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SOLUTE–SOLVENT INTERACTIONS ON THE SURFACE OF SILICA GEL. II

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SUMMARY

The interactions of solute and solvent on silica gel have been further examined and include adsorption isotherms for non-polar and polar solvents. The formation of a solvent bilayer on the surface of silica gel when using hydrogen-bonding polar solvents is further substantiated, and alternative explanations involving inhomogeneous site activity and steric hindrance are shown not to explain the bilayer formation. It is concluded that when polar-modifying solvents are employed in liquid chromatography at low concentrations, solutes interact with a primary layer of polar solvent without displacing the solvent. At higher concentrations solutes interact with the primary layer, displacing solvents in the second layer, but do not interact directly with the silica gel surface itself. However, for solutes eluted at high k' values or solutes that have a polarity similar to that of the modifying solvent, competition with the primary layer can take place. Under these circumstances, the solute interacts directly with the silica gel surface.

INTRODUCTION

In a previous paper[1], solute–solvent interactions on the surface of silica gel were examined. It was demonstrated that when a polar solvent mixture was used as a mobile phase, the solute did not compete with the polar modifying solvent for the silica gel surface, but that it interacted with the solvent layer itself to form a double layer. This sorption process by which the solute interacted with the layer of polar solvent on the silica gel appears to apply generally to all cases where the polar modifying solvent was capable of hydrogen bonding with the silica surface. Under these circumstances, competition by the solute for the surface occupied by the solvent only occurred when the solute had a polarity similar to that of the modifying solvent and/or where the solute was eluted at a k' value of 20 or more. These conclusions were drawn from experiments that demonstrated bilayer adsorption of polar solvents took place on the surface of silica gel and that any solute interacting with the silica gel surface interacted with the adsorbed layer of solvent and did not displace it unless eluted at a high k' value or had a polarity similar to that of the solvent.

Recently, alternative explanations have been put forward[2] to explain the isotherms that could be described by bilayer formation in an attempt to re-establish the

solute–solvent competition process to explain the retention of solutes on silica gel under all chromatographic conditions. In one case, it was suggested that the silica gel surface was inhomogeneous and contained two types of adsorption sites, high activity and low activity. A bilayer-type isotherm was exhibited because the high-activity sites were filled first and subsequently the low-activity sites. This explanation of the bilayer formation was, in fact, withdrawn[2], but at least it is theoretically possible and thus requires examination. A second proposal was that hydrogen-bonded solvents were sterically restricted and, therefore, only permitted half of the first layer to be formed. The second layer was, therefore, a type of mezzanine layer that was excluded from the surface by the rigidly held semi-monolayer. Under such conditions it was suggested that the solute was adsorbed as the second part of the monolayer; when this mezzanine layer was complete, the solute would then compete with any solvent in this mezzanine layer and displace it.

In this paper, both of these alternative explanations are examined and further experiments are reported which show that they are invalid. Further evidence demonstrating bilayer formation of polar solvent and the solute interaction with the polar solvent monolayer as opposed to the displacement of the adsorbed solvent is put forward in a conclusive manner.

THEORETICAL

There are two processes that have been suggested to explain the interaction of a solute with the surface of silica gel, namely, the competition process and the sorption process. The competition process is depicted in Fig. 1. The polar solvent component of the mobile phase, for example, ethyl acetate in n-heptane, is considered to form a layer over the surface of the silica gel. All solute molecules, shown as X in the diagram, compete with a molecule of ethyl acetate on the surface, displace it, and interact directly with the silica gel surface. This mechanism is considered by the proponents of the theory to describe all solute retention interactions irrespective of the k' value of the eluted solute or its polarity relative to that of the polar solvent. For example, the process would be expected to explain the retention of the relatively non-polar solute anisole eluted at a k' of 2.4 with a mobile phase composition of 0.35% ethyl acetate in n-heptane.
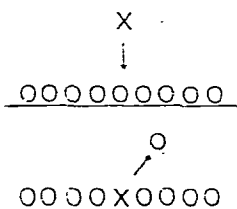
Fig. 1. The competition process. O, Solvent molecule; X, solute molecule.

