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SOLUTE-SOLVENT INTERACTIONS ON THE SURFACE OF SILICA GEL

III. MULTILAYER ADSORPTION OF WATER ON THE SURFACE OF SILICA GEL

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SUMMARY

Employing techniques of thermal treatment, infrared examination and chemical reaction, at least three layers of adsorbed water have been identified on the surface of silica gel equilibrated at 23°C with an atmosphere containing 50% humidity. Each layer contains about $8.5 \cdot 10^{20}$ molecules of water per gram of silica, which agrees well with previous reported data for polar and non-polar solute layers on the surface of the same silica gel. The second and third layers are weakly held and can be removed completely with dry solvents or by heating to 120°C. The first layer is very strongly held, removal commencing at about 200°C and is not complete until 650°C. This latter water loss is completely reversible. The silanol groups do not commence condensing to siloxyl groups until a temperature of 450°C is reached, and at 750°C, 75% of the silanol groups still remain and are not completely removed until temperatures in excess of 1000°C are reached. Conversion of silanol to siloxyl groups does not appear to be reversible.

INTRODUCTION

The concept of multilayer adsorption of water on the surface of silica gel is not novel. The multilayer adsorption of water on silica gel was discussed, amongst others, by Anderson and Wickersheim¹ in 1964, Mitchell² in 1966 and later by Linsen³ in 1970. More recently, Scott and Kucera^{4,5} experimentally verified that bilayer adsorption of the polar solvents ethyl acetate, tetrahydrofuran and methyl ethyl ketone took place on silica gel that had been activated by partial dehydration on heating at 200°C for 2 h. Scott and Kucera showed that non-polar solvents were adsorbed as a monolayer on silica gel, whereas polar solvents that would hydrogen bond to the silica gel produced bilayers. Furthermore, within experimental error, each layer of the bilayer of the polar solvent was shown to contain the same number of solvent molecules as the monolayer of non-polar, non-hydrogen-bonding solvents. However, silica gel heated to 200°C for 2 h still contains an extensive amount of hydrogen-bonded water, as discussed by Fripiat and Uytterhoeven⁶ and Fraissard *et al.*⁷ and demonstrated by

Scott and Kucera³. This suggests that the bilayer of polar solvents observed by Scott and Kucera^{4,5} was not formed on the silanol groups of the silica gel but on water molecules hydrogen bonded to the silanol groups of the silica gel. In fact, silica gel equilibrated with water could contain three or more layers of water molecules hydrogen bonded to themselves with the first layer hydrogen bonded to the silanol groups, as suggested by Anderson and Wickersheim¹ and Linsen². If this were so, silica gel employed in chromatography that had been activated by heat treatment for 2 h at 200°C or by solvent activation⁹ would consist of silica gel with one or perhaps two layers of adsorbed water. On top of this water layer would be either one layer of adsorbed solvent molecules if in contact with a non-polar solvent or two layers of hydrogen bonded solvent molecules if in contact with a polar solvent. Such a situation suggests that a far more complex silica gel surface was involved in chromatographic processes than was previously considered.

In this paper the nature of the water on the surface of silica gel is examined experimentally. The methods used include thermogravimetric analysis (TGA), thermal treatment and infrared (IR) examination, solvent extraction and chemical reaction with the silanol groups on the surface of thermally treated silica gel.

Examination of silica gel by thermal treatment

The silica gel used was Partisil 20, Batch No. A277 (Whatman, Clifton, NJ, U.S.A.). A bulk of the material was exposed to air in a desiccator containing 44% of sulfuric acid, which provided an atmosphere that had 50% humidity. All silica gel samples examined in this paper were equilibrated in this manner unless otherwise stated. A 16-mg amount of this material was subjected to thermogravimetric analysis using a Perkin-Elmer Model TCS-2 Thermogravimetric Analyzer. The results are given in Fig. 1, which shows the weight lost as a percentage of the total silica gel against temperature. The heating rate was 1°/min, and the temperature range was approximately 25–1000°C. Fig. 1 also includes a differential curve, but due to the very slow rate of heating, the differential curve is only sensitive at the lower temperatures where the weight change was more rapid. It is seen that there is a small peak in the differential curve occurring at about 30–40°C.

From the curve shown in Fig. 1 the mg loss per g of silica gel was calculated for every 10° temperature change. Due to the errors in reading from the chart in Fig. 1, the data was smoothed using a seventh-order polynomial smoothing procedure, and the resulting curve together with its differential is shown in Fig. 2. It is seen that there are three distinct temperature ranges where significant losses are obtained. The first range is between 25 and 150°C, the second between 350 and 700°C and the third between 800 and 1000°C with the differential curve showing maxima at about 100°C, 420°C and 960°C, respectively.

