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Title: A METHOD FOR INVESTIGATION OF SELECTIVE ADSORPTION FROM BINARY VAPOR MIXTURES

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An apparatus and procedure are described for investigating selective adsorption from a binary vapor mixture as a function of pressure. The technique measures both total mass adsorption and adsorbed-phase composition.

Development of the method is outlined. Possible sources of error are analyzed and are found to be either nonexistent or within experimental error.

Sets of data are offered to support the method and to illustrate applications of it. Preliminary correlations with other investigations are shown.

A Method for Investigation of Selective Adsorption from Binary Vapor Mixtures

by

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INTRODUCTION

Selective Adsorption

Investigations on adsorption by solids from binary mixtures have been rather scarce. Two aspects have been studied, adsorption from binary liquids and adsorption from the saturated vapor above such liquids. The first studies of both types were done in the 1920's.

Bartell and Sloan (4) were among the first to investigate selective adsorption from liquids when they studied the adsorption by carbon from non-aqueous binary solutions. The basic technique that they developed has been used with little modification by others. In their procedure, samples of adsorbent were immersed in several different concentrations of binary solutions. After equilibrium was reached, the new liquid concentrations were measured. The change in composition was a qualitative indication of which component had been preferentially adsorbed. Improvements in this technique have been in the area of measurement of the liquid composition. Bartell and Sloan used an interferometer for this purpose, Kipling and Tester (10) used a refractometer, and the most recent improvement was the use of a differential refractometer by Hanson (6, p. 16-17).

In subsequent studies on adsorption from non-aqueous binary

liquids Bartell and co-workers (1, 2, 3) first used the method of plotting data which has now become standard; the change in mole fraction of the solution is plotted versus the mole fraction of the original solution. The mole fraction is usually that of the more polar component. The change in mole fraction is defined as the initial value minus the equilibrium value so that a positive number indicates that the adsorbed phase is richer in the more polar component than the solution is. Using this representation a U-shaped curve (Figure 1) indicates adsorption of only one component over the entire concentration range. The more common S-shaped curve (Figure 1), which crosses the abscissa, indicates both components are adsorbed to some degree. If the crossing point were assumed to be the composition of the adsorbed phase, the observed shape of the curve would be the same as that expected.

Tryhorn and Wyatt (12, 13) were pioneers in the study of selective adsorption from binary vapor. Their technique consisted of placing weighed adsorbent samples in open tubes inside sealed tubes. The space between the inner and outer tubes contained a binary liquid. After equilibrium was reached, the samples were weighed, and the change in liquid concentration was measured. Results of their investigation on adsorption by charcoal from ethanol-benzene and acetone-benzene indicated that adsorption took place in three consecutive stages: adsorption in constant ratio, approximately the

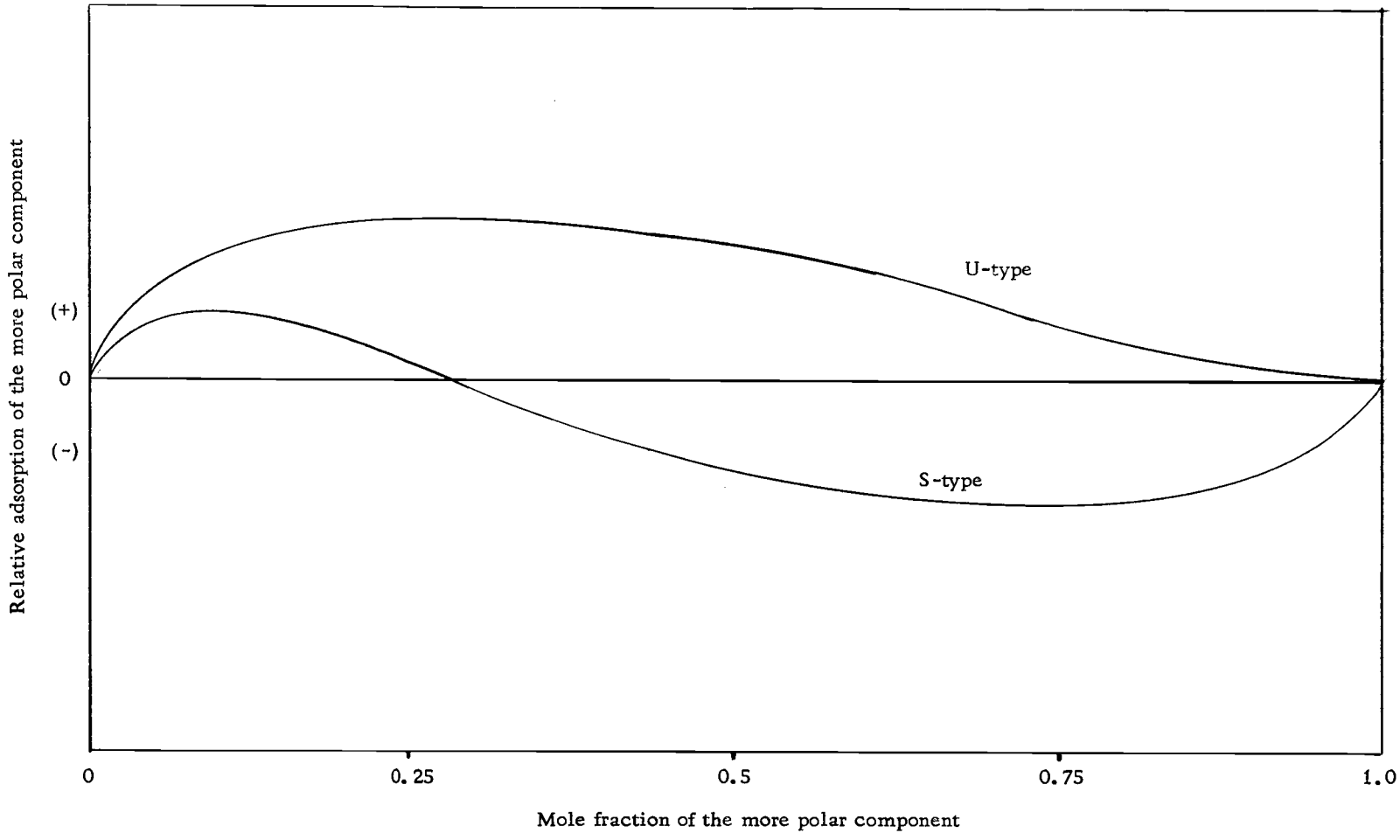


Figure 1. Typical isotherms for adsorption from solution.

same as the vapor; condensation of the adsorbate to a liquid; and adjustment of the adsorbed liquid to be in equilibrium with the bulk liquid.

