleaning of clay surfaces by washing or electrodialysing removes strongly adsorbed ions leaving the active spots free to adsorb benzene vapors. However, this effect is slight and is far from being an important factor in the vapor adsorption, as is evidenced by the experimental results.

It is well known that the particles of a clay are very large compared to molecular dimensions so that any pores involving the spacing of these particles must also be large by comparison. Spacing of the clay particles in an adsorbant by means of an aerogel formation does not increase benzene adsorption. In other words the formation of large pores or a greater amount of available particle area is not effective in greatly changing the adsorption.

The process of acid boiling greatly increases the adsorption by the Texas bentonite. It was mentioned that this effect is probably due to a large area increase caused by the formation of small silica capillaries which at the same time make possible the condensation. The silica tetrahedra have a greater amount of unsaturation, but the atoms probably have the same arrangement as they do in the clay so that
an orderly arrangement still obtains. The kind of acid used and the substances present in the boiling solution govern the nature of the capillaries formed. The addition of highly adsorbed metallic ions or molecules to the acid causes increased adsorption for benzene in certain pressure regions. This also seems to be a matter of governing the nature of the capillaries formed, or of forming a system of more uniform capillaries.

The present experiments show that the addition of Al₂O₃ and SiO₂ to acid boiled clay under certain conditions greatly increases the adsorption. This may be due to the presence of a highly active material in the larger pores of the clay enhanced by the action of the clay's own small capillaries. In certain other cases, however, the addition of SiO₂ or other oxides actually decrease the adsorption because apparently their methods of formation are such that adsorptive areas are blocked off.

In the preceding paragraphs it may appear that a distinction is being made between "capillary condensation" and surface adsorption. The indications from experiment are that these differences are of degree rather than kind, hence, when an active surface in a capillary adsorbs enough vapor so that no more material can enter, capillary condensation may be said to have occurred. In other words, the surface forces may be fundamentally the same, but their availability and relative amounts present under different treatments may depend upon structure.
SUMMARY

A revised apparatus for the measurement of vapor adsorption on relatively large samples has been presented. With this equipment the adsorption isotherms of benzene vapors for various natural and treated clays have been studied and interpreted on a basis of known facts about clay composition and structure.

The results show that the following generalizations may be made:

1. The adsorption of benzene varies somewhat with the internal structure of the clay particles. This difference is slight and is important only in that the structure may govern other properties of the clay. The montmorillonite type clay seems to have a greater adsorptive power than the kaolin type.

2. Clays which have a high degree of dispersion, i.e., those which have a large percentage of particles in the colloidal region exhibit a greater adsorption than those with large particles. Here again the differences are small, and the increased external surface is a minor factor in relation to other factors studied.

3. The spacing of clay grains to form a large-scale sponge-like structure is another factor of secondary importance in vapor adsorption. The presence of relatively large capillaries between grains and the increased particle surfaces which must be available do not exert forces which are noticeably different from those in the unchanged clays.

4. As might be expected from other adsorption studies,
the presence of exchangeable ions on the clay grains reduces the adsorption of benzene. For univalent and divalent ions this effect is very small and becomes relatively important in the case of the tetravalent ions. However, the effect is still of small consequence when certain other factors are considered.

5. By far the greatest changes in adsorption by clays are effected by forming capillaries or channels of near molecular sizes in the primary grain structures. The selective removal of iron and alumina by acid from the crystal structure of the clays leaves pores with active silica surfaces in which great amounts of vapor are adsorbed. This seems to be the factor of greatest magnitude in clay adsorption. Since the largest portion of the adsorption is governed by this factor, appreciable differences can be obtained under different conditions:

A. Different acids seem to form capillaries of different sizes or of different nature so that under identical conditions the effect of one acid is not the same as that of another.

B. The addition of highly adsorbed metallic ions to the acid treating solution seems to promote the formation of uniformly active spaces giving greater adsorption in certain pressure regions.

C. The addition of silica or alumina gels to an acid treated clay alter the adsorption. If the gel is allowed to form in the sponge-like
structure, the adsorption is reduced, probably because the active surfaces have been partially covered. If the state of subdivision of the material added is controlled, the activity of the treated clay is enhanced. It is likely that this is due to the formation of active spaces which operate in conjunction with the active spaces on the clay.

3. Certain natural clays have higher adsorption curves than other natural clays having the same internal structure and grain size. This, and the fact that inflection points occur in their isotherms seem to indicate that the capillary formation has taken place partially in nature.
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