From the differential curve in Fig. 2, one can conclude that there are three different sources of water loss from silica gel; weakly held material having a peak evolution temperature of about 100°C, very strongly held material having a peak evolution temperature of about 420°C and water probably produced by the condensation of silanol groups to siloxyl groups that has a peak evolution temperature of 960°C. Examination of the early peak of the curve shown in Fig. 1 shows a small step in the TGA curve and a small peak in the differential curve occurring at about 35°C. This could indicate two sources of weakly adsorbed water. Due to the time

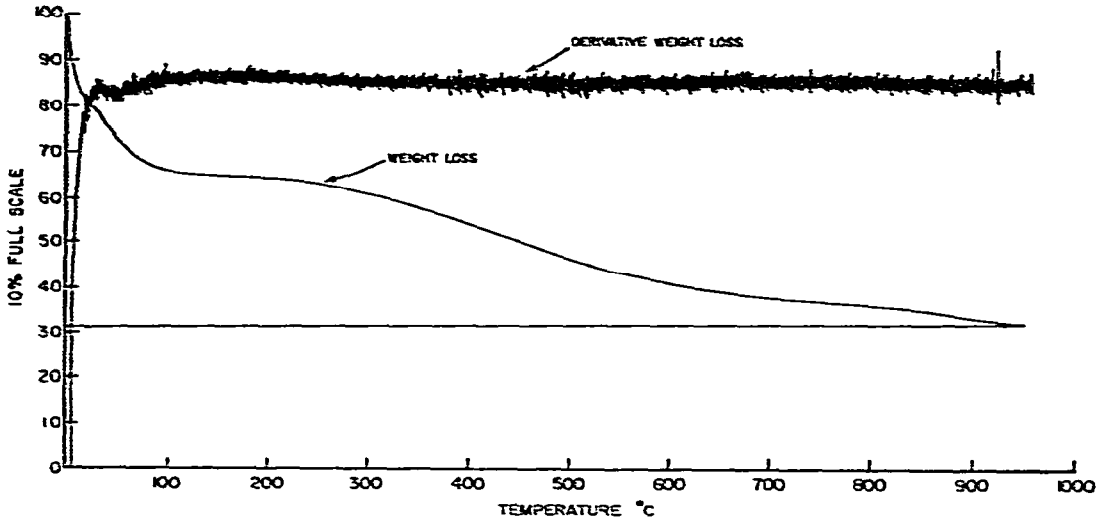


Fig. 1. Thermogravimetric curve of silica.

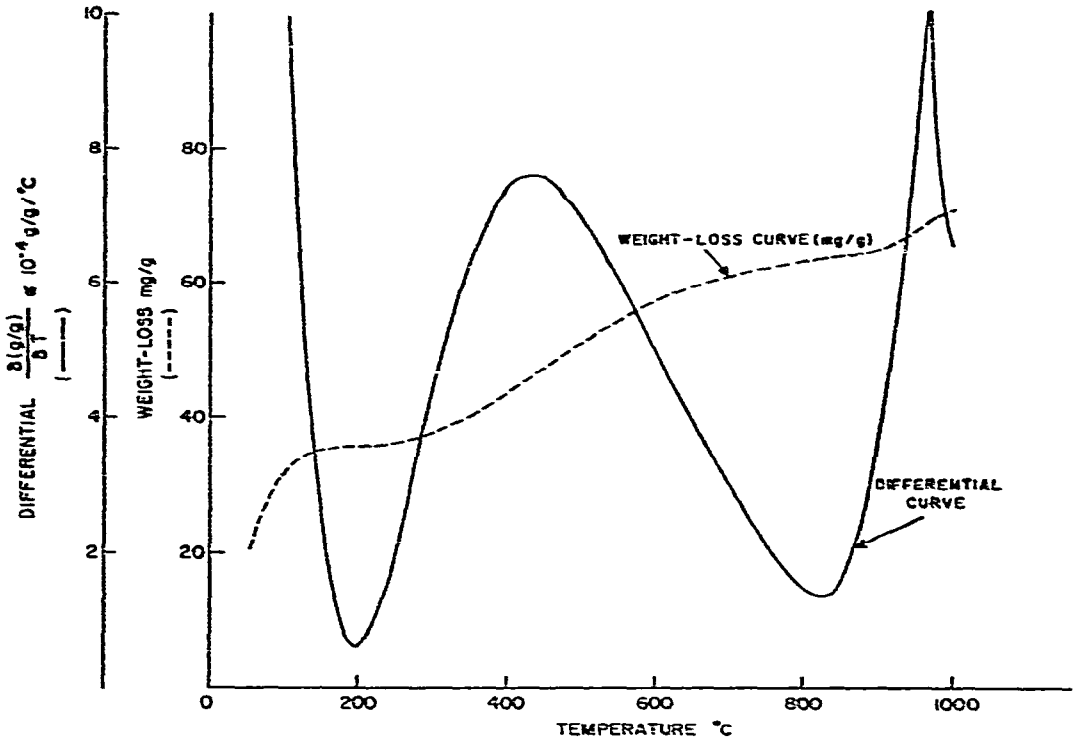


Fig. 2. Curves relating weight-loss and differential weight-loss of silica to heating temperature (taken from thermogravimetric curve).

required for setting up the thermogravimetric equipment, some water is lost from the sample initially before recordings are taken. It was, therefore, of interest to determine by a separate experiment the water lost at 110°C and 1100°C.

