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## SOLUTE-SOLVENT INTERACTIONS ON THE SURFACE OF SILICA GEL

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### SUMMARY

The nature of the silica gel surface when in contact with different solvents was examined and it was found that for non-polar, non-hydrogen-bonding solvents, a monolayer of solvent is adsorbed on the surface. For polar or hydrogen-bonding solvents, at low concentrations of polar solvent a monolayer is formed, but at higher concentrations extensive bilayer coverage is produced. For polar solvents under conditions of monolayer coverage only, and for solutes eluted up to a  $k'$  value of 10, it appears that during chromatographic development the solutes interact with the polar monolayer but do not displace it. Under conditions where bilayer coverage exists and again for solutes eluted up to a  $k'$  value of 10, the solute appears to displace the bilayer only and interacts directly with the monolayer without displacing it.

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### INTRODUCTION

Silica gel is the most commonly used stationary phase in high-performance liquid chromatography (HPLC); it is used, *per se*, directly as a column packing and also forms the basis of the various bonded phases that are now available. In fact, it would be difficult to imagine modern liquid chromatography, in its present state of development, without the essential ingredient, silica gel. Despite the extensive use of silica gel in chromatography over many decades, the exact nature of the interactions that occur at the surface, which result in its unique retention characteristics, is still largely a matter of conjecture. In order to identify the interactions that occur at the surface of silica gel, which result in solute retention, a number of questions have to be asked and answers found to them:

(1) When silica gel is in contact with the eluting solvent, is the surface freely available to the solute or is it coated with a layer of solvent?

(2) If the surface is coated with a layer of solvent, how thick is it? How does the extent of surface coverage depend on the nature of the interacting solvent and its concentration in the mobile phase?

(3) If a layer of solvent covers the surface, does the solute interact with the solvent layer or does it displace the solvent and interact directly with the surface? Can both types of surface interaction occur?

(4) If solutes can either interact with the solvent layer or displace the solvent

and interact with the surface, what factors determine the type of interaction that will predominate?

In this work, experiments were designed and carried out to answer some of these questions and to elucidate the nature of the interactions that can occur on the surface of a silica gel stationary phase during chromatographic development. The work was divided into two parts. Firstly, the nature of solvent interaction with the silica gel surface was investigated, employing both stoichiometric experiments and a chromatographic approach. Secondly, the interaction of solutes with a solvent-silica gel system was examined, again using both stoichiometric methods and a chromatographic procedure.

### SOLVENT-SILICA GEL INTERACTIONS

In order to investigate the nature of the silica gel surface when in contact with different solvents, present over a range of concentrations, it is helpful to determine the form of the adsorption isotherms. The adsorption isotherms of isopropanol, tetrahydrofuran, ethyl acetate and *n*-butyl chloride were determined, employing different concentrations of each solvent in *n*-heptane, by the following procedure.

A known mass of silica gel (Partisol 20), that had been heated to 200° for 4 h to remove physically adsorbed water and having a surface area of 408 m<sup>2</sup>/g as determined by the B.E.T. procedure from nitrogen adsorption was placed in a 70-ml flask and 50 ml of *n*-heptane were added. All solvents used in both the adsorption isotherm experiments and subsequent chromatographic experiments were dried over alumina activated at 300°. All solvents so treated were found to be anhydrous with respect to the Karl Fischer Test. The flask was sealed with a PTFE-lined serum cap and 100 μl of the solvent were added by means of a syringe. The mixture was equilibrated for 30 min at 25 ± 0.1° in a thermostat with continuous shaking, then allowed to stand for 20 min in the bath to permit the silica gel to settle. Duplicate samples were withdrawn, a known mass of *n*-decane was added as an internal standard and the sample subjected to gas chromatographic (GC) analysis. A Hewlett-Packard 5710A gas chromatograph was employed, fitted with an automatic sample injector and computer data-processing facilities. The chromatograph was operated at 70°. A 9-ft. column was used, packed with 10% PEG 20M on Chromosorb W. After each sample had been taken for analysis, a further 100 μl of the solvent were added and the process was repeated. From the concentration of solvent in the solvent mixture determined by GC, the volume of the solvent mixture and the mass of solvent added, the mass of solvent adsorbed by the stationary phase was calculated. Careful corrections were made for volume changes resulting from the addition of the solvent and the removal of the samples, together with the volume change on mixing when appropriate. The results obtained, shown as curves relating concentration of solvent on the silica gel in milligrams per gram and concentration of solvent in *n*-heptane in percent (w/v) for the four solvents are shown in Fig. 1. It can be seen that isopropanol is rapidly adsorbed by the silica gel and tends to flatten out at a solvent concentration of less than 1%. The adsorption of ethyl acetate and tetrahydrofuran is less rapid but nevertheless the curve also tends to flatten at concentrations between 5 and 10%. *n*-Butyl chloride, however, behaved differently in that the isotherm tended to become flat only at solvent concentrations in excess of 40% (w/v) in the solvent mixture. It

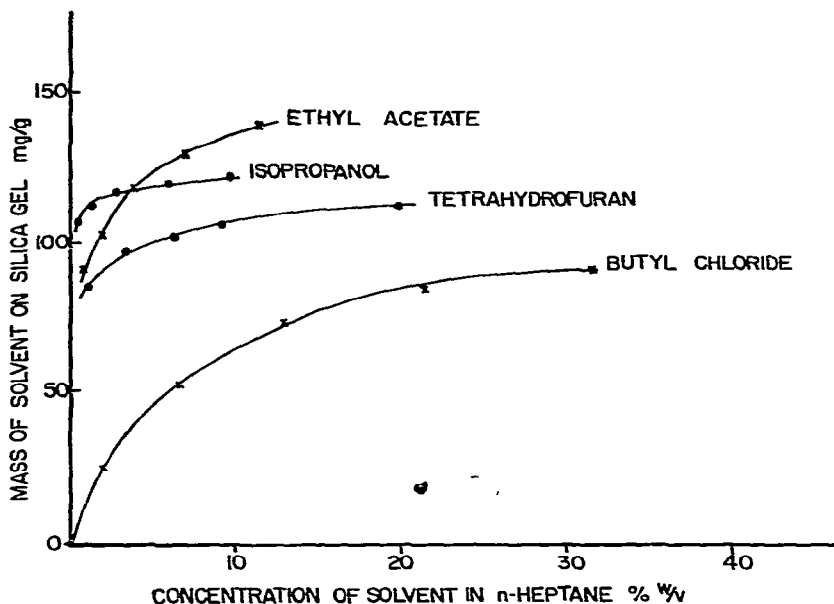


Fig. 1. Adsorption isotherms for *n*-butyl chloride, ethyl acetate, tetrahydrofuran and isopropanol on silica gel in *n*-heptane.

should be noted that the results for *n*-butyl chloride closely fitted the Langmuir function for single-layer adsorption whereas the curves for the other three solvents did not. This divergence will be discussed in detail later.