If the adsorbed film is assumed to be a liquid in equilibrium with the bulk liquid through the saturated vapor, adsorption from saturated vapor may be used as an extension of the standard liquid technique. Although the standard liquid technique can measure only the relative amounts of the two components adsorbed, vapor phase methods can measure quantitative adsorption. Kipling and Tester (10) used this advantage to determine individual adsorption isotherms for components that they had also studied by the standard liquid method. Their results enabled them to propose two theories of adsorption which would not have been obvious from liquid phase data alone.

To our knowledge, methods for measuring adsorption from binary vapors at less than saturated vapor pressures have not been reported. In this investigation an attempt was made to develop a method for studying selective adsorption as a function of pressure. Data are offered in support of the technique and as a preliminary correlation with some of the results obtained by Hanson (6), who studied adsorption from binary liquid mixtures by an organoclay complex.

Clay Structures and Properties

To the layman the term clay implies a fine-grained substance which becomes plastic when wet. More scientific definitions refer to particle size or crystal structure. To the geologist, clay means particles no larger than four microns in diameter, while soil science limits the size to two microns. The chemical definition applies to a variety of minerals with different types of layer structures. Further information on the different types of clays may be found in textbooks by Grim (5) and van Olphen (14).

Of interest in this investigation is the structure of hectorite clay. It is helpful to begin with a description of the structure of talc, the prototype of hectorite. Each talc particle consists of a stack of platelets analogous to a deck of cards. A simplified model of a talc platelet would be a stack of four sheets of oxygen atoms with the outer layers close-packed and the inner layers hexagonal but expanded. Smaller magnesium atoms are located in octahedral holes between the two inner layers, and silicon atoms are located similarly in tetrahedral holes between each outer layer and its inner neighboring layer (Figure 2).

For a more accurate description, some additional details must be added. The outer oxygen layers look like close-packed sheets with one-fourth of the atoms missing, forming a two-dimensional

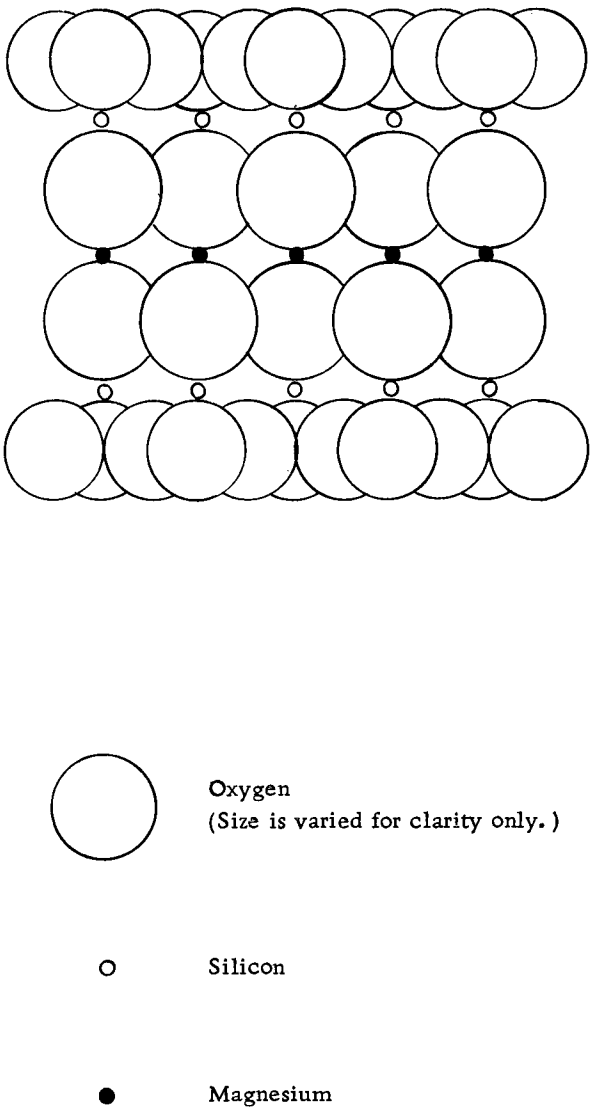
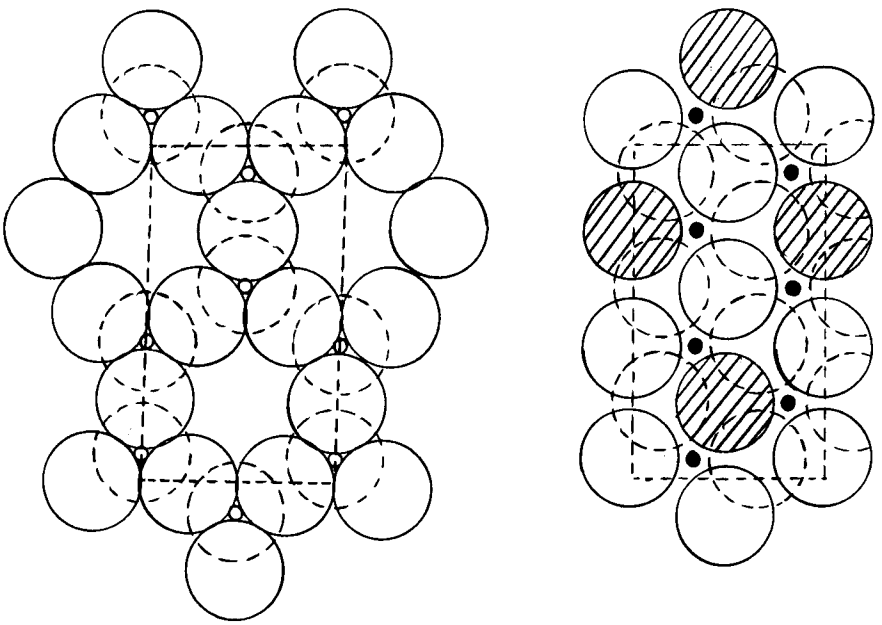


Figure 2. Simplified model of a talc platelet.

hexagonal network (Figure 3a). The inner layers have no missing oxygen atoms, but the atoms are separated more than they would be in a close-packed layer (Figure 3b). The expansion allows each oxygen in an inner layer to be directly below either a space in its neighboring outer layer or a group of three oxygens which form a tetrahedron with the fourth oxygen. The previously mentioned magnesium and silicon atoms are located, respectively, in the octahedral holes between the inner layers and in the tetrahedral holes between the inner and outer layers. Those oxygen atoms which are below the spaces in the outer layers are actually hydroxide groups.