The second process suggested to explain solute retention on the surface of silica gel is sometimes called the sorption process, but unfortunately this implies a single phenomenon that explains all solute behavior on silica gel irrespective of the nature of the solute eluted in a similar manner to the competition process. In fact, no single

process can describe the retention characteristics of solutes throughout the entire k' range of elution. The nature of the silica gel surface in contact with a polar solvent contained in an inert solvent such as n-heptane is shown in Fig. 2A and B. In Fig. 2Aa the conditions are depicted where the second layer of solvent is scarcely formed due to the concentration of the polar solvent being low and in the order of 1–3 %. Under these conditions, solute molecules having a polarity less than that of the polar solvent will sorb directly on to the surface of the first layer of the polar solvent with no competition and no displacement of the polar solvent. This is depicted in Fig. 2Ab. If the solute has a polarity similar to that of the polar solvent so that it would be eluted at a high k' value, then competition can take place and the polar solvent can be displaced[1]. Such a solute would be eluted at k' value of 20 or more. In Fig. 2Ba the conditions are depicted where the second layer of solvent has been well formed, and this occurs when the polar solvent is present at concentrations of the order of 10–20 % (w/v) in the nonpolar solvent. Under these conditions, a molecule of solute will compete with a molecule of polar solvent in the second layer only, displace it, and adsorb on the primary layer of solvent as shown in Fig. 2Bb. The process outlined above has been supported by carefully designed experiments demonstrating bilayer formation in polar, hydrogen-bonding solvents and the adsorption of solutes onto the primary layer without displacement of the polar solvent[1].
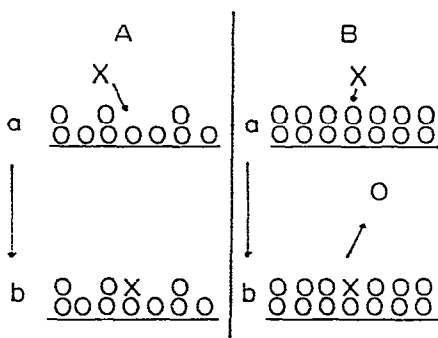

Fig. 2. The sorption process. O, Solvent molecule; X, solute molecule.

INHOMOGENEITY OF THE ACTIVE SITES

One alternative explanation for the bilayer isotherm behavior that was put forward and that would still permit the competition process to explain solute retention was as follows. It was suggested that there were two types of sites, high activity and low activity, and the "first layer" formed by the polar solvent was formed solely on the high-activity sites. The "second layer" formed on the low-activity sites, thus producing a bilayer adsorption isotherm. This situation is depicted in Fig. 3A. If the second layer was formed, then the solute molecule competed with the solvent molecule in the second layer, displaced it, and adsorbed again on a low-activity site. This alternative explanation is not unreasonable as one could imagine the high-activity sites consisted of silanol groups and the low-activity sites silanol groups which had water hydrogen bonded to them. It is well known that such a situation can exist in silica gel. To prove or disprove this alternative explanation, it is necessary to make the silica gel

homogeneous in site activity and to determine the adsorption isotherm under these conditions. If a bilayer adsorption isotherm is still maintained, then this could not be explained by site inhomogeneity and two layers must indeed be formed on the surface.
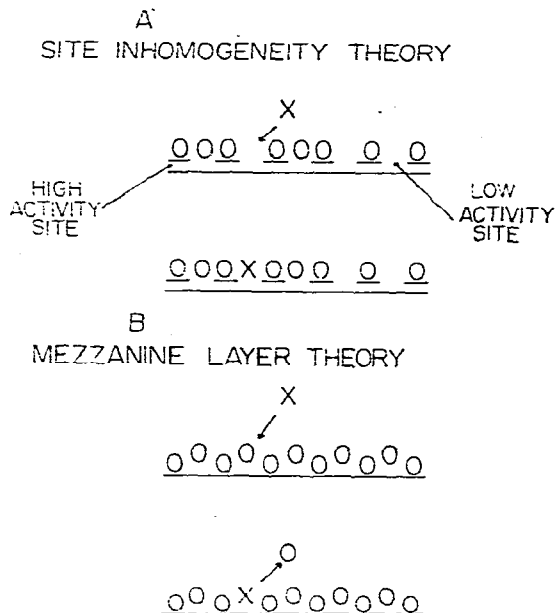

Fig. 3. (a) Site inhomogeneity theory; (b) mezzanine layer theory. ◯, Solvent molecule; X, solute molecule.