Duplicate samples of about 0.7 g of silica gel were rapidly transferred from the desiccator to a closed, preweighed silica crucible, and the mass of silica added determined. The loss of weight after heating for 2 h at 110°C and 1100°C, respectively, was measured, and the results are shown in Table I. The mass lost between 110°C and 1100°C is calculated by difference. It is seen from Table I that the initially adsorbed water lost at 110°C constitutes about 4.8% of the silica gel and that lost between 110°C and 1100°C about 3.8% of the silica gel. Thus the two types of water evolved between 350°C and 650°C and between 800°C and 1100°C, respectively, as shown in Fig. 2, constitute a total of about 3.8% of the total mass. The total loss of water on heating the material to 1100°C was 8.6%.

TABLE I

LOSS OF WEIGHT (% w/w) OF SILICA GEL ON HEATING AT 110°C AND 1100°C

	<i>1</i>	<i>2</i>	<i>Mean</i>
Loss on heating to 110°C	4.91	4.67	4.79
Loss on heating to 1100°C	8.63	8.50	8.57
Loss on heating from 110°C to 1100°C (by difference)	3.72	3.83	3.78

The exact nature of these different types of water evolved at different heating temperatures has been the subject of much discussion. De Boer and Vleeskens^{10,11} considered that water lost below the temperature of 100°C was physically bound water, and at 120°C all physically absorbed water has been lost. Heating at higher temperatures, these workers consider, depletes the surface hydroxyl groups. Lange¹², however, considered that even at 180°C strongly bound water still remains, whereas Young and Burch¹³ considered that at 180°C some chemically bound water has been evolved. It was, therefore, of interest to determine the source of the water being lost at 100°C, 420°C and 960°C, and in what form the material was contained by the surface.

The nature of the water lost on heating silica gel to 100° C

As the water lost at temperatures up to 100°C was likely to be weakly held to the silica gel, an attempt was made to determine this water by direct titration using the Karl Fischer procedure. A Metrohm Karl Fischer Automat, Model 547, was employed and 1 g of the equilibrated silica gel titrated directly. Duplicate analyses were performed, and the results obtained are shown in Table II.

The possibility of extraction of this weakly held water by dry solvents was also investigated. A 1-g amount of the equilibrated silica gel was placed in a tube contained by a sintered glass frit and the silica extracted using four separate 5-ml volumes of dry ethyl acetate under anhydrous conditions. The system used was closed, and when open to the atmosphere was surrounded by dry nitrogen to ensure no water was adsorbed from the atmosphere. The 5-ml extracts were bulked together and the water again determined by the Karl Fischer method. The above procedure was repeated

TABLE II

WATER CONTENT OF SILICA GEL BY KARL FISCHER DETERMINATION AND SOLVENT EXTRACTION

<i>Water contents (%)</i>	<i>Method of measurement</i>
4.93	Karl Fischer
4.96	Karl Fischer
4.78	Extraction by dry ethyl acetate and by Karl Fischer determination
4.31	Extraction by dry tetrahydrofuran and by Karl Fischer determination

using dry tetrahydrofuran as the solvent and employing an identical procedure. Both the ethyl acetate and tetrahydrofuran were dried prior to use by passage of the solvent through alumina activated at 300°C, and blank Karl Fischer determinations on the dried solvents demonstrated that no measurable quantity of water was present. The results expressed as % (w/w) of water extracted from the silica gel by the two solvents are also included in Table II. Comparing the water content as determined directly by Karl Fischer and also by solvent extraction with the weight loss on heating to 110°C shown in Table I, it is seen that all values are in close agreement. It follows, therefore, that the water loss on heating the silica gel to 100°C is weakly held and could be described as adsorbed moisture on the silica gel. It also follows that when activating silica gel using dry solvents such as the sequence described by Scott and Kucera¹⁴ consisting of ethanol, acetone, ethyl acetate, ethylene dichloride and heptane merely removed this physically adsorbed water, and the activity of the silica gel procedure would be similar to that obtained if the silica gel were heated to about 150°C.

The nature of the water loss on heating silica gel that exhibits a maximum at 420°C

The water lost at 420°C must have a fairly high energy of binding and could result from strongly hydrogen bonded water on the silanol groups or from pairs of silanol groups so close that they readily form siloxyl groups with the evolution of water. In the first instance an attempt was made to identify the nature of this water and to determine whether the loss of water resulted from the evolution of hydrogen bonded material or the condensation of silanol groups by IR examination. About 3 mg of silica gel equilibrated at 50% humidity were pressed into a 300-mg KBr disc at 10,000 kg/cm². The IR spectra were obtained, and the water absorption between 3000 and 4000 wavenumbers was measured. The disc was then heated at 25° intervals to 400°C, the spectra being measured at each temperature. Examples of the spectra obtained before heating are shown in Fig. 3, and the graph relating the area of the absorption peaks between 3000 and 4000 wavenumbers against heating temperature is shown in Fig. 4. The spectra for samples heated above 400°C were of little quantitative value due to the partial fusion of the potassium bromide as it approached its melting point, and the resulting interference effect. It is seen that the characteristic free water absorption pattern persists until 400°C, and by extrapolation appears to become negligible at 600°C, and thus the water providing the absorption appears to have been completely evolved at this temperature. This is confirmed by spectra previously taken at 600°C⁵ where it was shown that the absorption bands between 3000 and 4000 wavenumbers had completely disappeared at this temperature.