#### GRADIENT ELUTION EFFECTS

The rapid adsorption of polar solvents on to silica gel at low concentrations in the solvent mixture has a very significant effect on gradient elution procedures, particularly when using solvents with widely different polarities. This effect, which causes solute displacement in normal gradient chromatographic development, has been discussed theoretically<sup>1</sup> but has not been demonstrated experimentally. The adsorption isotherms of *n*-butyl chloride, ethyl acetate and isopropanol were therefore determined for the sequential addition of the three solvents in *n*-heptane using the same analytical procedure as previously described. Firstly, 1.4 g of *n*-butyl chloride was added in small portions sequentially to 10 g of silica gel in equilibrium with 100 ml of *n*-heptane. Using the GC analysis procedure, the concentrations of *n*-butyl chloride in the *n*-heptane and on the silica gel were determined and calculated after each addition. After 1.4 g of *n*-butyl chloride had been added, 1.5 g of ethyl acetate was then added, also in small increments, and the concentrations of both solvents on the silica gel and in *n*-heptane were determined. Finally, 2 g of isopropanol were added in the same manner and the distribution of all three solvents in the system was determined. The results obtained are shown in Fig. 2 as curves relating the mass of each solvent on the silica gel and in the solvent mixture against the total mass of solvent added. It can be seen from Fig. 2 that the concentrations of *n*-butyl chloride

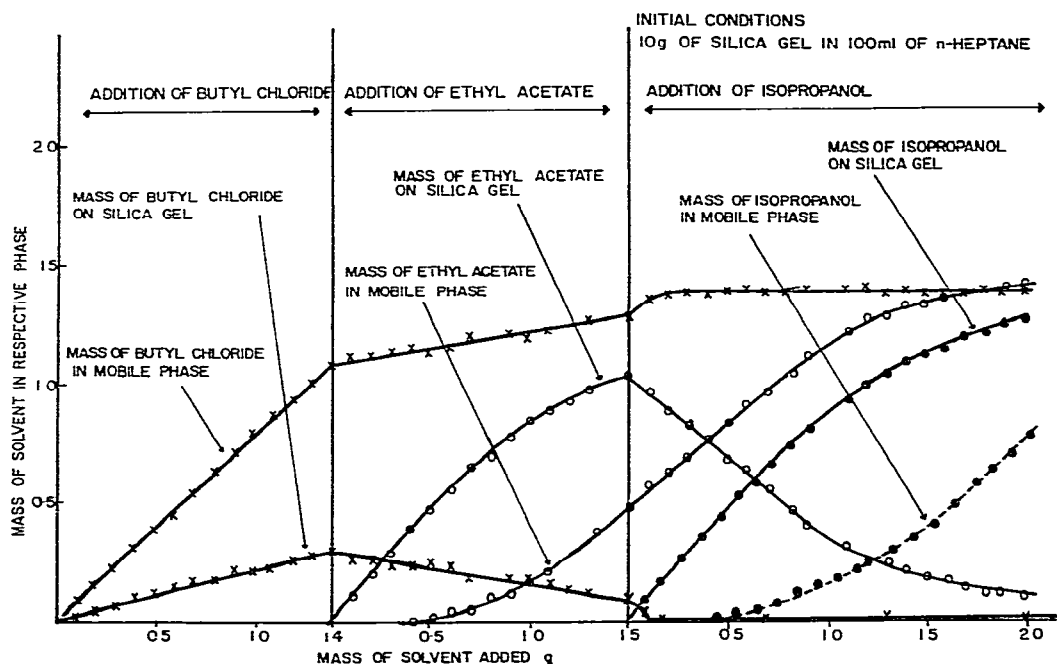


Fig. 2. Mass distribution of mixtures of *n*-butyl chloride, ethyl acetate and isopropanol in contact with silica gel.

on both the silica gel and in the solvent appear to increase linearly with the amount of *n*-butyl chloride added. This apparent linearity arises from the fact that the values are at the lower end of the Langmuir adsorption isotherm for *n*-butyl chloride and therefore tend to be linear. On addition of ethyl acetate, however, the mass of *n*-butyl chloride decreases on the silica gel and increases in the solvent mixture as the ethyl acetate is adsorbed on the silica gel, causing displacement. It should be noted that the mass of ethyl acetate in the solvent is negligible until about 0.5 g of ethyl acetate has been added to the system. It should also be noted that even when the concentration of ethyl acetate on the silica gel is 0.1 g/g, some *n*-butyl chloride still resides on the surface, suggesting that the *n*-butyl chloride is forming a double layer. On addition of isopropanol, the *n*-butyl chloride is rapidly displaced from the silica gel and remains solely in the solvent mixture. It should also be noted that as the isopropanol is added, the concentration of isopropanol on the silica gel increases almost linearly during the addition of the first gram of solvent. Simultaneously, the mass of ethyl acetate increases linearly in the solvent and falls linearly from the silica gel, suggesting an almost stoichiometric displacement of ethyl acetate from the silica gel by isopropanol. It should also be noted that there is no significant amount of isopropanol in the solvent until about 0.5 g of isopropanol has been added. Again, it should be observed that even when there is a concentration of *ca.* 0.12 g/g of isopropanol on the silica gel, there is still a significant amount of ethyl acetate on the surface, suggesting the formation of a double layer. In Fig. 3, the same results are presented but in the more conventional form of curves relating concentration of