MEZZANINE LAYER FORMATION

If the polar solvent molecules were indeed hydrogen bonded on the surface of the silica gel, it has been suggested[2] that some immobilization or steric hindrance occurs on the surface and that bilayer formation consists of a two-part monolayer adsorption. The first layer formed was construed to be rigidly held, but the surface was incompletely covered owing to steric hindrance. It was further suggested that the second layer was layed down either by interacting with the already adsorbed solvent or by long-distance interactions with the silanol groups fitting between the molecules of the previous layer but not actually reaching the surface of the silica gel. This situation is depicted in Fig. 3B. If the mezzanine layer has not been completely formed, it was concluded that the solute molecules would interact with the lower layer and help to build up the mezzanine layer, and thus no polar solvent molecule would be displaced. If the mezzanine layer, however, was nearly complete, it was thought that a solute molecule could compete with this mezzanine solvent molecule, displace it, and become part of the mezzanine layer itself. This alternative explanation, in the authors' opinion, is highly unlikely, but again it needs to be addressed in order to establish the type of solute–solvent interaction that takes place on the surface of silica gel. It should be pointed out at this stage that if indeed the steric hindrance does take place resulting from regular hydrogen bonding to the silanol group and a mezzanine layer is formed, then one would expect the first layer to contain a considerably lower number of mole-

cules of a hydrogen-bonded solvent on the surface, relative to the number of non-polar, nonsterically hindered solvents such as butyl chloride or chloroform, which would be expected to cover the surface completely. In a similar manner, the second or mezzanine layer would also contain a fraction of the number of molecules contained in a saturated monolayer. The total number of molecules in the two layers from a bilayer isotherm would therefore be expected to equal roughly the total number of molecules in the monolayer found from a non-polar solvent which exhibited a Langmuir type of isotherm.

MEASUREMENT OF ADSORPTION ISOTHERMS OF ETHYL ACETATE ON SILICAS THAT HAVE INHOMOGENEOUS AND HOMOGENEOUS SITE ACTIVITY

The preparation of silica gel with varying degrees of site homogeneity has been described[3] and it has been shown that silica heated above 700°C provides homogeneous surface where the retention of solutes is linearly related to the amount of hydroxyl groups present. It was therefore decided to prepare a series of silica gels with different site homogeneity by heating samples to various temperatures for 8 h. Eight-gram samples were heated at 200, 300, 400, 500, 600 and 700 °C respectively for 8 h and then cooled in a desiccator containing phosphorus pentoxide. Thermogravimetric analysis curves were then obtained for a sample of each of the silica gels so treated, and the curves are shown in Fig. 4. It is seen that the loss on heating at 1000 °C of silica gel previously heated at 500 °C is less than half that for silica gel heated at 200 °C. Further, silica gel heated at 700 °C has a loss on heating less than one-eighth that heated at 200 °C. Attempts were made to obtain the IR spectra for the silica heated at the different temperatures. However, it was found that in making the potassium bromide pellet the silica gel rapidly adsorbed water and the spectra changed with the time taken to press the pellet. An alternative procedure was therefore used in which the pellet was made using 10 mg of silica gel pressed with 300 mg of potassium bromide into a 1-cm disc at 10,000 kg/cm². The pellet was then heated to the various temperatures for 3 h,
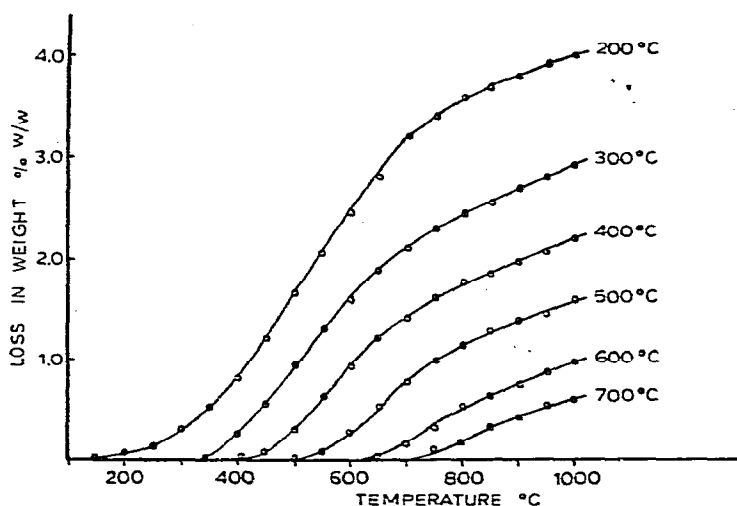

Fig. 4. TGA curves for silica gel heated for 3 h at different temperatures.

and immediately after removal from the oven and cooling in a desiccator containing phosphorus pentoxide, the IR spectra were measured.