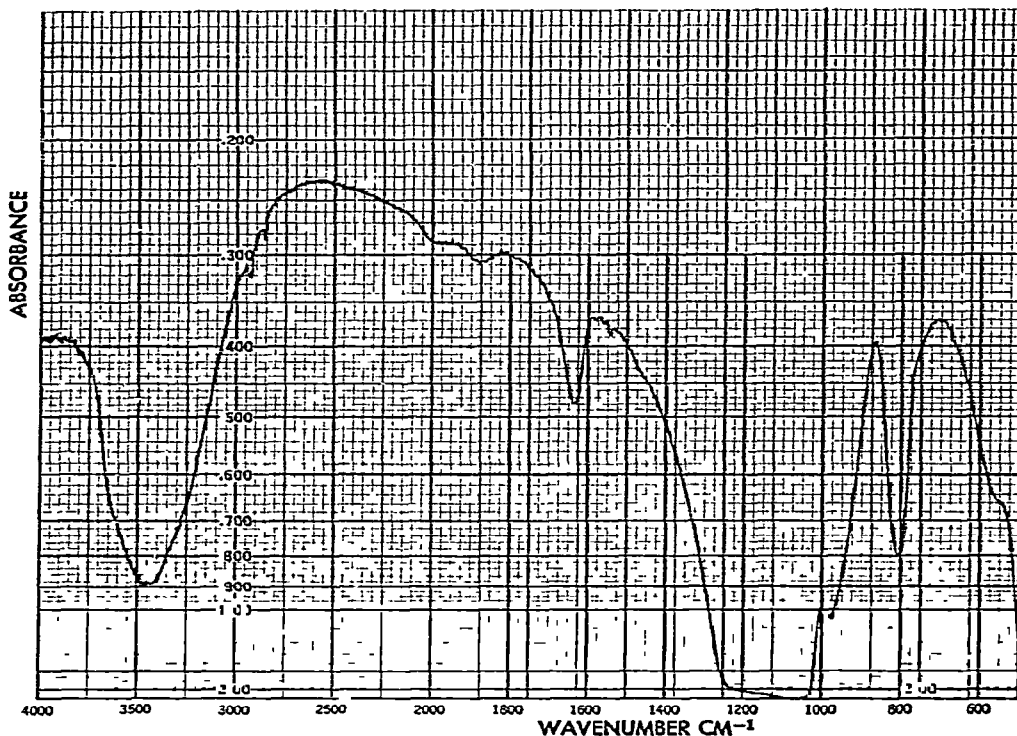


Fig. 3. Inf.ared spectra of silica gel.

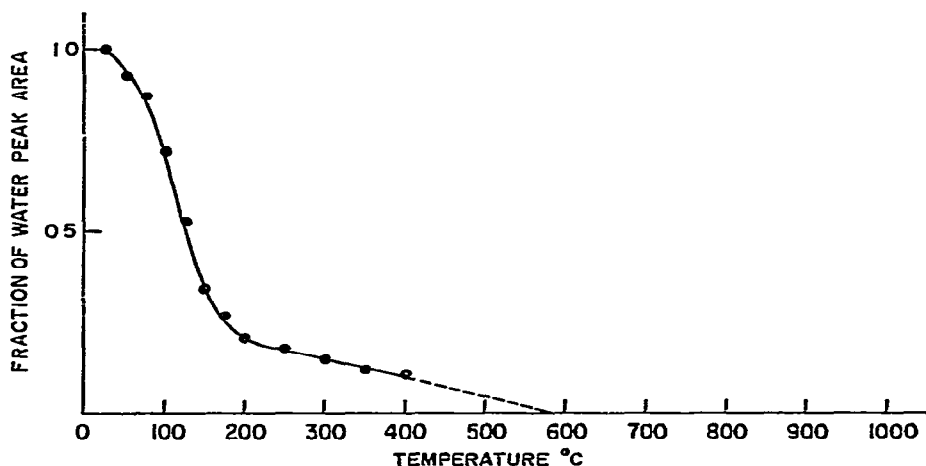


Fig. 4. Graph of relative area of water adsorption peaks between 4000 and 2000 cm^{-1} for silica gel heated at different temperatures.

From the IR spectra shown in Fig. 3 it is seen that the absorption band between 3000 and 4000 wavenumbers is broad and is characteristic of hydroxyls from water. Similar absorption would be expected by silanol groups. However, at 600°C this absorption peak disappears, and it has been shown⁸ that there are still significant

numbers of silanol groups remaining. It would appear, therefore, that the absorption between 3000 and 4000 wavenumbers was likely to result from strongly hydrogen-bonded water only.