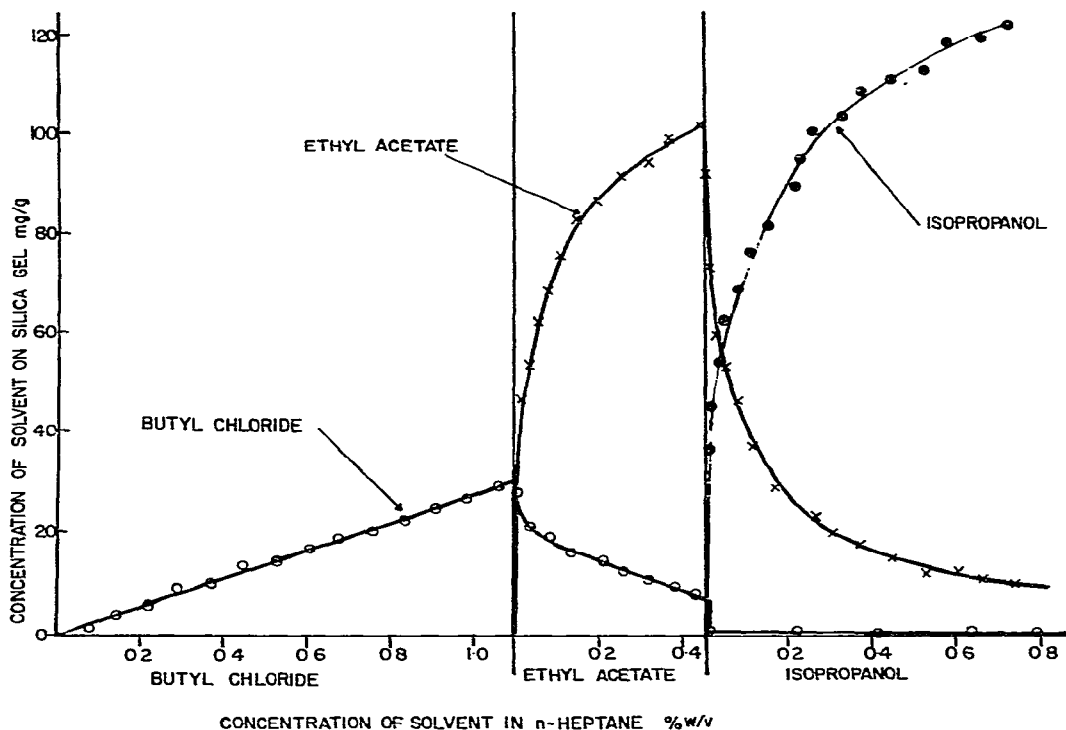


Fig. 3. Composite adsorption for *n*-butyl chloride, ethyl acetate and isopropanol on silica gel.

solvent on the stationary phase to the concentration of solvent in the mixture. The displacement effects of the more polar solvents are clearly shown and the residual concentrations of *n*-butyl chloride and ethyl acetate on the surface in the presence of ethyl acetate and isopropanol, respectively, are more apparent.

#### ADSORPTION ISOTHERM FOR NON-POLAR SOLVENTS

The adsorption isotherm for *n*-butyl chloride and chloroform obtained by the method previously described are shown in Fig. 4. The adsorption isotherm for single-layer coverage of a surface, as developed by Langmuir, takes the following form:

$$N_A = \frac{c}{A + Bc} \quad (1)$$

where  $N_A$  is the surface area covered by the adsorbed monolayer of solvent,  $c$  is the concentration of the solvent in the solvent mixture and  $A$  and  $B$  are constants. In the original adsorption isotherm developed by Langmuir for the adsorption of gases on solids, the concentration  $c$  was replaced by  $P$ , the partial pressure of the adsorbed gas in contact with the surface. The partial pressure was employed because it was directly proportional to the number of gas molecules per unit volume and thus controlled the probability of a gas molecule striking the surface. In an analogous

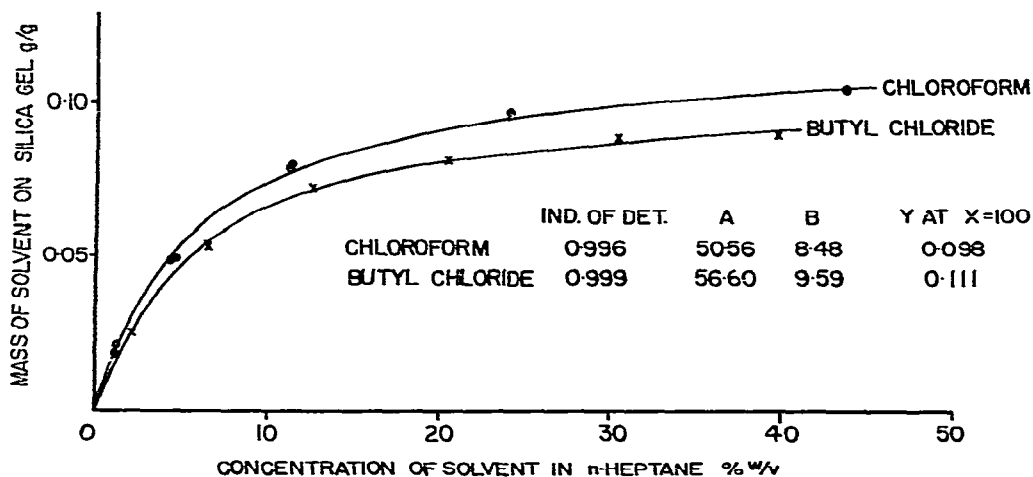


Fig. 4. Adsorption isotherms for chloroform and *n*-butyl chloride on silica gel. Data curve fitted to the function  $Y = X/(A + BX)$ . Ind. of Det. = index of determination.

manner, at constant temperature the concentration of the adsorbing solvent in the solvent mixture is also directly related to the probability of the molecule striking the adsorbing surface.

The results shown in Fig. 4 were curve-fitted to the function given in eqn. 1 and the curves shown are the theoretical values obtained from the curve-fit, which are seen to match closely the experimental data. The index of determination for chloroform and *n*-butyl chloride were 0.996 and 0.999, respectively, confirming that the isotherms are of the Langmuir type and that only a monolayer of adsorbed solute molecules is formed. Langmuir monolayer-type adsorption of solvents on silica gel appears to be confined to non-polar solvents and does not describe the adsorption isotherm of polar solvents or solvents that can form hydrogen bonds with the hydroxyl groups of the silica gel. It should be noted from Fig. 4 that when the surface of the silica gel is completely covered with a monolayer of chloroform and *n*-butyl chloride, *i.e.* when the concentration of solvent is infinite, there are 0.118 and 0.104 g/g on the surface of the silica gel, respectively. As the specific gravities of *n*-butyl chloride and chloroform are 0.886 and 1.483, respectively, the maximum concentration of solvent will be 88.6 and 148.3% (w/v), respectively. Inserting the values in eqn. 1 using the constants *A* and *B* from the curve-fit function, it can be calculated that there will be 0.098 and 0.113 g/g of *n*-butyl chloride and chloroform, respectively, on the surface of the silica gel when the pure solvents are employed as the mobile phase. This means that under these conditions, the two solvents would cover only about 95% of the available surface. This coverage applies only to the system at 25°.

The area covered by the solvent per gram of silica gel,  $a_s$ , can be calculated from

$$a_s = \frac{m}{M} \cdot N_a S$$

where *m* is the mass of solvent adsorbed per gram at complete coverage, *M* is the

molecular weight of the solvent,  $N_a$  is Avogadro's number and  $S$  is the effective surface area per molecule. The value of  $S$  was taken as the area, in square Ångstroms, in the form of a rectangle or square that would completely enclose molecular models (constructed to scale) of *n*-butyl chloride and chloroform. The area values for *n*-butyl chloride and chloroform determined in this way were 45.66 and 43.0 Å<sup>2</sup>, respectively. Employing the above equation, the areas covered by *n*-butyl chloride and chloroform were found to be 309 and 256 m<sup>2</sup>/g, respectively. These values are significantly lower than 408 m<sup>2</sup>/g as measured by the B.E.T. test. The difference can be accounted for by the fact that the molecules are in motion and thus the effective area of coverage per molecule will be significantly greater than that calculated by the method given above. Further, the smaller nitrogen molecule used in the B.E.T. test will have access to surfaces contained in pores that would exclude the larger molecules of chloroform and *n*-butyl chloride.