The IR spectra obtained are shown in Fig. 5. It can be seen that the absorption between 3000 and 4000 wavenumbers progressively decreases as the silica gel temperatures rises and that at 600 °C there is very little absorption in this region, and at 700 °C it has virtually disappeared. This is surprising because Hockey[4] stated that the infrared absorption between 3000 and 4000 wavenumbers can be related directly to the silanol groups on the silica gel. At 700 °C there is no absorption in this wavelength range but the silica gel still has very significant retentive capacity and a considerable number of hydroxyl groups are still present. It is, therefore, to be concluded that the absorption between 3000 and 4000 wavenumbers is largely due to the hydroxyl groups of the chemically bound water, which has been shown to be no longer present at temperatures in excess of 600 °C (ref. 3). The adsorption isotherms for ethyl acetate in n-heptane on the silica gels heated at 200 °C, 500 °C and 700 °C were determined in the manner previously described[1].
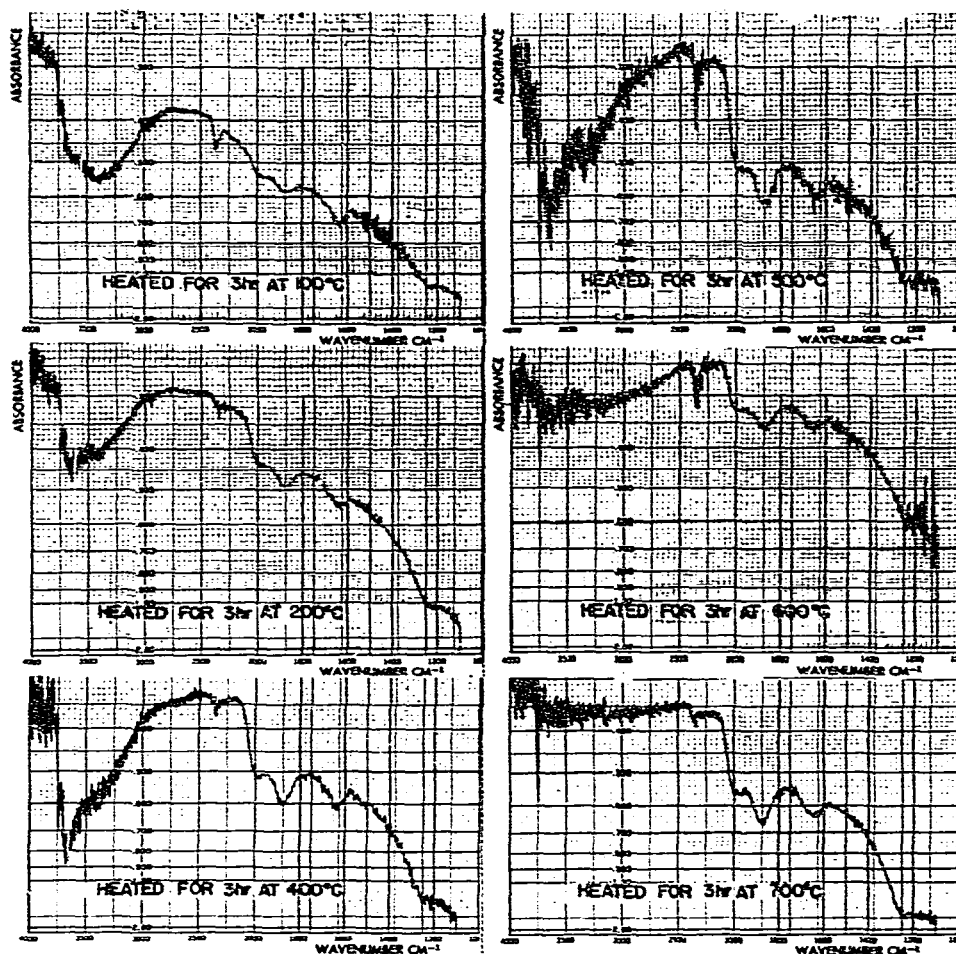

Fig. 5. IR spectra of silica gel heated to different temperatures in KBr discs. A 10-mg amount of silica gel was pressed with 300 mg of KBr into a 1-cm disc at 10,000 kg/cm^2.