Another representation of the same structure is the condensation of two silicate layers with a brucite layer between them. The silicate layers are two-dimensional polymers of silicate tetrahedral units interconnected at their bases with all the bases in the same plane. Brucite is a two-dimensional magnesium hydroxide polymer with the magnesium atoms octahedrally coordinated by two layers of hydroxide groups. The three layers are condensed through sharing oxygen atoms, or, alternatively, replacing two-thirds of the hydroxide groups in the brucite layer with the oxygen atoms in the vertices of the silicate tetrahedra. The remaining hydroxide groups are situated below the holes formed by the hexagonal network of tetrahedral silicate bases. The thickness of one of these platelets is of



a. Tetrahedral sheet

b. Octahedral sheet

Oxygen

Hydroxide

Silicon

Magnesium

Dotted lines indicate unit cell.

Figure 3. Structural units of talc.

the order of 10 Å, while the length and width are hundreds of angstroms or greater.

Hectorite is the result of the isomorphic substitution of univalent lithium for about one-ninth of the divalent magnesium atoms in the octahedral (brucite) layer of the talc structure. Since talc is electrically neutral, the charge difference between Li and Mg causes a positive charge deficiency in the structure of the platelet. This deficiency shows up as sites of excess negative charge, and these are distributed throughout the platelet. To maintain electrical neutrality, hectorite platelets have external cations situated on their surfaces near the negative charge sites. Since these cations are too large to penetrate the lattice, they are easily exchangeable. A quantitative measurement of this property is the cation-exchange capacity, CEC, in milliequivalents of exchangeable cation per 100 grams of dry clay. Clays in the class called montmorillonoids, of which hectorite is an example, have CEC values from 80 to 150 meq/100 g.

A result of the exchangeable cations is the ability to swell in the presence of water. The combination of hydration of the cations and adsorption of water molecules by the oxygen surface through hydrogen bonds releases enough energy to overcome the attractive force between platelets. Depending upon the particular combination of clay and exchangeable cation, the clay may adsorb up to 0.5 g

water vapor per gram of clay, and the volume of the clay may double. In the liquid the clay may adsorb up to 10 g water/g clay as the platelets become separated by approximately 100 Å and form a gel. If anhydrous clay particles are analogous to decks of cards, the hydrous gel may be thought of as a "house of cards" structure.

According to Hofmann and others (7), interlaminar swelling does not take place in the absence of exchangeable cations, as in talc. Since the distance between platelets would be smaller with no cations between them, the attractive forces (van der Waals) between them would be greater. Either the energy released by adsorption of water on the surface of the platelet is not enough to overcome these larger attractive forces, or the platelets are too close for the water molecules to penetrate between them.

Organoclays

The adsorbent properties of a swelling clay may be changed by transforming it into an organic cation-exchange complex. In this case the exchangeable metal cations are replaced by alkylammonium cations. The alkyl groups tend to orient themselves parallel to the oxygen surface by forming hydrogen bonds. Adsorbent properties vary depending on the size of the alkyl groups. Large alkyl groups cover more of the oxygen surface of the platelet and make the organoclay quite hydrophobic. As might be expected the complex is

also organophilic.

Mechanistically similar to the clay-water system, organoclays form gels with organic solvents. According to Jordan (8, 9), the solvents must have some polar character to form a good gel. The house of cards structure necessary for the formation of a gel is a result of the solvation of the alkyl groups of the complex by the organic liquid. First, however, the platelets must be separated enough to expose their surface to the bulk liquid. Polar molecules or polar groups on larger molecules are the only species having high enough adsorption energies on the oxygen surface to overcome the attractive forces between platelets. The best solvents for gel formation combine polar and non-polar properties, such as nitrobenzene or a binary mixture such as ethanol in heptane.

EXPERIMENTAL

The System

In order to obtain correlation with a liquid phase study done by Hanson (6), the dimethyldioctadecylammonium salt of hectorite was chosen as the adsorbent for this investigation. This organoclay is manufactured under the trade name of Bentone-38 by the Baroid Division of the National Lead Company. The as-received material was extracted with 2-propanol in a Soxhlet extractor for 48 hours, dried in a vacuum oven at 40 - 50 degrees C. for 12 hours, and hand ground to 120 mesh. The extraction was done to remove any excess quaternary ammonium salt that might have been physically adsorbed on the organoclay and to provide a reproducible starting material.

The binary vapor mixture, toluene and 2-propanol, was chosen from several liquid mixtures studied by Hanson (6, p. 18). This particular combination was selected because it was at first thought desirable for the two components to have similar vapor pressures. Bulk samples of the binary mixtures were prepared in liquid form and stored in glass-stoppered containers to prevent concentration change by evaporation. Toluene and 2-propanol were both of reagent grade.

Apparatus

The vacuum system consisted of two sections on the same manifold, one for measuring total mass adsorption and one for measuring composition of the adsorbed phase, both as functions of pressure. Pressure was measured with a mercury manometer and a McLeod gauge. All adsorption sample chambers were thermostated to 25.0 ± 0.1° C. with a water bath.