#### ADSORPTION ISOTHERM FOR POLAR SOLVENTS

Attempts to fit a Langmuir function to the isotherms for tetrahydrofuran, ethyl acetate and isopropanol shown in Fig. 1 proved that the isotherms were not Langmuir in type for monolayer coverage. The function describing the adsorption isotherm for double-layer coverage was therefore developed as follows. It should be pointed out that the development of the isotherm equation for double-layer adsorption is a simple extension of that used by Langmuir.

Let a solution of a polar solvent, at a concentration of  $c$  g/ml, be in equilibrium with a silica gel surface of unit area as depicted in Fig. 5. Under the conditions of equilibrium, let a monomolecular layer of  $N_1$  molecules and a bimolecular layer of

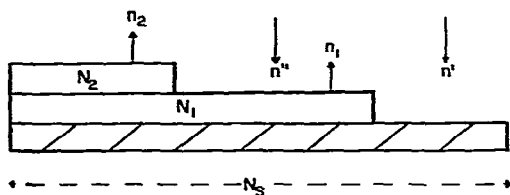


Fig. 5. Illustrations of bilayer adsorption.

$N_2$  molecules coexist. Let the maximum number of polar solvent molecules that can cover unit area of surface as a monomolecular layer be  $N_3$  and the number of molecules striking and adhering to the exposed silica gel surface and the exposed monolayer per unit time be  $n'$  and  $n''$ , respectively. If the numbers of molecules leaving the exposed monolayer surface and the bilayer surface per unit time are  $n_1$  and  $n_2$ , respectively: then under conditions of equilibrium

$$n' = n_1$$

and

$$n'' = n_2$$

At a given constant temperature

$$n' = a_1 c (N_s - N_1)$$

where  $a_1$  is a constant. Furthermore,

$$n_1 = b_1 (N_1 - N_2)$$

Equating  $n_1$  and  $n'$  and rearranging, we obtain

$$N_2 = N_1 \left( 1 + \frac{a_1}{b_1} \cdot c \right) - \frac{a_1}{b_1} \cdot c N_s \quad (2)$$

In a similar manner

$$n'' = a_2 c (N_1 - N_2)$$

and

$$n_2 = b_2 (N_2)$$

where  $a_2$  and  $b_2$  are also constants. Equating  $n_2$  and  $n''$  and rearranging, we obtain

$$N_2 = \frac{a_2 c N_1}{b_2 + a_2 c} \quad (3)$$

Equating eqns. 2 and 3, solving for  $N_1$  and letting  $g_1 = a_1/b_1$  and  $g_2 = a_2/b_2$ , we obtain

$$N_1 = \frac{g_1 (1 + g_2 c) N_s c}{(1 + g_1 c) (1 + g_2 c) - g_2 c} \quad (4)$$

Substituting for  $N_1$  from eqn. 4 in eqn. 2 to obtain an expression for  $N_2$  and simplifying:

$$N_2 = \frac{g_1 g_2 c^2 N_s}{(1 + g_1 c) (1 + g_2 c) - g_2 c} \quad (5)$$

Now the total number of molecules on the surface,  $N$ , will be given by

$$N = N_1 + N_2$$

Thus, substituting for  $N_1$  and  $N_2$  from eqns. 4 and 5 and simplifying:

$$N = \frac{g_1 c N_s (1 + 2g_2 c)}{1 + g_1 c + g_1 g_2 c^2}$$

Expressing as a partial fraction:

$$N = 2N_s - \frac{N_s (2 + g_1 c)}{1 + g_1 c + g_1 g_2 c^2}$$



As the number of molecules is directly proportional to the mass of solvent,  $N$  and  $N_s$  can be replaced by  $M$  and  $M_s$ , where  $M$  is the total mass of solvent adsorbed on the surface and  $M_s$  is the total mass of solvent constituting a monolayer. Thus

$$M = 2M_s - \frac{M_s(2 + g_1 c)}{1 + g_1 c + g_1 g_2 c^2} \quad (6)$$

or

$$M = A - \frac{(A' + ABc/2)}{1 + Bc + Dc^2} \quad (7)$$

where

$$A = 2M_s$$

$$B = g_1$$

$$D = g_1 g_2$$

i.e.

$$M_s = A/2$$

$$g_1 = B$$

$$g_2 = D/B$$

Owing to the limited number of points in the isotherm for ethyl acetate shown in Fig. 1, this work was repeated using the same technique but determining the isotherm over a concentration range of 0-4% of ethyl acetate in *n*-heptane. Twenty-six data points were obtained experimentally over this concentration range and the results obtained are shown in Fig. 6 as curves relating the mass of ethyl acetate adsorbed on the silica gel to the concentration of ethyl acetate in the mobile phase.

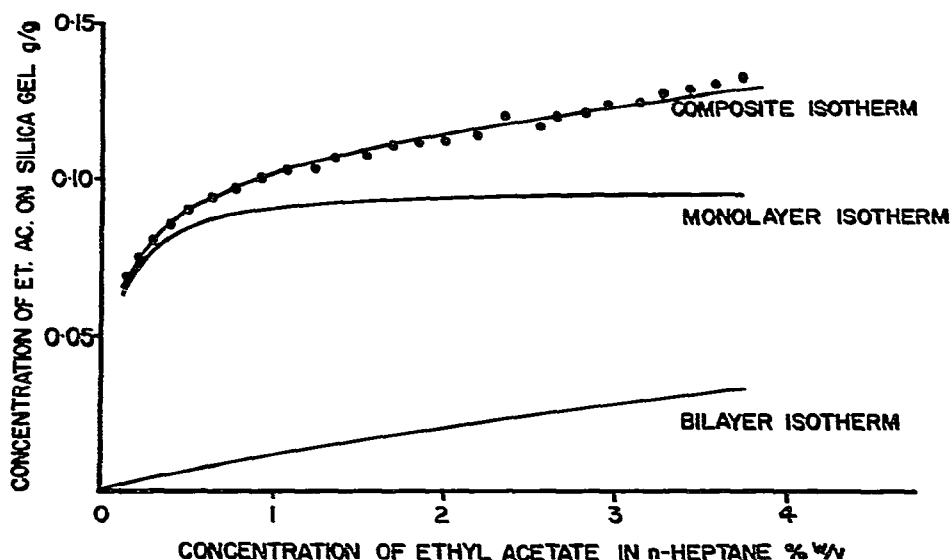


Fig. 6. Composite adsorption isotherm for ethyl acetate on silica gel. Data curve fitted to the bilayer Langmuir-type function  $Y = A - (A + ABx/2)/(1 + Bx + Cx^2)$ .