It is a possibility, however, that the water lost between 350°C and 700°C was caused by the formation of siloxyl groups from closely associated silanol groups, and this possibility at this point has still not been eliminated. It is also possible, although highly unlikely, that such types of silanol groups could show an absorption between 3000 and 4000 wavenumbers, whereas the more stable silanol groups may not. If the water evolved at these intermediate temperatures arose from silanol groups, however, this would be because due to their spacial arrangement they were unstable and readily formed the siloxyl groups which would then be the more stable structure. It follows, therefore, that such a loss of water would be irreversible. The more stable siloxyl groups would not readily react again with water to reform the unstable silanol groups. If, on the other hand, the loss of water at these intermediate temperatures resulted from the evolution of hydrogen bonded water, then the process would be readily reversible, and if the material was exposed to water vapor under equilibrium conditions, water would be adsorbed by hydrogen bonding on those sites where it had been lost. Temperatures of 300°C and 400°C being required to release hydrogen bonded water, at first sight, appear unreasonably high. However, many other sources of hydrogen-bonded water such as water of crystallization which is bonded in the crystal structures requires such temperatures to release it from the crystals. For example, uranium sulfate [$U(SO_4)_2 \cdot 4H_2O$] loses four molecules of water at 300°C, zinc arsenate [$ZnHAsO_4 \cdot 4H_2O$] loses one molecule of water at 327°C and thorium sulfate [$Th(SO_4)_2 \cdot 9H_2O$] loses all nine molecules of water at 400°C. At the extreme ytterbium chloride ($YbCl_2 \cdot 6H_2O$) loses its six molecules of water at 865°C¹⁵.

It follows, therefore, that the water lost between 200°C and 1000°C by the silica gel should be investigated for reversibility. As a result the following experiments were carried out.

The reversibility of water adsorbed on a thermally treated silica gel

Approximately 1 g of silica gel equilibrated in an atmosphere of 50% humidity was heated to 135°C for 2 h, and the loss of weight was determined. The sample was then heated to 200°C for 2 h and the loss again recorded. The sample was then wetted with water that had been purified by passage through a reversed-phase chromatographic column and allowed to stand overnight (16 h). The sample was then heated to 135°C again for 2 h and again the loss of weight recorded. This process was repeated increasing the temperature by 50° intervals after each stage, the loss of weight of the silica was measured and then re-equilibrated with water and heated to 135°C and again the net weight loss measured. The results obtained are shown as percentage loss in weight against temperature in Fig. 5. The upper curve is a loss on heating to the different temperatures, the lower curve is the loss after subsequent rehydration with water. It is seen that up to 850°C with subsequent rehydration after heating, re-adsorption of water occurs in a reversible manner. Subsequent to this temperature when the silanol groups are being rapidly eliminated (between 850°C and 1050°C), the amount of water adsorbed on rehydration progressively decreases. In Fig. 6 the difference between the two curves in Fig. 5 is plotted against temperature. The curve represents the amount of water that can be re-adsorbed after heating to a

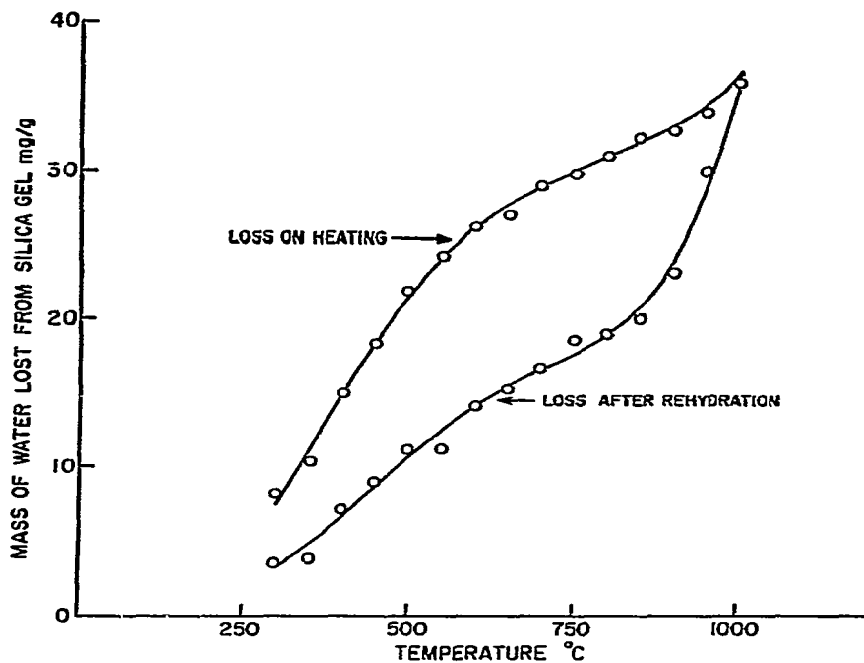


Fig. 5. Graph of water lost on heating and rehydration against temperature.