The section of the apparatus used for total mass adsorption measurement (Figure 4) was similar to an apparatus described by McBain and Bakr (11). Adsorption samples in tin foil buckets were suspended from helical quartz springs. These assemblies were enclosed in vertical glass tubes connected to the vacuum system. To minimize thermal effects on the spring lengths, the portions of the tubes containing the springs were enclosed in an air bath thermostatted to 30.0 ± 0.2° C. The samples were suspended about 50 cm from the ends of the springs by glass extension rods to make possible the control of their temperatures more accurately with the previously mentioned water bath. Mass adsorption was measured by following coded marks on the glass extension rods with a cathetometer. The force constants of the quartz springs were approximately 1 mg/mm, and the cathetometer accuracy was 0.1 mm, for a mass error of 0.2 mg (difference of two readings). The tin buckets weighed about 125

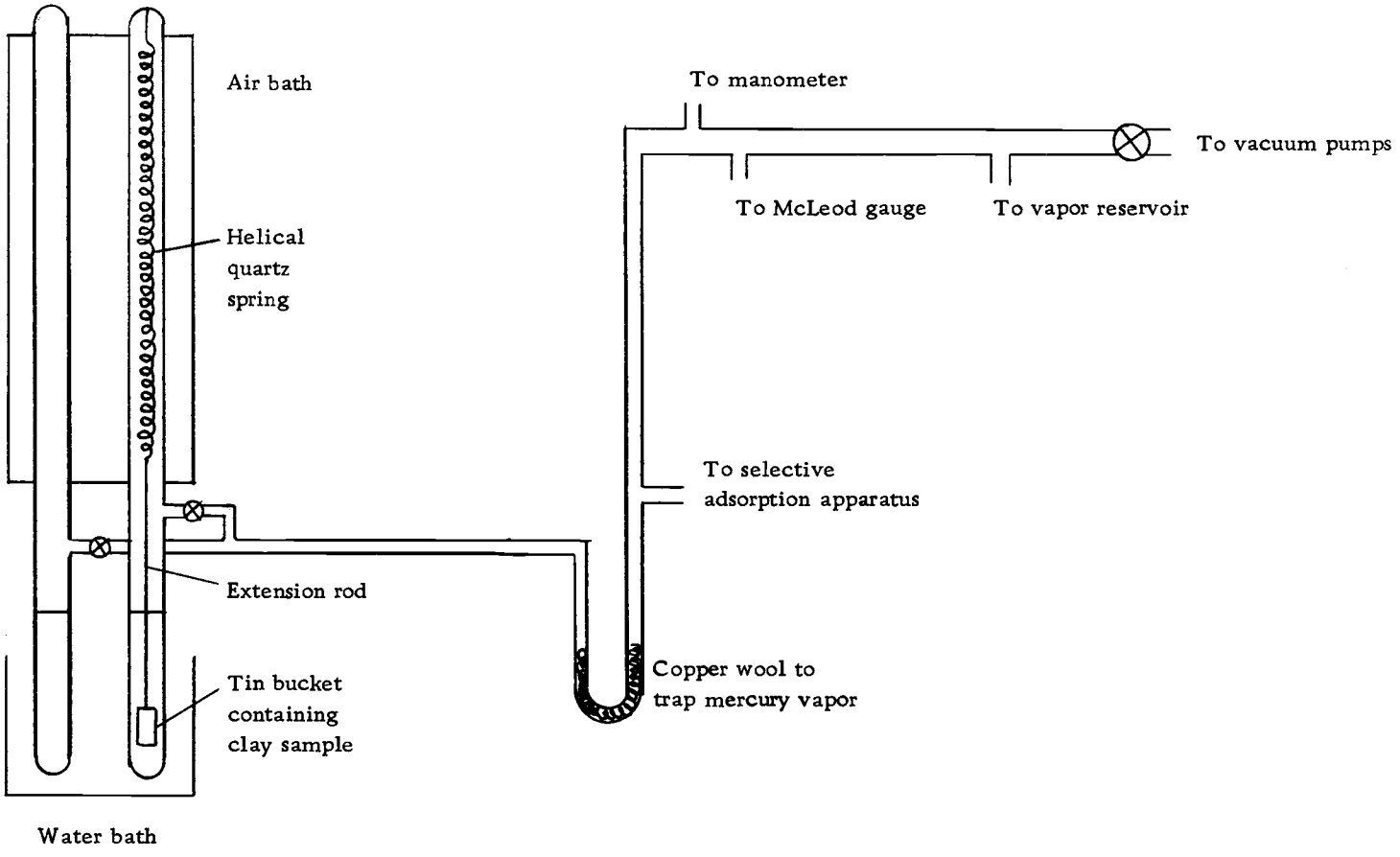


Figure 4. Mass adsorption apparatus.

mg and the adsorption samples about 250 mg.

The composition of the adsorbed phase was measured by desorption and condensation of the adsorbed layer, with composition of the condensed liquid determined by a refractometer. A discussion of the evolution of this technique may be found in Technical Development. This portion of the vacuum system (Figure 5) consisted of an adsorption sample chamber and a removable cold finger with stopcocks to isolate them from the main system and from each other. The cold finger also had a stopcock to let in air to facilitate its removal. The adsorption sample was about 10 g and temperature was controlled to 25.0 ± 0.1° C. by the water bath.

The refractometer was a Bausch and Lomb Precision Refractometer with a sodium light source. Temperature was controlled to 25.00 ± 0.01° C. Accuracy of the instrument was 0.00002 units near the refractive index of toluene and 0.00005 units near that of 2-propanol. These values correspond to 0.0002 and 0.0005 mole fraction units, respectively.

Vapor samples were obtained from a reservoir in liquid form. The reservoir (Figure 6) had two stopcocks, one above for outgassing the liquid and one below for releasing small amounts of liquid into the vacuum system to form the vapor. The lower stopcock was Teflon and was greased with Dow Corning silicone grease.