The points were curve-fitted to eqn. 7 and it can be seen that a close fit is obtained between the experimental points and the function that describes bilayer formation. It should also be stressed, however, that the points tend to fall slightly below the line between concentrations of 1 and 2.5% (w/v) of ethyl acetate in *n*-heptane and above 3% (w/v) they tend to lie above the theoretical line. There can be two reasons for this. Firstly, in the development of the theoretical equation it was assumed that the sites were homogeneous and all had the same activity. In practice, this is known not to be so and it is strongly suspected that there is a small proportion of sites that have significantly higher activity than the average. An alternative explanation for the slight discrepancy in Fig. 6 between the experimental points and the theoretical line is that it is possible that a third layer of ethyl acetate is formed on the silica gel. The experimental values used to construct the curve in Fig. 6 are included in Table I to permit workers to test the values for a trimolecular layer isotherm or to fit the results to alternative functions that they may feel appropriate. The constants found for *A*, *B* and *D* in eqn. 7 and the values for  $M_s$ ,  $g_1$  and  $g_2$  are also included in Table I. If it is

TABLE I

## ISOTHERM DATA FOR ETHYL ACETATE ON SILICA GEL

Constants of the function  $M = A - \frac{A + ABC/2}{1 + BC + DC^2}$ .  $A = 0.1931$ ;  $B = 14.0099$ ;  $D = 1.9601$ ;  $M_s = 0.0966$ ;  $g_1 = 14.0099$ ;  $g_2 = 0.1399$ .

*Concentrations of ethyl acetate*

<i>In mobile phase</i> <i>C</i> (% w/v)	<i>On stationary phases (g/g)</i>			
	<i>M</i>	( <i>Calculated</i> ) $M_c$	( <i>First layer</i> ) $M_c^I$	( <i>Second layer</i> ) $M_c^{II}$
0.1372	0.0697	0.0651	0.0639	0.0012
0.2047	0.0764	0.0741	0.0721	0.0020
0.3059	0.0813	0.0821	0.0789	0.0032
0.4074	0.0862	0.0872	0.0828	0.0045
0.5139	0.0908	0.0912	0.0855	0.0057
0.6464	0.0940	0.0949	0.0877	0.0073
0.7810	0.0971	0.0980	0.0892	0.0088
0.9248	0.0997	0.1007	0.0904	0.0104
1.0791	0.1018	0.1033	0.0913	0.0120
1.2552	0.1026	0.1059	0.0921	0.0138
1.3709	0.1060	0.1074	0.0925	0.0149
1.5584	0.1070	0.1097	0.0931	0.0167
1.6919	0.1101	0.1112	0.0934	0.0179
1.8638	0.1113	0.1131	0.0937	0.0194
2.0540	0.1114	0.1150	0.0940	0.0210
2.2092	0.1134	0.1165	0.0942	0.0223
2.5317	0.1167	0.1193	0.0946	0.0247
2.6650	0.1198	0.1204	0.0947	0.0257
2.8307	0.1213	0.1217	0.0948	0.0269
2.9593	0.1246	0.1227	0.0949	0.0278
3.1372	0.1254	0.1240	0.0951	0.0290
3.2914	0.1275	0.1251	0.0951	0.0300
3.4440	0.1295	0.1262	0.0952	0.0310
3.6154	0.1306	0.1273	0.0953	0.0320
3.7603	0.1332	0.1282	0.0954	0.0329

tentatively assumed that the number of molecules from the solvent striking the exposed surfaces, whether they be the bare silica gel surface or the monolayer, will be approximately equal, then the ratio of  $g_1$  to  $g_2$  will indicate the tenacity by which the first layer is held to the silica gel relative to that by which the second layer is held to the first layer. It can be seen from the results that the first layer appears to be held two orders of magnitude more strongly to the silica gel surface than the second layer is held to the ethyl acetate monolayer surface. This also suggests that when polar solvents that can form hydrogen bonds with the silica gel are employed at very low concentrations, the silica gel is, in fact, acting as a hydrogen-bonded phase. From the values shown in Table I for the constants in the curve-fitted equation, it can be seen that a single-layer coverage of ethyl acetate would be equivalent to a mass of 0.097 g/g. Using a value determined for the surface area of the ethyl acetate molecule of  $46.7 \text{ \AA}^2$  as previously defined, the surface coverage of the silica gel by the ethyl acetate can be calculated to be  $308 \text{ m}^2/\text{g}$ . This value is in agreement with the values obtained for chloroform and *n*-butyl chloride monolayer coverage. Employing eqns. 4, 5 and 6 and substituting values for  $M_s$ ,  $g_1$  and  $g_2$  as derived and shown in Table I, the individual isotherms for the monolayer and the bilayer can be calculated. The curves showing the formation of the monolayer and bilayer are included in Fig. 6. It can be seen that up to a concentration of 0.35% (w/v) of ethyl acetate in *n*-heptane, only the monolayer is being formed to any significant extent, the bilayer being a second-order effect. At 1% (w/v) of ethyl acetate in *n*-heptane, however, the monolayer is almost completely formed and any increase in ethyl acetate on the silica gel results from the formation of a second layer. As the specific gravity of ethyl acetate is 0.903, the pure solvent ethyl acetate would be equivalent to a concentration of 90.3% (w/v). At this concentration, using eqns. 4 and 5 it can be calculated that the monolayer is complete but the second layer is only 91% complete. This, of course, assumes that second-layer coverage will have the same surface area as the first layer, which may not necessarily be the case.

#### CHROMATOGRAPHIC SUPPORT OF MULTILAYER ADSORPTION

Single- or double-layer adsorption of a solute-solvent onto silica gel can be easily examined and confirmed by a chromatographic procedure. Consider the retention of *n*-butyl chloride in *n*-butyl chloride-*n*-heptane mixtures over a range of concentrations. Assume that *n*-butyl chloride is retained by an interaction with exposed silica gel surfaces:

$$V' = KN_B$$

where  $V'$  is the corrected retention volume,  $K$  is the distribution coefficient of *n*-butyl chloride between the *n*-butyl chloride-*n*-heptane mixture and silica gel and  $N_B$  is the area of the exposed silica gel surface. From the Langmuir adsorption isotherm given in eqn. 1,

$$N_B = N_A - \frac{N_A Ac}{1 + Ac}$$

where  $N_A$  is the total surface area of the silica gel,  $A$  is a constant and  $c$  is the concentration of *n*-butyl chloride in the mobile phase. Thus

$$N_B = \frac{N_A + N_A A c - N_A A c}{1 + A c} = \frac{N_A}{1 + A c}$$

and

$$V' = K N_B = \frac{K N_A}{1 + A c}$$

or

$$\begin{aligned} \frac{1}{V'} &= \frac{1 + A c}{K N_A} \\ &= B + D c \end{aligned}$$

or

$$\frac{1}{k'} = B' + D' c$$

It follows that if only monolayer coverage is possible, a plot of  $1/k'$  against  $c$  will give a straight line over all solvent concentrations where monolayer coverage is taking place. This is in accordance with the findings of Soczewiński<sup>2</sup>.

The values of  $k'$  for *n*-butyl chloride over a range of concentrations in *n*-heptane were determined at  $25 \pm 0.1^\circ$  employing a 25 cm  $\times$  4.6 mm I.D. column packed with Partisil 10 in conjunction with a refractive index detector. The results obtained are shown in Fig. 7 as the curve for  $1/k'$  against *n*-butyl chloride concentration. It can be seen that an excellent linear correlation is obtained over the entire concentration range examined, confirming the existence of a monolayer of *n*-butyl chloride on the silica gel up to a mobile phase consisting of 17.5% (w/v) of *n*-butyl chloride in *n*-heptane.