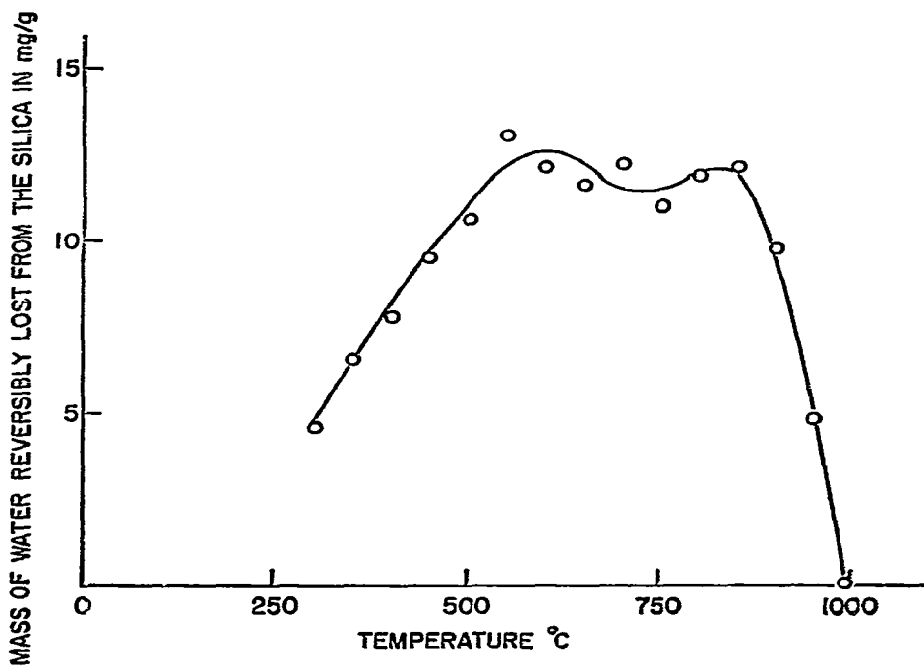


Fig. 6. Graph of mass of water lost reversibly from silica gel against heating temperature.

given temperature. It is seen that a maximum is reached at about 500°C which compares with the maximum water loss in Fig. 2 at 420°C. It follows that part of the water lost at intermediate temperatures, viz., between 350 and 700°C, is indeed reversible and appears to consist largely of hydrogen-bonded water.

The relationship between silanol group loss and heating temperature of the silica gel

The silanol content of the silica gel was determined by exhaustive reaction with dimethyloctylsilyl chloride after heat treatment of the gel at given temperatures. Due to the fact that some of the silanol groups would be in pores inaccessible to the silyl reagent, the extent of reaction would not be directly *equivalent* to the total number of silanol groups remaining on the silica. However, changes in the dimethyloctyl content of the silica will be directly *proportional* to the total number of silanol groups that remain on the silica after thermal treatment. It follows that such a process permits the extent of siloxyl formation with temperature to be followed on a relative basis.

Approximately 150 mg of silica gel were heated to the appropriate temperature in a platinum crucible for 90 min. The silica was then allowed to cool in a desiccator over phosphorus pentoxide. The silica sample was then divided approximately into two halves and rapidly transferred to two phials (capacity 2 ml), and 1 ml of a 25% (v/v) solution of dimethyloctylsilyl chloride in xylene added carefully with a dropper to each of the phials which were then sealed in a blow pipe flame. The phials were then heated in an oven at 125°C for 5 days. It was previously established that heating the phials for longer periods than 5 days produced no further reaction. After the 5 days had elapsed, the phial was opened with a glass file and the contents filtered under vacuum on a fine scintered filter, washed with 1.5 ml of xylene followed by 1.5 ml of acetone and then twice with 1.5 ml of methanol. The residual silica was then dried at 80°C under vacuum and examined in two ways.

(1) The carbon content of each duplicate sample was determined by microanalysis, and the carbon taken as the average value obtained for each of the duplicate samples. The results obtained are shown as curves relating the average carbon content to the temperature at which the silica was heated prior to reaction in Fig. 7.

(2) Equal quantities from each pair of duplicates were mixed, and about 2 mg added to 300 mg of potassium bromide which was pressed into a disc at a pressure of 10,000 kg/cm². The IR absorption between 3000 cm⁻¹ and 2800 cm⁻¹ wavenumbers was measured and a typical spectrum is shown in Fig. 8. The respective peaks on the chart for the methyl and methylene groups were cut out and weighed. The results plotted as peak mass in mg per mg of sample against the temperature to which the silica had been heated prior to reaction are shown in Fig. 9.

It is seen that the scatter of the results from the IR examination is far greater than that obtained by microanalysis; thus, the latter results have to be given more credence. Both methods clearly indicate that silanol groups are not lost until the silica has been heated to about 450°C, and even at 750°C only about 25% of the original silanol groups have been converted to siloxyl groups. This agrees well with the results shown in Fig. 3.