The results obtained are shown in Fig. 6, relating mass of adsorbed ethyl acetate per gram of silica gel to the concentrations of ethyl acetate in the mobile phase. The results were curve fitted to both the Langmuir isotherm function for monolayer adsorption and to the isotherm function for bilayer adsorption[1]. It was found that the data did not correlate with the monolayer adsorption isotherm but gave an excellent correlation with the bilayer adsorption isotherm. The curves shown in Fig. 6 are the theoretical curves from the curve fit procedure and the points are experimental. It can be seen that even for silica gel heated at 700°C, where there is no hydrogen-bonded water remaining on the surface and where it has been previously shown that the surface is homogeneous, giving a linear relationship between hydroxyl content and solute retention, the bilayer adsorption function still applies and two layers of solvent molecules are being built up on the surface. It follows that the suggested possibility of high and low-activity sites causing the bilayer-type adsorption isotherm to be formed is false and, where the solvent can hydrogen bond to the surface, true bilayer adsorption occurs.
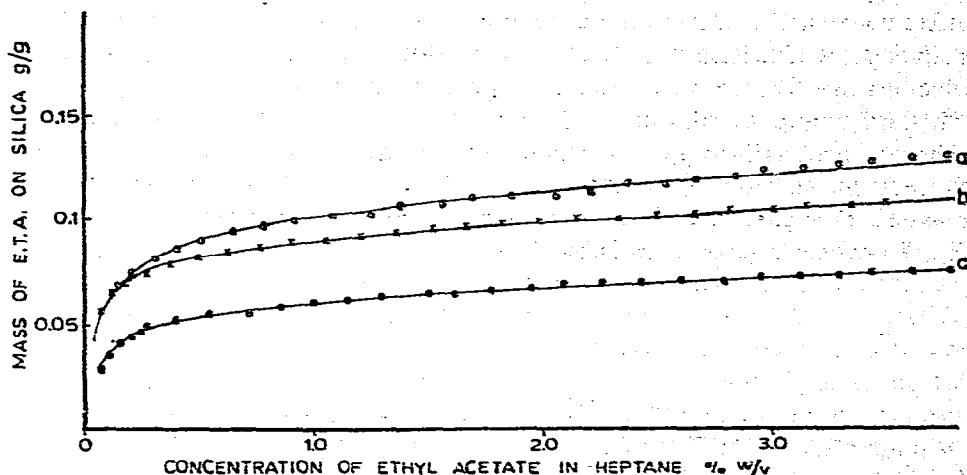

Fig. 6. Adsorption isotherms for ethyl acetate on silica gel heated at different temperatures. Data curve fitted to the bilayer Langmuir-type function $y = A - (A + ABx/2)/(1 + Bx + Cx^2)$. (a) Partisil 20 heated to 200°; (b) Partisil 20 heated to 500°; (c) Partisil 20 heated to 700°.

QUANTITATIVE AND QUALITATIVE NATURE OF THE BILAYER FORMED ON THE SURFACE OF SILICA GEL

Many attempts have been made to assess quantitatively the nature of an adsorbed layer of solvent molecules on the surface of silica gel. In the past this has been done by taking the surface area as given by the BET test, and by making certain assumptions, calculating the probable surface area of the adsorbed molecule when in contact with the surface of the silica gel. The result arrived at in this way is dependent on a number of assumptions. Assumptions are sometimes made that the area that could be explored by the small nitrogen molecule could also be explored by the much larger solvent molecule; that is, that the solvent molecules were in no way excluded from any surfaces areas seen by the nitrogen. Assumptions are also made on the effective sur-

face area of the nitrogen molecule and further still on the effective surface area of the
adsorbed solvent molecule. Varying these assumptions within reasonable limits can
give widely different values for the number of molecules adsorbed on the surface. The
mezzanine layer theory requires that the surface is only roughly half covered with
solvent molecules which are sterically hindered and the second layer that fits between
the primary layer completes the surface coverage. Thus, for the mezzanine layer
theory to be valid, the primary layer would be expected to contain approximately half
as many molecules as the primary layer of an adsorbed non-polar solvent obeying the
Langmuir single layer-type isotherm. By making the necessary assumptions as to the
pertinence of the surface area given by the BET test and the size of the molecules ad-
sorbed on the surface, a value for the primary layer of the mezzanine-type system can
indeed be made to equal approximately half that of the adsorbed monolayer of non-
polar solvents. However, by making alternative assumptions for the magnitude of the
above physical properties the contrary can be proved and it is therefore necessary to
obtain a quantitative evaluation of the surface layer without employing controversial
assumptions.