All other stopcocks in the entire system were glass and were

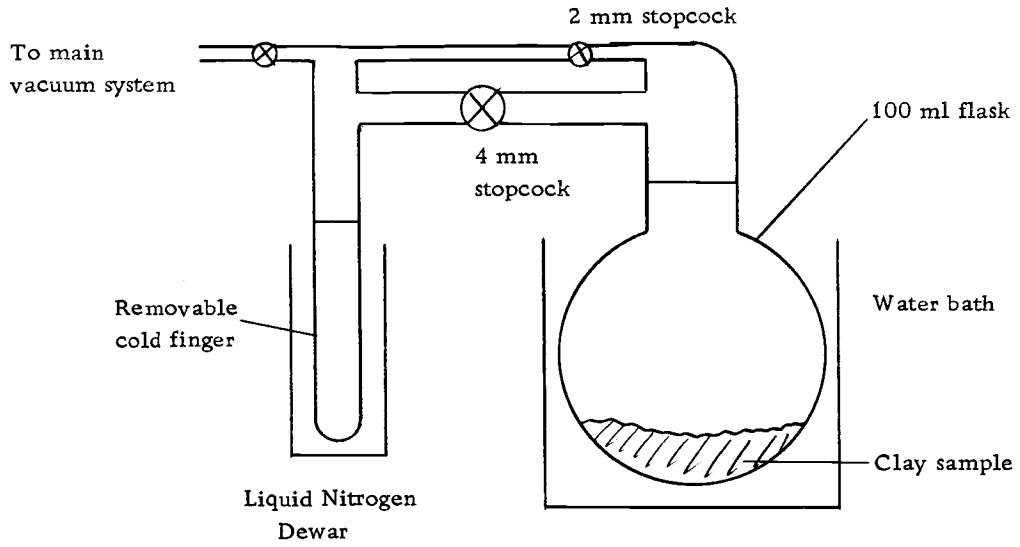


Figure 5. Adsorbate composition apparatus.

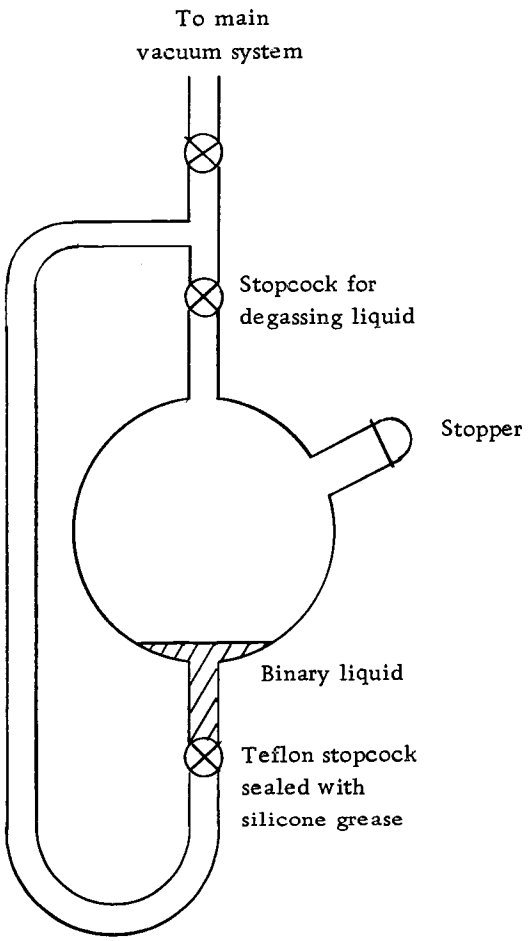


Figure 6. Binary mixture reservoir.

greased with Apiezon "N" hydrocarbon grease. Ball and socket joints were sealed with Apiezon "W" black wax except for the removable cold finger, which was sealed with Apiezon "T" grease.

Procedure

To begin a mass adsorption run, samples of about 250 mg were weighed into the previously weighed tin buckets, and their weight was determined by difference to 0.2 mg. The buckets were then suspended on the quartz springs, the chambers were sealed, and cathetometer readings were taken. The system was evacuated slowly (over at least a 30 minute period) to prevent bumping of the powdered samples due to the escaping of adsorbed gases. Then the diffusion pump was turned on, and the system was allowed to outgas overnight at 0.001 torr or less.

Before any binary vapor was allowed into the system, another cathetometer reading was made to correct the adsorption sample weights for weight loss on outgassing and to provide a starting point for the mass increase measurements. Small amounts of previously outgassed binary liquid were then let into the system to vaporize and to come to equilibrium with the organoclay samples. Spring displacement and pressure readings were taken at each equilibrium point before a new pressure increment was added. Equilibrium times varied from one hour at the low end of the pressure scale to two

hours or more at the saturated vapor pressure (approximately 30 torr) end of the scale.

For selectivity measurements (composition of the adsorbed phase) a 10.0 ± 0.5 g sample of organoclay was sealed into its chamber, evacuated as carefully as the samples in the buckets, and outgassed overnight. Small amounts of vapor were allowed into the system until the desired pressure had been reached at equilibrium, about one hour after the last vapor increment had been added. Equilibrium time was established by constant weight readings on the previously mentioned gravimetric apparatus, which was used concurrently to check the performance of the system as a whole. For this purpose the two sections were connected and exposed to the same vapor sample.

After equilibrium was reached, the organoclay sample and adjacent cold finger were isolated from the rest of the system. The cold finger was immersed in liquid nitrogen, and a 2 mm stopcock between them was opened very slightly to prevent too fast desorption and resultant bumping of the organoclay powder. After 10 to 15 minutes the stopcock was opened completely. At the end of 30 minutes total time a 4 mm stopcock between the sample chamber and the cold finger was opened to enable faster desorption of the residual adsorbate. After a total of 60 minutes the cold finger was isolated, air was let into it through a drying tube, and the liquid

nitrogen was removed.

When the cold finger had warmed enough so that the ice that had formed on it had barely melted, it was removed from the vacuum line and the liquid sample was withdrawn with a ground glass hypodermic syringe and needle. The liquid sample was then introduced between the prisms of the refractometer, and the reading taken was compared with a standard curve made from the bulk liquid samples. The smallest sample that would give a reading was about two drops, which corresponded to the amount obtained at 0.3 - 0.4 torr.

Technical Development

Initial trials to develop a vapor phase selective adsorption technique involved an attempt to parallel as closely as possible the liquid phase technique used by Hanson (6, p. 18-21). As mentioned before, his method consisted of measurement of the change in mole fraction of the liquid in contact with the organoclay. To parallel this method, a technique was developed to measure the change in mole fraction of the vapor in equilibrium with the adsorbent. This information combined with the total adsorbed mass, the system volume, and the pressure would have enabled calculation of the composition of the adsorbed phase.

The first problem encountered was measurement of the vapor composition. Several methods were considered: quantitative infrared

absorption by the vapor, gas-liquid chromatography analysis of the vapor condensed into a liquid, and refractive index of the condensate. Since high accuracy was needed, the spectroscopic and chromatographic techniques were rejected. Their accuracy was thought to be no better than several percent, while the refractometer offered an accuracy of better than 0.001 mole fraction.