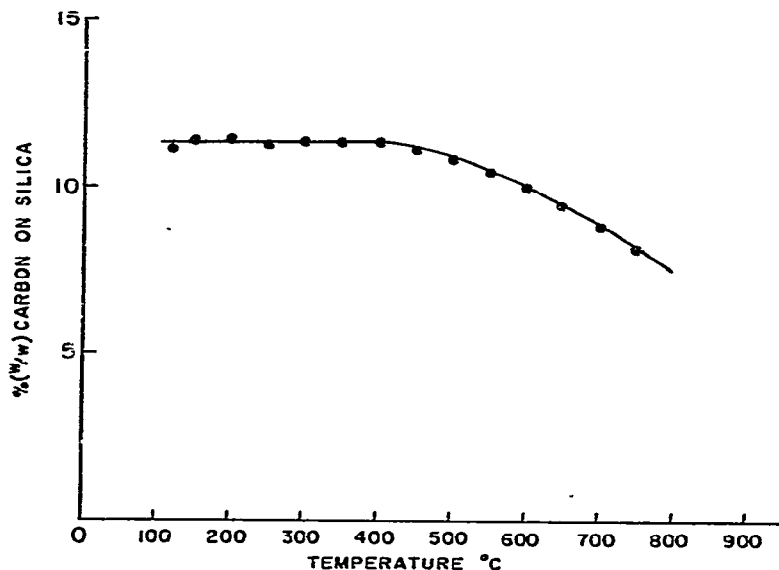
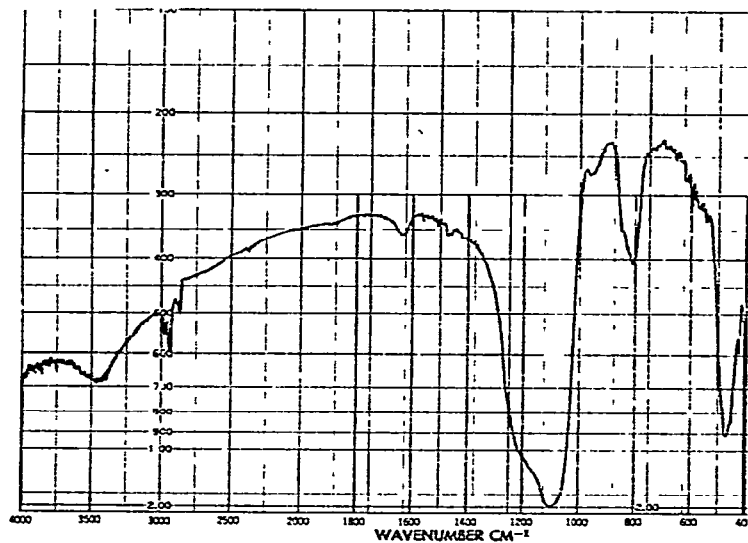
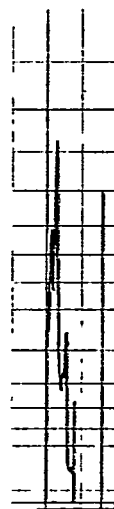


Fig. 7. Graph of % (w/w) carbon content of silica against temperature of activation for different silica samples reacted with dimethyloctylsilyl chloride.



Transmission Spectra



Amplified Adsorption Spectra

Between 2700 and 3000cm⁻¹

Fig. 8. Infrared spectra showing CH₂ and CH₃ stretching bands for a dimethyloctyl bonded phase.

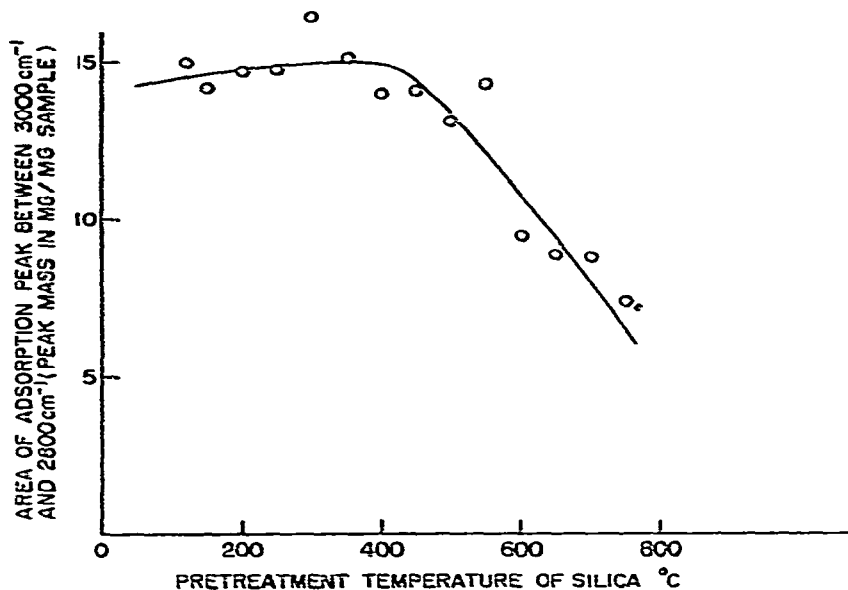


Fig. 9. Graph of adsorption peak area for methyl and methylene groups (3000 cm^{-1} through 2800 cm^{-1}) taken as peak mass per mg of silica against pretreatment temperature of silica.

CONCLUSIONS

Multilayer adsorption of water on silica gel which has been suggested by Anderson and Wickersheim¹, Mitchell² and Linsen³ has been substantiated. Two layers of water have been identified with certainty, and three or even four appear to be highly likely. The precise manner in which water is adsorbed onto the surface is not known, but a likely form is shown schematically in Fig. 10. It should be emphasized