It is first necessary to determine experimentally the amount of solvent on the
surface of a silica gel when there is no hydrogen bonding and thus no steric hindrance,
and the molecules are free to move and thus produce a maximum coverage of the
surface. Such data would be obtained from the adsorption isotherms of non-polar
solvents on the surface of silica gel that provided monolayer coverage only. Such data
have already been published[1] for chloroform and butyl chloride and data for a third
non-polar solvent, benzene, have been obtained in the same manner. The data are
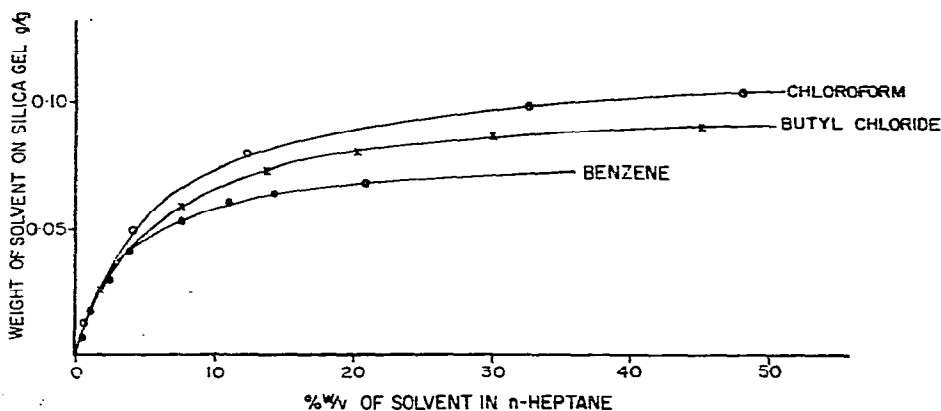shown in Fig. 7 and summarized in Table I.

Fig. 7. Langmuir adsorption isotherms for three non-polar solvents. Data curve fitted to the
Langmuir function $y = x/(A + Bx)$.

It can be seen that the data fit the Langmuir isotherm function with correlation
coefficients of 0.99 and better, and in Fig. 7 the curves are obtained from the theoreti-
cal curve fit and the points are experimental. The reciprocal value of constant B from
Table II gives the maximum mass of solvent on the surface for complete monolayer
coverage. By dividing this figure by the molecular weight and multiplying by Avo-
gadro's number, we find the total number of molecules on the surface of 1 g of the silica

TABLE I

RESULTS FROM CURVE FITTING THE DATA FROM THE ISOTHERMS FOR BENZENE, BUTYL CHLORIDE AND CHLOROFORM ON SILICA GEL TO THE LANGMUIR FUNCTION $y = x/(A + Bx)$

Solvent	Index of determination	A	B	Mass of solvent on surface when completely covered (g/g)	Molecular weight of solvent	No. of molecules on surface when completely covered
Benzene	0.999	45.54	12.30	0.0813	78.1	$6.3 \cdot 10^{20}$
Butyl chloride	0.999	56.60	9.59	0.1043	92.6	$6.8 \cdot 10^{20}$
Chloroform	0.996	50.56	8.48	0.1179	119.4	$6.0 \cdot 10^{20}$
					Mean:	$6.4 \cdot 10^{20}$

gel. This is shown in the last column in Table II. It can be seen that all three solvents, although providing significantly different masses adsorbed per gram of silica gel and having significantly different molecular weights, give closely the same figure for the total number of molecules on the surface of 1 g of silica gel. The mean value was taken as the maximum number of molecules that could be adsorbed on the surface when there was no steric hindrance to inhibit complete coverage.

It was now necessary to determine the mass of solvent per gram of silica gel to form the monolayer of a bilayer system for some solvents that are known to hydrogen bond to the surface of the silica gel. In a previous paper[1] only one solvent, ethyl acetate, was investigated and so data for a further two polar solvents were obtained using the same method; the solvents chosen were methyl ethyl ketone and tetrahydrofuran. The results obtained were curve fitted to the bilayer function and the results are shown in Fig. 8, with the data summarized in Table I. The curves in Fig. 8 are the theoretical curves from the curve-fit procedure and the points are experimental.