After the measurement of the vapor composition was solved, a need for a more reproducible vapor composition became apparent. The first attempts at producing the binary vapor had consisted of mixing the components in the system from separate liquid reservoirs and calculating the mole fraction from the partial pressures read on the manometer. This technique was not sensitive enough to provide several different mixtures of the same composition, which were needed to measure adsorptive selectivity at several different pressures.

The simplest solution to the reproducibility problem was to mix the components in liquid form and let amounts into the system which were small enough to vaporize completely. A special reservoir was built (Figure 6) which had a stopcock to outgas the liquid and one to release the liquid into the system. The stopcock in contact with the liquid was Teflon greased with silicone grease. Although a glass stopcock may have been satisfactory, the Teflon was selected because it was easy to clean the silicone from it. Ease of cleaning was an

important factor since even the silicone grease deteriorated after about four days in contact with the toluene-2-propanol mixture.

At this point in the development several disadvantages began to cause increased concern about the practicality of this technique. The largest change in vapor composition came at low pressure (< 4 torr), but the amount of vapor in the system at this pressure did not provide enough condensate to give a good refractometer reading. A system volume large enough to give a good refractometer reading at low pressure would have been of the order of 100 liters, which would have been somewhat impractical. Also, it was laborious to make the calculations necessary to transform vapor composition change, total mass adsorption, system volume, and pressure into adsorbed-phase composition.

A technique was then formulated for essentially a direct measurement of the adsorbed-phase composition. It involved desorbing and condensing the adsorbed layer and measuring the composition of the resulting liquid with the refractometer. The amount of organoclay large enough to provide a workable refractometer sample at equilibrium pressure of one torr was calculated to be about 10 g.

A sample this large caused some bumping during desorption because much of the vapor was trapped by the bulk of organoclay particles above it. To minimize bumping from this cause, the

adsorbent was contained in a 100 ml round-bottom flask sealed onto the vacuum system. The flask was large enough to let the organo-clay sample spread out and expose enough surface area to minimize physically trapped gases. Even with this precaution it was necessary to desorb the vapor slowly at first, particularly when a large amount of vapor had been adsorbed.

The assumption that the composition of the condensate is equal to the adsorbed-phase composition is quite accurate. Assuming complete desorption of the adsorbed layer, the only error would be from the unadsorbed vapor being condensed along with the adsorbate. The error would be appreciable only if the number of moles of unadsorbed vapor were significant compared with the number of moles of adsorbate.

To test the validity of the equality of the adsorbate and condensate composition, the ratio of the number of moles of adsorbate to the number of moles of unadsorbed vapor was calculated. To calculate the number of moles of adsorbate a linear function was chosen as an estimate of the actually somewhat S-shaped adsorption isotherm. The slope of this line was approximately equal to that of the linear portion of the experimental curve, and it was chosen to give a calculated value less than or equal to the actual number of moles adsorbed at any given pressure. The number of moles of unadsorbed vapor was calculated from the ideal gas law using a generous chamber

volume estimate of 200 ml. The ratio of the calculated amounts of adsorbate and unadsorbed vapor was 56 for 2-propanol, which corresponds to 1.8 percent of the condensate having been unadsorbed vapor. Similar calculations for toluene gave a value of 1.0 percent, and the binary mixtures should give values between these two percentages. Percentages of this magnitude translate into a maximum of 0.005 units of error in the mole fraction of the adsorbed layer. This maximum can happen only if the vapor is a single component and only at a mole fraction of 0.5. However, the vapor could never be considered a single component, and it is usually close to the composition of the adsorbate except at low pressures (Figure 7). For this reason and because of the generous estimates in the calculation of the error, the true systematic error must be close to or within the refractometer accuracy of 0.0005 mole fraction units.

For the measurements of the condensate composition to have any validity with respect to the adsorbate composition, the adsorbed layer had to be desorbed completely. Organoclay samples of 250 mg were observed to desorb completely in the gravimetric apparatus in about 30 minutes. This experiment was performed with a short path length to the cold finger and with a minimum passage diameter of about 5 mm. The configuration of the desorption path was similar to this for the apparatus used to measure the adsorbed-phase composition. The path from the 10 g organoclay sample to the cold finger

was of comparable length, and it contained a 2 mm stopcock and a 4 mm stopcock in parallel. One hour was judged to be sufficient desorption time for the 10 g adsorbent sample. To prevent bumping the first 30 minutes of desorption of large adsorbate samples was done through the 2 mm stopcock only. Small adsorbate samples were desorbed through both stopcocks for almost the full hour. Small samples, for which complete desorption was most critical with respect to percentage of total sample, were thus assured of the most complete desorption. Further support of the adequacy of the 60-minute desorption time was observed when several samples desorbed for 90 and 100 minutes showed no measurable difference when compared with the 60-minute samples.

Equilibrium time was determined gravimetrically; the adsorbate was assumed to have attained composition equilibrium when it had attained constant weight. The gravimetric apparatus, used in conjunction with the composition apparatus, reached equilibrium in 60 minutes. As further validation of this time, adsorbate samples which had been equilibrated up to two and one-fourth hours showed no measurable difference from the 60-minute samples.

Since the adsorbate seemed to show an increase in toluene at low relative pressures (Figure 7), explanations other than selective adsorption by the organoclay were sought. One possible explanation that required further investigation was the possibility that the increase

in toluene was from selective adsorption of the 2-propanol liquid by the glass surface of the cold finger. If this were happening, the smaller condensate samples would be expected to contain the larger amounts of toluene, just as was observed. To test this idea a small amount of vapor was condensed in the cold finger without having been in contact with the organoclay. The condensate showed no change in composition when compared with the bulk liquid in the reservoir. Since the sample was small enough to have shown a relatively large increase in toluene if it had been exposed to the organoclay, the observed changes in condensate composition must have been entirely due to selective adsorption by the organoclay.

The most difficult problem in the development of this technique was the elimination of vacuum leaks. The adsorbate composition could not be measured accurately unless the vacuum system would maintain a pressure of 0.001 torr for at least two hours. Since this pressure was close to the minimum capability of the system, leaks were frequent problems. Apparently only small amounts of air were necessary to increase either the equilibrium time and/or the desorption time to greater than the time allowed.