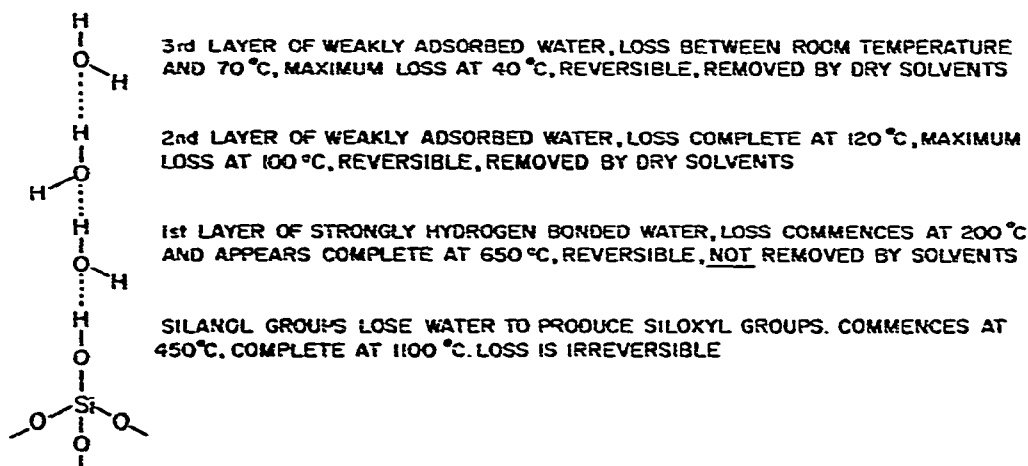


Fig. 10. Schematic impression of multilayer formation of water on silica gel.

that this diagram does not portend to give a real impression of the spatial distribution of the hydroxyl groups but is merely a diagrammatic representation of the multilayer formation. The contemporary impression of the nature of the surface of silica gel has been summarized by Wren¹⁶ from the many publications on the subject, and much of the work demonstrated in this paper has shown that the model described by Wren in many instances is incorrect. In view of this, the conclusions arrived at from this work will be contrasted where appropriate against the description of silica gel given by Wren. The third weakly held layer is lost at a maximum rate from the surface at about 35°C, and is completely removed at 70°C. This layer can be removed when the silica is washed with dry solvents. The second layer still weakly held is also completely removed by heating to 120°C and, as with the third layer, is also completely removed by dry solvents. The first layer is very strongly held by hydrogen bonding and does not commence to leave the surface until a temperature of 200°C is reached and is not completely removed until about 650°C. This is in conflict with the summary by Wren when he states all free water can be removed by heating to 170°C and where he also states that silica gel is fully activated as an absorbent if devoid of free water. If the silica gel is only activated by heating to a temperature of 200°C or by solvent treatment, the loosely bound second and third layers of water only are removed, but the first layer of strongly hydrogen-bonded water remains. Thus, it is water hydrogen bonded to each silanol group that is the interacting moiety on the surface of the silica gel. Thus, the active silica is not devoid of free water but is devoid of only loosely bound water with strongly bound water remaining. It follows that the solvent layer (monolayer for non-polar solvents and bilayer for polar solvents) formed when the silica gel is in contact with the mobile phase is interacting with the first layer of hydrogen bonded water and not the silanol groups themselves. Thus, bilayers of polar solvents such as ethyl acetate or alcohol are complimentary to the second and third layers of water that are found under equivalent conditions and are probably produced in the same way.

The silanol groups are not converted to siloxy groups until the silica gel is heated to 450°C, and even then the decomposition is slight. Significant loss of silanol groups does not appear to take place until 750°C, at which temperature 75% of the original silanol groups still remain. The removal of the silanol groups has been confirmed to be irreversible. This also is in conflict with the results of other worker's conclusions as summarized by Wren where he states that at temperatures above 170°C condensation of silanol groups starts to occur, liberating fixed water, and, in fact, the decomposition of silanol groups does not start until 400°C. The results described in this paper also refute the conclusions that water lost above 170°C is irreversible. It is interesting to note that from Table I the first layer of water and the water evolved from the condensation of the silanol groups constitute 3.78% (w/w) of the silica or 0.0378 g/g of silica. The hydrogen bonded water layer, therefore, constitutes about 0.0252 g/g of silica, which is equivalent to $8.5 \cdot 10^{20}$ molecules of water per g of silica. It is also interesting to compare this figure with the results obtained in Part I⁴ and Part II⁵ of this series of papers on interactions on the surface of silica gel. The value of $8.5 \cdot 10^{20}$ molecules/g of silica compares well with the mean number of non-polar solute molecules per g of the same silica (*viz.*, $6.40 \cdot 10^{20}$ molecules/g) for monolayer formation previously determined⁵ for the same silica gel. The difference is accounted for by those silanol groups that were contained in pores inaccessible to the solvent. The

value of $8.5 \cdot 10^{20}$ also compares well with the mean number of polar solvent molecules per g of the same silica for each layer of a bilayer system (*viz.*, $6.9 \cdot 10^{20}$ molecules/g). If the mean maximum carbon content of the silica reacted with dimethyloctylsilyl chloride (11.37%, w/w) is converted to molecules per gram of silica which is equivalent to the number of silanol groups reacted, it is found that $5.71 \cdot 10^{20}$ molecules are present on the surface. Thus, if a value of $8.5 \cdot 10^{20}$ silanol groups per gram of silica is taken as the maximum number of dimethyloctyl groups that could be placed on the surface, then the silanization proceeded to about 67% completion. Thus, 67% of the silanol groups were available to the silanyl reagent and have been reacted. It is also interesting to note from Table I that the loss of water on heating to 100°C appears equivalent to about 2.0 layers of water, assuming a single layer is equivalent to 2.52% (w/w) water on the silica gel. Thus, a third layer of water in the system examined is confirmed. Three or more layers of water adsorbed on the silica gel may completely fill the smaller pores of the silica and thus establish the beginning of the so-called "condensation effect".

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