It should be pointed out that at a concentration of 17.5% (w/v) of *n*-butyl chloride in *n*-heptane, the  $k'$  value of *n*-butyl chloride was less than 0.1 and there was little retention, indicating the almost complete coverage of the silica gel surface by the *n*-butyl chloride. It can be calculated from the constants for the Langmuir equation given in Fig. 4 that at this concentration only 20% of the silica gel surface remains exposed.

With a solvent that can produce two layers on the surface of the silica gel, for example ethyl acetate, the curve relating  $1/k'$  for ethyl acetate against ethyl acetate concentration in the mobile phase would be different. For concentrations up to 0.5% (w/v) of ethyl acetate in *n*-heptane, the ethyl acetate would interact primarily with the exposed silica gel surface as relatively little double layer has been formed. Thus, between 0.0 and 0.5% (w/v) of ethyl acetate in *n*-heptane, a graph of  $1/k'$  against ethyl acetate concentration should give a straight line. Above 2% (w/v) of ethyl acetate in *n*-heptane, however, the monolayer has been almost completely formed, so that ethyl acetate is largely interacting with a primary layer of ethyl acetate on the silica gel

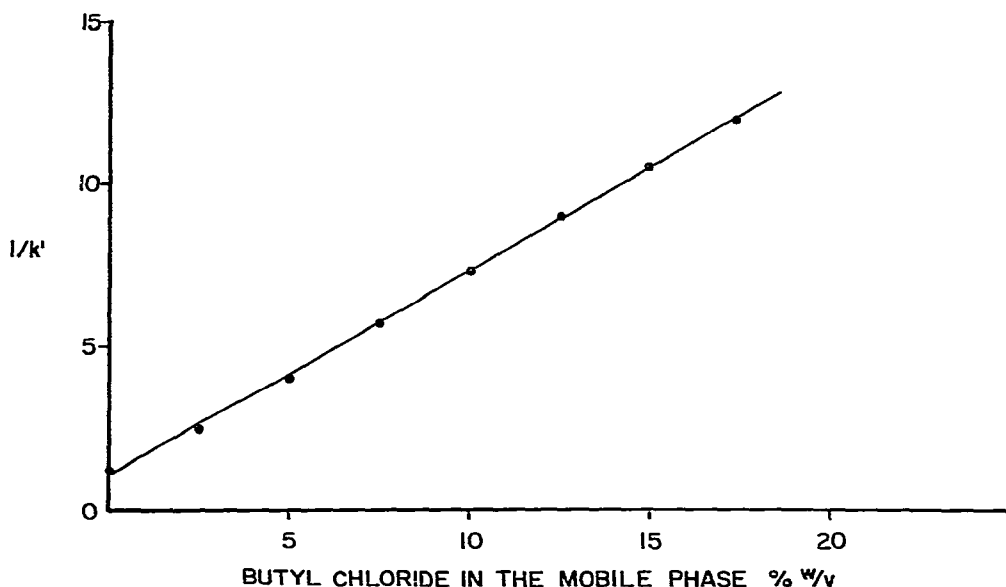


Fig. 7. Graph of  $1/k'$  for *n*-butyl chloride against concentration of *n*-butyl chloride in the mobile phase.

surface. Above 2% (w/v) of ethyl acetate, therefore, another straight line would be produced on plotting  $1/k'$  against ethyl acetate concentration but it would have a different slope to the previous one. The value of  $k'$  for ethyl acetate in ethyl acetate-*n*-heptane mixtures was determined in a manner similar to that described previously. In the upper part of Fig. 8, the curve relating  $1/k'$  for ethyl acetate against ethyl acetate concentration in *n*-heptane between 0 and 0.5% (w/v) is linear. Under these circumstances the ethyl acetate is interacting directly with the silica gel surface and as it becomes covered less surface is available and the retention and  $k'$  fall. Thus, the reciprocal function,  $1/k'$ , increases linearly to a point at which the concentration of ethyl acetate in *n*-heptane is 0.5% (w/v). In the lower curve a straight line is produced for  $1/k'$  plotted against ethyl acetate concentration in the range 1.5–20% (w/v). At 1.5% (w/v) the primary layer of ethyl acetate has been completely formed and thus ethyl acetate is now not interacting with the free silica gel surface but with the primary layer. As the primary layer builds up, less surface is available for the ethyl acetate to interact with and thus the retention volume falls and  $1/k'$  increases. The two linear functions shown in Fig. 8 clearly substantiate the stoichiometric methods, and at low concentrations a monolayer of ethyl acetate is formed whereas at high concentrations the second layer of ethyl acetate is deposited on the surface of the silica gel.

#### SOLUTE-SOLVENT-STATIONARY PHASE INTERACTIONS

The method of interaction of a solute with silica gel and the conditions under which the surface of the silica gel can be covered with a single or double layer of adsorbed solvent molecules remain to be identified. This can be achieved by examining the interaction of a series of solutes with silica gel under conditions such that only a

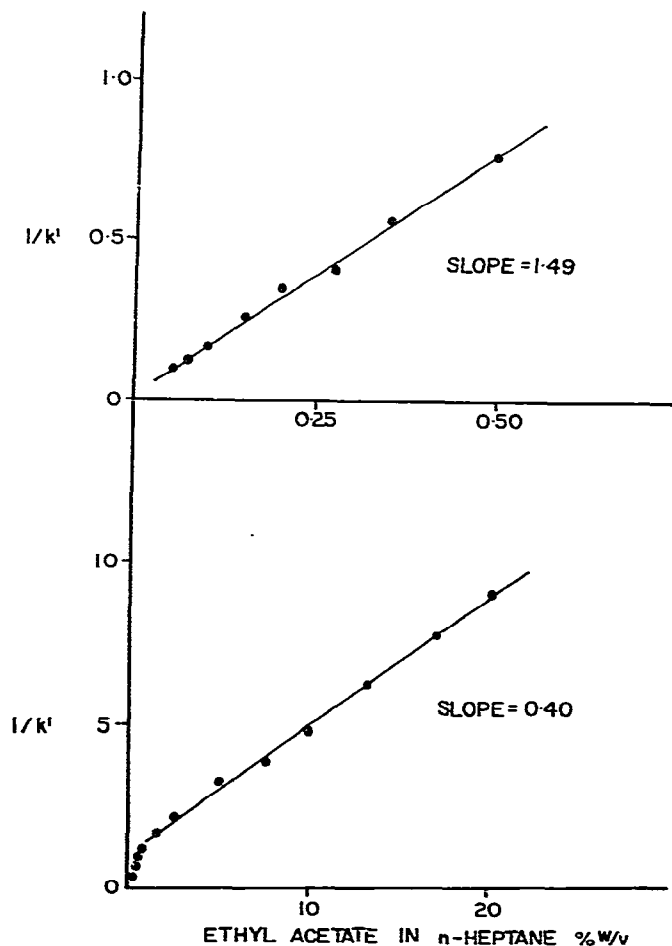


Fig. 8. Graphs of  $1/k'$  for ethyl acetate against concentration of ethyl acetate in the mobile phase.

monolayer of adsorbed molecules exists and a double layer predominates. If ethyl acetate is chosen as the polar component of the solvent, then from Fig. 4 it can be seen that at 0.35% (w/v) of ethyl acetate in *n*-heptane the monolayer of ethyl acetate on the silica gel is almost completely formed but only a small proportion of the surface is covered by a double layer. Conversely, at about 13% (w/v) of ethyl acetate in *n*-heptane the monolayer coverage is complete and the double layer coverage is becoming significant.