APPLICATIONS

Selective Adsorption Curves

Measurements of the adsorbate composition may be displayed graphically by plotting the mole fraction of the polar component of the adsorbate versus the pressure (Figure 7). For convenience the pressure may be replaced by the relative pressure, P/P_o, where P_o is the saturated vapor pressure of the binary mixture. Since P_o is intended only as an approximate reference point, Raoult's law and Dalton's law provide sufficient accuracy for its calculation.

A curve of this type was plotted for each of several different vapor compositions (Figure 7). In each case the adsorbate mole fraction approached that of pure toluene at low relative pressure. The smoothness of these curves supports the experimental method developed in this investigation by demonstrating its potential precision. In addition, the small difference between the mole fractions of the adsorbate and the initial vapor, except at very low relative pressures, indicates that the composition of the unadsorbed vapor at equilibrium must be close to the composition of the adsorbate. This conclusion supports the assumption that the compositions of the adsorbate and desorbed condensate are equal within experimental error. The basis for this assumption was outlined in Technical Development.

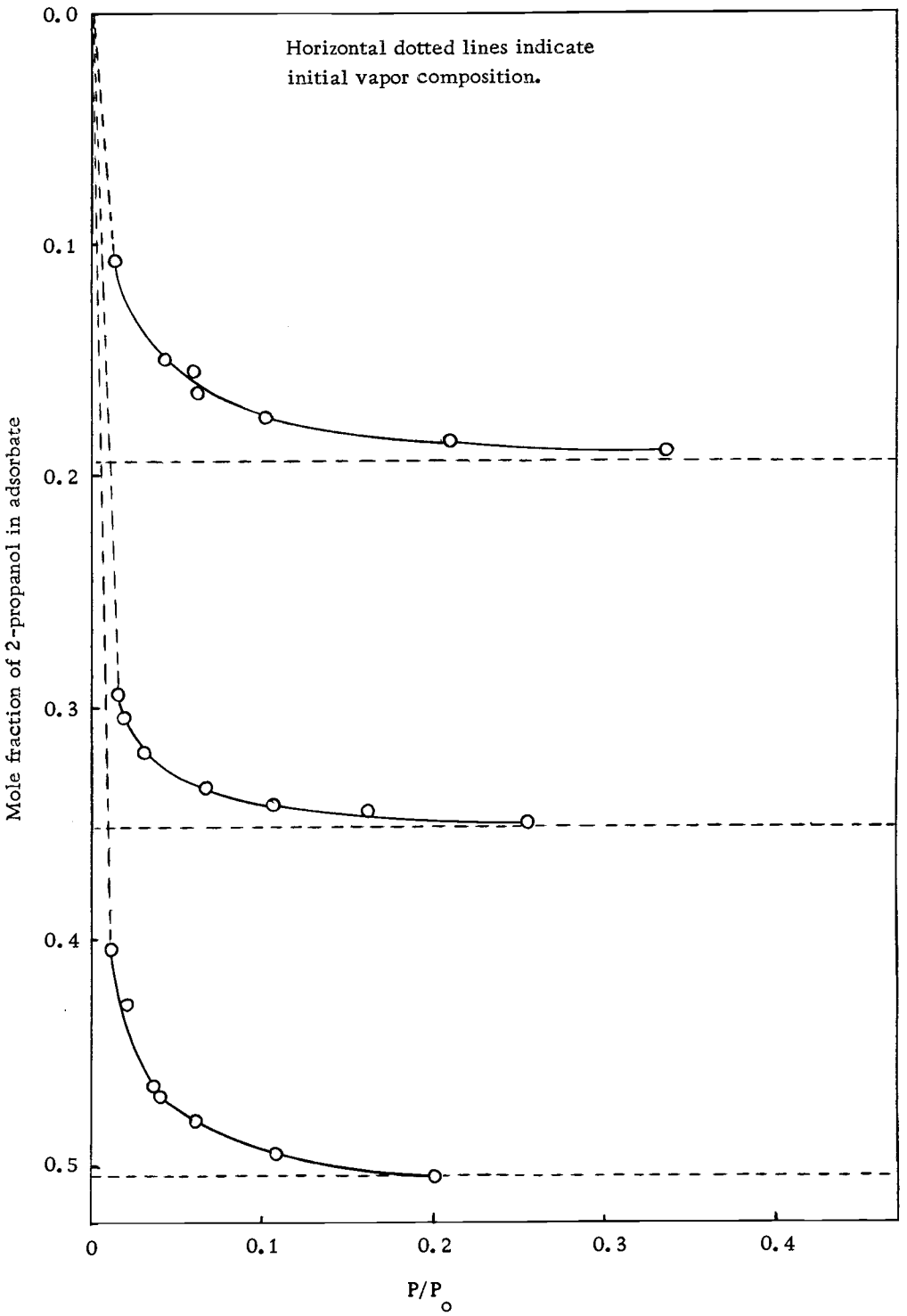


Figure 7. Selective adsorption curves.

Even the larger differences between the adsorbate and the initial vapor at low relative pressures would probably not cause a measurable error in the adsorbate composition determination. Furthermore, if a systematic correction were necessary at low pressures, the corrected value for the adsorbate composition would be higher in toluene than the uncorrected value. Since the correction is in the same direction as the observed increase due to selective adsorption, the observed change would not be nullified by such a compensation.

These selective adsorption curves also support a conclusion by Tryhorn and Wyatt (13) mentioned earlier. In their studies on adsorption from saturated binary vapor, they hypothesized that the first stage of adsorption took place in a constant ratio approximately equal to the composition of the vapor. This idea is supported by the nearly constant composition of the adsorbate (except at low relative pressures) and the asymptotic approach to the composition of the vapor, which are shown in the curves.

Some preliminary correlations with liquid phase studies by Hanson (6, p. 26) are also possible. He found that for a 2-propanol-toluene mixture adsorbed by Bentone-38 the crossing point of the S-type isotherm came at a mole fraction (2-propanol) of about 0.35. If the crossing point is assumed to be the composition of the adsorbed phase, the adsorbed layer is therefore richer in toluene. This correlates with the increase in toluene observed on the adsorbate composition curves at low relative pressure. Even though

the two cases are not equivalent, some of the same forces may be acting in both. In addition the curve corresponding to an initial vapor composition of 0.35 seems to show a slower increase in toluene than the other two curves as the pressure is decreased. This may indicate a "reluctance" to deviate from a possible favored composition. However, such a conclusion would need more data for support.