It can again be seen that the data fit very closely the bilayer adsorption isotherm function and it was found that the data did not fit the simple monolayer Langmuir adsorption isotherm function. From the constants A in Table I, which was the total mass of solvent adsorbed when both layers were complete, the mass of solvent comprising the first layer was obtained by dividing the constant A by 2. The mass of sol-

TABLE II

RESULTS FROM CURVE FITTING THE DATA FROM THE ISOTHERMS OF TETRAHYDROFURAN, METHYL ETHYL KETONE AND ETHYL ACETATE ON SILICA GEL TO THE BILAYER FUNCTION $y = A - (A + ABx/2)/(1 + Bx + Cx^2)$

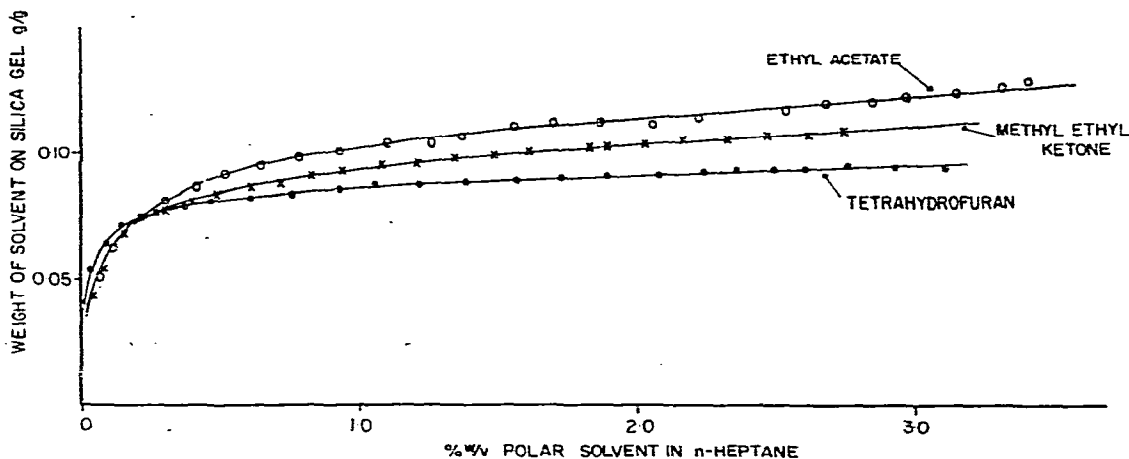| Solvent	A	B	C	Mass of solvent on surface when completely covered by a monolayer only (g/g)	Molecular weight of solvent	No. of molecules on surface when completely covered by a monolayer only
Ethyl acetate	0.1931	14.0	1.96	0.0965	88.1	$6.6 \cdot 10^{20}$
Methyl ethyl ketone	0.1724	22.6	3.29	0.0862	72.1	$7.2 \cdot 10^{20}$
Tetrahydrofuran	0.1660	39.5	2.38	0.0830	72.1	$6.9 \cdot 10^{20}$
					Mean:	$6.9 \cdot 10^{20}$

Fig. 8. Adsorption isotherms for different polar solvents on silica gel. Data curve fitted to the bilayer Langmuir-type function $y = A - (A + ABx/2)/(1 + Bx + Cx^2)$.

vent that completely covered the surface in the monolayer was then divided by the molecular weight of the solvent and then multiplied by Avogadro's number. The data for the three solvents are shown in the last column in Table II. It can be seen that close agreement is again obtained for each solvent and that the average value of the number of molecules occupying the monolayer only of the bilayer system was $6.9 \cdot 10^{20}$. This figure agrees well with the values obtained for the non-polar solvents that obeyed the Langmuir isotherm function for monolayer coverage and thus shows that the same number of molecules is contained in the monolayer of a non-polar solvent system as in the first layer of a bilayer solvent system. It follows that the hydrogen bonding of the polar solvent of the silica gel does not sterically hinder the development of the first layer of the bilayer system and the first layer contains the same number of molecules as the monolayer of a non-polar solvent. Thus, a mezzanine layer cannot exist and, in fact, the bilayer system is a simple double layer, with each layer containing the same number of molecules.