The possible displacement of ethyl acetate from silica gel by solutes was investigated by employing the stoichiometric procedure described previously. The flask containing 10 g of Partisil 20 was equilibrated with a 0.35% (w/v) solution of ethyl acetate in *n*-heptane, the solvent mixture analysed and the amount of ethyl acetate in the solvent mixture determined by GC. Solute were then added to the mixture in small increments and equilibrium was established after the addition of each amount of solute. The solute mixture was then analysed for both ethyl acetate

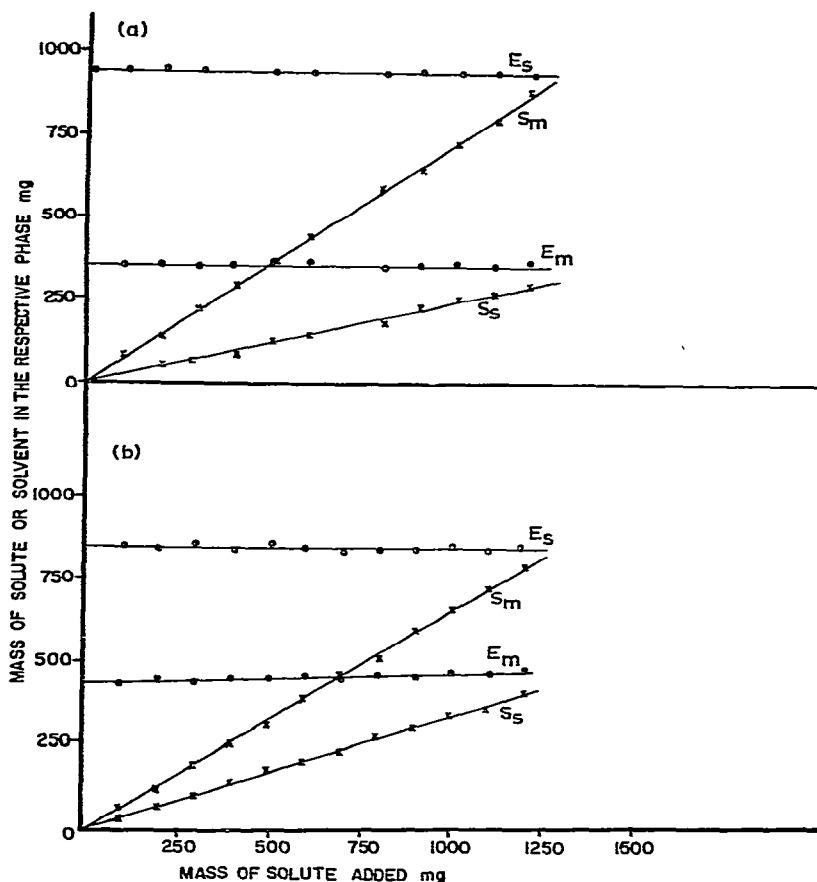


Fig. 9. Curves relating mass of solute and solvent in the two phases to total mass of solute added.  $E_m$  = mass of ethyl acetate in mobile phase;  $E_s$  = mass of ethyl acetate on silica gel;  $S_m$  = mass of solute in mobile phase;  $S_s$  = mass of solute on silica gel. (a) Concentration of ethyl acetate, 0.35% (w/v); volume of mobile phase, 100 ml; solute, anisole,  $k' = 2.4$ ; mass of silica gel, 10.04 g. (b) Solute, nitrobenzene,  $k' = 4.7$ ; mass of silica gel, 10.28 g.

and solute. Appropriate temperature programming was employed for the GC analyses to ensure the elution of the solute in a reasonable time. The solutes employed were anisole, nitrobenzene, *m*-dimethoxybenzene and benzyl acetate, which, when chromatographed on a liquid chromatographic column of silica gel employing a mobile phase of the same composition (0.35%, w/v), would elute at  $k'$  values of 2.4, 4.7, 10.5 and 27.0, respectively. The results obtained are shown in the form of graphs relating the mass of ethyl acetate and solute in the mobile phase together with the mass of solute on the silica gel against the mass of solute added to the system. In Figs. 9 and 10, it can be seen that during the addition of the solutes with  $k'$  values of 2.4, 4.7 and 10.5, little or no change in concentration of ethyl acetate in the solvent mixture is observed even though the silica gel was holding up to 30–40 mg of the solute per gram on its surface. This clearly indicates that no ethyl acetate is displaced from the silica gel and that the solutes are interacting with the primary layer of ethyl