Individual Component Isotherms

Total mass adsorption isotherms from binary vapors may be separated into individual component isotherms (Figure 8) if the adsorbate composition is measured simultaneously. More information may be incorporated into the individual isotherms than into the total isotherm because the ordinate of the component curve may be expressed as moles adsorbed per unit mass of adsorbent. Since the adsorbate composition is not constant, the ordinate of the total mass adsorption curve may be expressed only as mass adsorbed per unit mass of adsorbent. The separation of the components and the change in ordinate units would probably simplify theoretical treatment of the adsorption isotherm. Not enough data has been obtained to make any theoretical analysis worthwhile.

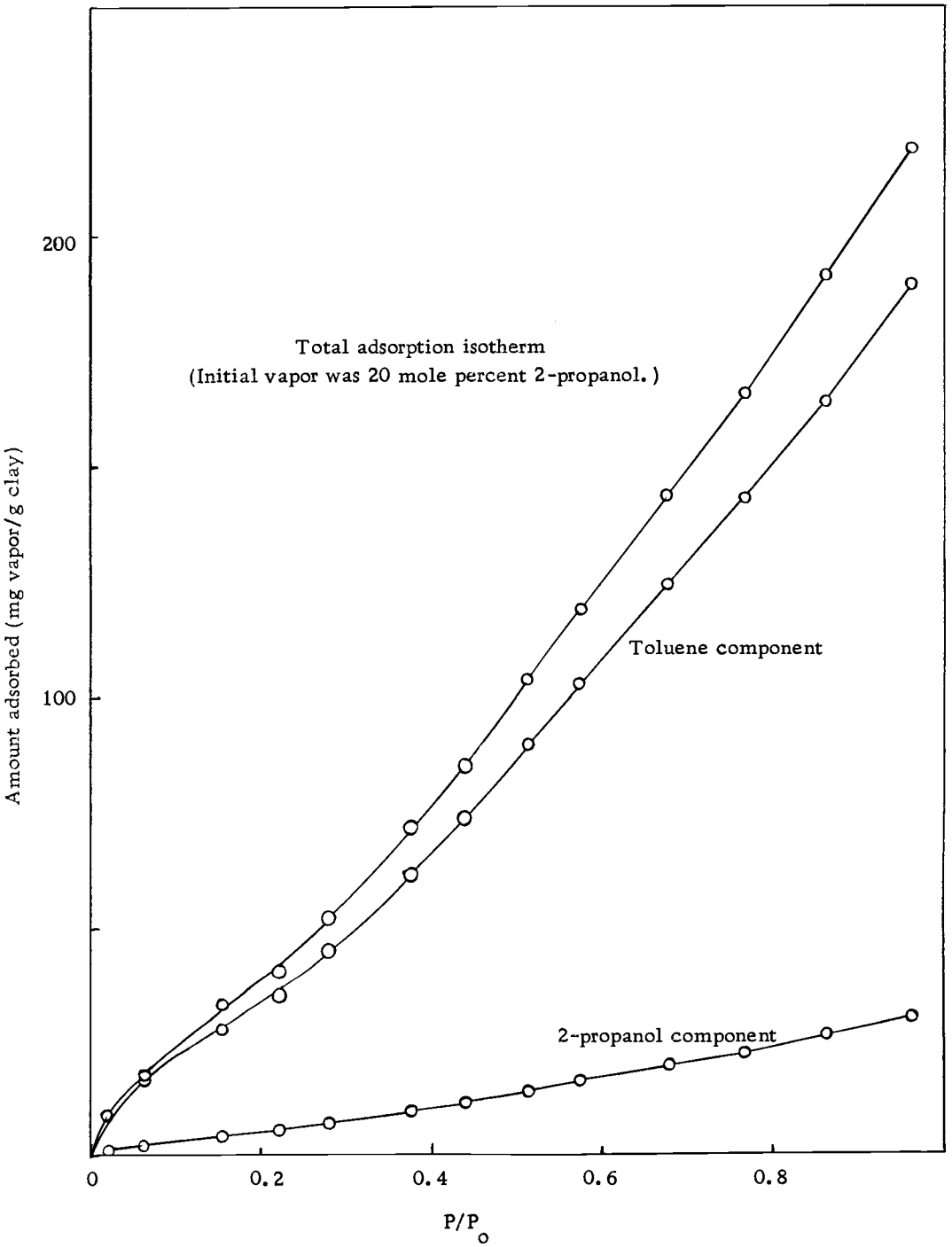


Figure 8. Individual component isotherms.

CONCLUSION

Summary

An apparatus and procedure for investigating selective adsorption from a binary vapor mixture as a function of pressure have been described. The apparatus was designed to measure both total mass adsorption and adsorbed-phase composition.

Development of the method for measuring adsorbate composition was begun by first trying to parallel a standard liquid phase technique as closely as possible. Limitations in the practicality and facility of the technique necessitated the changeover to direct measurement of the adsorbate composition, which was done by desorption and condensation of the adsorbate followed by refractometric measurement of the condensate composition. Possible sources of error were analyzed and were found either nonexistent or within experimental error.

Sets of data were offered in support of the method and as illustrations of applications of the method. The data also showed some correlations with conclusions drawn from other techniques.

Suggestions for Improvement

The main improvement in the technique would be to construct a system with several adsorbent sample chambers. Each should have

its own manometer and cold finger so that several data points (possibly an entire run) could be gathered in one operation. Anyone attempting this should become fully familiar with the idiosyncracies of a single-sample apparatus, however.

Stopcocks of the no-grease variety would be another worthwhile improvement. Most of the previously mentioned idiosyncracies were caused by the vapors attacking the stopcock grease and causing vacuum leaks.

Suggestions for Further Work

The following systems are proposed for additional investigation in this area:

1. Additional data for 2-propanol-toluene on Bentone-38.
2. Mixtures of toluene and other polar molecules.
3. Mixtures of toluene and a saturated hydrocarbon.
4. Mixtures of benzene and any polar molecule.
5. Other adsorbents (silica gel, charcoal, other clays, etc.).

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