DISCUSSION AND CONCLUSIONS

The results obtained from the determination of the adsorption isotherms of ethyl acetate on silica gels that have been subjected to different thermal treatments indicate that the bilayer type Langmuir adsorption isotherms do not result from site inhomogeneity. Past work[3] has clearly shown that silica gel heated to temperatures in excess of 600°C has a very homogeneous surface where retention characteristics are linearly related to hydroxyl content. Thus, the bilayer adsorption isotherm truly indicates that two layers of solvent molecules are adsorbed on the surface, the second layer being superimposed on the first. From the adsorption isotherms, determined for both non-polar solvents and polar solvents that could hydrogen bond to the silica gel, it has been shown that for monolayer coverage the surface contains about $6.5 \cdot 10^{20}$ molecules. Close agreement is obtained for the number of molecules on the surface with monolayer coverage for the three non-polar solvents, as well as the three polar solvents. It should also be noted that all the solvents used have roughly the same

TABLE III

MOLECULAR DIAMETERS AND MOLECULAR AREAS OF SOLVENTS EXAMINED

Solvent	Mean molecular diameter[5] (Å)	Mean molecular area[5] (Å²)	Mean molecular area[6] (Å²)
Butyl chloride	6.9	37.4	35.6
Chloroform	6.3	31.2	28.6
Benzene	6.6	34.2	33.7
Ethyl acetate	6.8	36.3	34.1
Methyl ethyl ketone	6.6	34.2	31.9
Tetrahydrofuran	6.4	32.2	29.9

mean molecular diameters and surface areas, as shown in Table III. The values in Table III were obtained using the following equation[5]:

$$\text{Mean molecular diameter (Å)} = \left(\frac{MW \cdot 3.16}{d} \right)^{1/3}$$

where MW = molecular weight of solvent and d = density of solvent. This procedure assumes that the molecules can be assumed to be spheres; therefore, it should be emphasized that the values in Table III cannot be considered absolute but only relative. Included in Table III are surface areas measured from the silhouettes of molecular models taken in three dimensions in the manner described by Amoore[6]. It is seen that both methods give similar values and that the values for all compounds are approximately the same.

It follows that the mezzanine layer theory resulting from incomplete coverage of the primary layer due to steric hindrance cannot explain the bilayer adsorption function obtained for polar solvents. In a previous paper[1] it was shown that employing the mobile phase consisting of 0.35% (w/v) of ethyl acetate, up to 60 mg/g of dimethoxybenzene, eluted at $k' = 10.5$, could be adsorbed without displacement of any ethyl acetate. At a concentration of 0.35% (w/v) of ethyl acetate in n-heptane, 88% of the primary layer is formed, which contains $5.8 \cdot 10^{20}$ molecules of ethyl acetate.

The 60 mg of dimethoxybenzene is equivalent to $2.6 \cdot 10^{20}$ molecules and thus the total number of molecules on the silica gel is $8.4 \cdot 10^{20}$. From the bilayer adsorption isotherm a monolayer would contain $6.6 \cdot 10^{20}$ molecules and, therefore, there is an excess of $1.8 \cdot 10^{20}$ molecules that have formed a bilayer consisting of solute molecules. The solute molecules are, therefore, interacting with the monolayer of ethyl acetate and not with the silica gel.

From the results obtained in this paper and that published previously[1], the following can confidently be concluded:

(1) Polar solvents can hydrogen bond to activated silica gel to form a double layer, the extent of coverage depending on the concentration of the organic polar solvent. At low concentrations and up to about 1% (w/v) of polar solvent, the first layer is being formed. At concentrations above 1%, the formation of the first layer is nearly complete and the second layer is being formed.

(2) Solutes that are moderately retained or have polarities less than that of the polar solvent do not displace the primary layer. At low concentrations of polar

solvent where the second layer is incompletely formed, they interact directly with the primary layer, forming a second layer of solute molecules. At higher concentrations where significant amounts of the second layer of solvent are formed, solute molecules can displace solvent molecules of the second layer and interact with the surface of the first layer, but do not displace solute molecules from the first layer and cannot interact with the silica gel surface itself.

(3) For solutes that are strongly retained or have polarities similar to that of the solvent, displacement of the primary layer may take place and the solute molecules can thus interact directly with the silica gel surface.

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