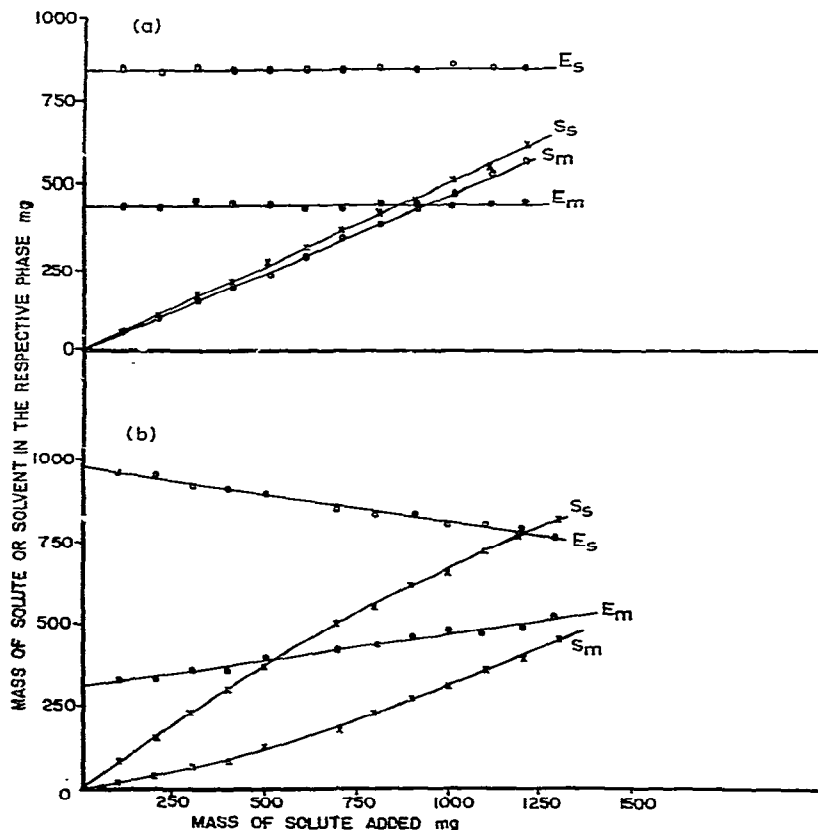


Fig. 10. Curves relating mass of solute and solvent in the two phases to total mass of solute added. Symbols as in Fig. 9. (a) Concentration of ethyl acetate, 0.35% (w/v); volume of mobile phase, 100 ml; solute, *m*-dimethoxybenzene,  $k' = 10.5$ ; mass of silica gel, 10.23 g. (b) Solute, benzyl acetate,  $k' = 27.0$ ; mass of silica 10.17 g.

acetate on the surface. Thus, in normal chromatographic development for solutes eluted up to  $k' = 10$ , which includes most LC analyses, retention of the solute is achieved by interaction with the primary solute-solvent layer on the surface. For benzyl acetate, however, eluted at  $k' = 27$ , as shown in the lower set of curves in Fig. 10, displacement of the primary layer of ethyl acetate does occur and thus indicates that solutes eluted at very high  $k'$  values can compete with a primary layer of solvent and displace it. This effect, however, occurs outside the  $k'$  range normally used in analytical liquid chromatography.

The stoichiometric approach could not be employed for ethyl acetate mixtures at concentrations where the double layer was predominant, as the precision of the GC analysis was not adequate to identify unambiguously small displacements of ethyl acetate. In order to investigate double layer displacement, therefore, a chromatographic procedure was used. A 25 cm  $\times$  4.6 mm I.D. column was employed in conjunction with a high-pressure Valco sampling valve and an LDC refractive index detector. The mobile phase employed was 13% (w/v) solution of ethyl acetate in



*n*-heptane. Referring to Fig. 6, it can be seen that at this concentration the monolayer has completely formed and a significant proportion of the double layer exists. Samples of 5 ml of ethyl acetate, 2-phenylethanol, 3-phenyl-1-propanol and methanol at concentrations of 0.5% (w/v) were injected onto the column. The frontal analysis curves obtained are shown in Fig. 11. The first chromatogram demonstrates the response of the detector to 25 mg of ethyl acetate. It can be seen that all three solutes displace ethyl acetate from the silica gel. It should be noted that the negative ethyl acetate displacement peak from methanol is twice the size of the ethyl acetate displacement peaks for the other two solutes. The other two solutes were eluted at  $k'$  values of 4.6 and 9.5, respectively. From the results shown in Figs. 2 and 3 it can be concluded that methanol would displace both the primary ethyl acetate layer and the major portion of the secondary layer. The fact that the other two solutes displaced only half the ethyl acetate that is displaced by methanol gives a strong indication that the solutes are displacing the secondary layer only and are still interacting directly with the primary layer and not the surface of the silica gel.

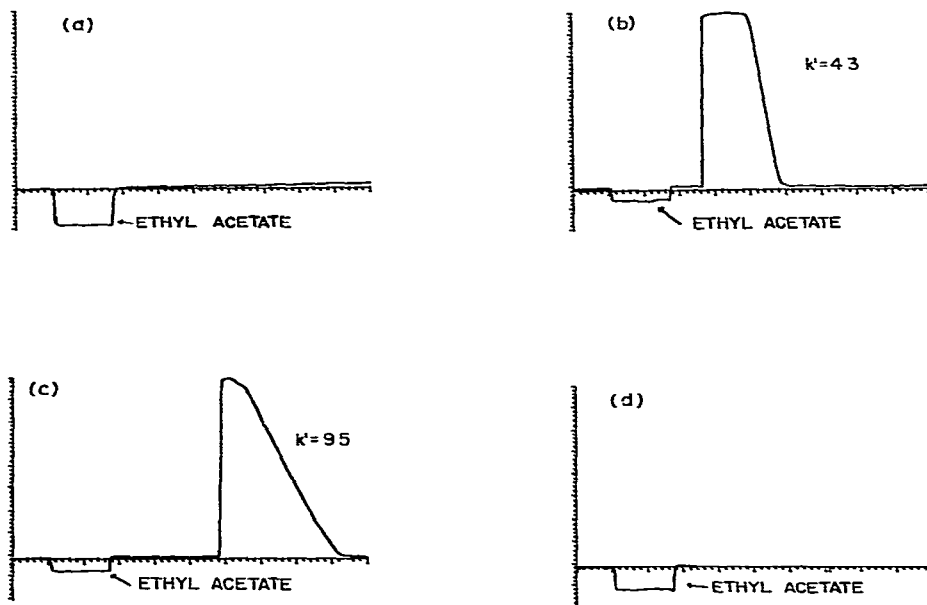


Fig. 11. Frontal analysis chromatograms demonstrating solvent displacements from silica gel by solutes. Column, 25 cm  $\times$  4.6 mm I.D., Partisil 10. Mobile phase, 13% (w/v) ethyl acetate in *n*-heptane. Sample volume, 5 ml. Sample concentration, 0.5% (w/v). Flow-rate, 1 ml/min. Solute: (a) ethyl acetate; (b) 2-phenylethanol; (c) 3-phenyl-1-propanol; (d) methanol.

## CONCLUSIONS

Silica gel in contact with solvents or solvent mixtures adsorbs solvent molecules on its surface to give single- or double-layer coverage. Single-layer coverage results from contact with non-polar or non-hydrogen-bonding solvents. Double layers are not formed or, if there are interactions forming double layers, they are very

weak and thus a stable bilayer appears not to exist. Silica gel in contact with polar or hydrogen-bonding solvents can give both mono- and bilayer coverage depending on the concentration of the polar solvent in the solvent mixture. The hydrogen-bonded monolayer is firmly held to the silica gel and in fact can be considered as a hydrogen-bonded phase. The hydrogen-bonded monolayer is formed rapidly and can be complete when only a fraction of 1% of polar solvent is contained in the solvent mixture. The second layer of solvent forms more slowly, is less rigidly held and only provides significant coverage with ethyl acetate at solvent concentrations in excess of 2-3% (w/v). There are indications that at high solvent concentrations a third layer might be formed. At low concentrations of polar solvent, where the primary layer is nearly complete and only a small proportion of the secondary layer exists, solutes eluted up to a  $k'$  value of 10 appear to interact with the primary layer only and do not displace it. At concentrations where a significant proportion of the surface is covered with a bilayer of polar solvent, solutes eluted up to a  $k'$  value of 10 appear to displace the secondary layer of solvent and again interact with a primary layer but do not displace it.

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