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EMPIRICAL CORRELATION OF LAYER THICKNESS AND SUPPORT PORE SIZE IN "CHEMICALLY BONDED" PHASES*

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SUMMARY

In analogy to earlier experience with non-extractable polymers, conventional "bonded phases" produced from silicone monomers do also show a variation of layer thickness with the pore size of the support. The effect is small but noticeable: as a rule of thumb for the range between 1 and 400 m²/g, doubling the pore diameter means an increase in layer thickness by 15 to 20%. No obvious differences are found in this context among layers formed from mono-, di-, or trifunctional silanes.

INTRODUCTION

So-called "chemically bonded phases" may be obtained from the reaction of silicone monomers with silicic surfaces. Their preparations and properties have been extensively researched and reviewed[1-3]. Yet there exists little factual knowledge on the true structure of the bonded layers —mainly because, by definition, they cannot be extracted and must therefore be characterized by *in situ* analytical methods.

In contrast to synthetic methods employing silicone *monomers*, "bonded" (*i.e.* non-extractable) layers can also be prepared on silicic and other type supports by using *polymers* as starting substances. These polymers are coated onto the supports, heat-treated and subjected to exhaustive extraction[4]. While bonded phases of the first variety (from silicone monomers) are often described in stoichiometric terms, a similar attempt with the polymers of the second variety would appear much less creditable —in fact, practically nothing is known about their interfacial structure.

There has been but scant overlap between bonded phases of the two varieties, since the first is used mainly in liquid chromatography (LC), the second in gas chromatography (GC). One of our continuing interests, however, has been to know whether there are more similarities between the two types of phases than the obvious one of their non-extractability.

The layer thickness of phases made from polymers increases with decreasing surface area of the support[5]. While this effect correlates (nominally and very approx-

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* Taken from Ph.D. research of P. P. Wickramanayake.

imately) with pore size, its raison d'être has not yet been established. When large polymer molecules fill up sizeable portions of small pores, however, some steric correlation between the two does not appear too unreasonable.

In contrast, the layer thickness of conventional bonded phases made from small silicone monomers with, at least in theory, defined stoichiometries, should *not* be dependent on pore size —at least not within the normal range of GC and LC supports. This view, we presume, reflects the generally held opinion.

Still it was interesting for us to investigate a possible change in thickness of conventionally bonded layers with surface area or pore size. (For a correlation of surface area and pore size in silica gels, see ref. 6.) This is because the distinction between "polymeric" and "monomeric" thin layers is not as clear-cut as it may appear on first sight.

First, polymers can depolymerize or otherwise fragment or react on an active support surface. In this context, note a recent, very interesting paper by Schomburg et al.[21]. Conversely, silane monomers, such as are used in bonded-phase synthesis, may form polymers —either directly if they are di- or trifunctional, or indirectly after rearrangement if they are monofunctional. Obvious for both cases, the reaction environment (acidity, temperature, catalytic activity of the support, presence of trace amounts of water, presence of oxygen, etc.) will play a role in determining what happens on the surface.

Second, it is quite common to find that a distinction is made in the literature of bonded phases between those that originate from monofunctional and those that are formed from di- or trifunctional silanes. In analogy to polymer chemistry, the former are often viewed as restricted to "monomeric" behaviour, while the latter are suspected of "polymeric" engagements. Perhaps this view has also been encouraged by a widely used picture, namely that of "bristles on a brush" originating from monofunctional reagents. That this picture should be important to chromatographers is understandable, since it is often associated with facile mass transfer. Against this, of course, one can argue that homogenous layers of only a few Ångstroms —because such is their thickness in conventional "bonded phases"— that are, furthermore, under the influence of a strong surface field, render such distinctions between "monomeric" and "polymeric" structures largely meaningless. Experimental evidence, in our opinion, largely supports the latter argument. Be that as it may, however, it is obviously important for a study such as this to include both monofunctional and difunctional reagents.

Third, and a bit removed from the chromatographic context, is the fact that surfaces are often characterized by their interaction with reactive silanes, for instance in determining the "number of silanol groups". These numbers, in turn, may wind up in studies on the stoichiometry of silanization reactions, thereby completing a circular argument. In such arguments, any unrecognized influence of pore size (pores that are considered easily accessible to the reagents) could have further detrimental consequences on the accuracy of conclusions drawn from experimental data.

For our purposes, which were mostly empirical in nature, a relatively "clean" experimental system and the exclusion of moisture were all that were called for.

EXPERIMENTAL

Supports and reagents

Chromosorb P (Johns-Manville) was purified as described ealier[7]. Chromosorb W was washed in a Soxhlet for 6 days with refluxing 6 N HCl. Porasils (Waters Assoc.) were refluxed with 6 N HCl until no further colour was extracted by the acid. They were then rinsed with excess of distilled water and dried in a vacuum desiccator at 110°C for 6 h. Silica gel 62 (Grace) was extracted with 6 N HCl in a Soxhlet for 2 days, rinsed with excess distilled water, and dried at 150°C in a vacuum desiccator.

All silicone monomers were purchased from Petrarch Systems (Levittown, PA, U.S.A.) and were used without further purification. Transfers of these chemicals were done in a drybox. Hexadecane, octane and toluene were cleaned by passage through silica gel followed by fractional distillation under dry nitrogen.

Synthesis of bonded phases

Their synthesis followed, with minor modifications, the conventional approach; but it was carried out in the same apparatus developed earlier for the bonding of polymers[8]. The support was covered with hexadecane in a round-bottomed flask and a simple tube acting as condenser was attached. The outlet of the condenser was connected to the fume hood by a polyethylene tube terminating in a glass capillary (to prevent any back-diffusion of air). A stream of very dry nitrogen [prepurified grade, further dried over silica gel and molecular sieve 5A, and run through a heated cartridge containing a scavenger for oxygen and water (Supelco)] was bubbled through the support/hexadecane suspension; and this mixture was refluxed for two hours. During that time, the colder portions of the condenser were externally heated with a hot-air gun to remove any condensed and/or adsorbed water. Then the hexadecane was allowed to cool down to room temperature while the nitrogen flush was maintained. After cooling, the silicone monomer was injected into the flask through a rubber septum fitted to the condenser top. The reaction mixture was again brought to boil and refluxed for six hours. After cooling under nitrogen, the non-bonded reagent was removed by a 10-h extraction with dry toluene in a continuous extractor[9].

Elemental analyses

These were done at Galbraith Laboratories and Guelph Chemical Laboratories. The data obtained on some randomly selected samples analysed by both laboratories were in close agreement.

Calculations

Purely for calculation purposes, the organic material is assumed (1) to be present on the whole BET surface, (2) to have a density of one and (3) to consist of silyl (not siloxyl) units, e.g. R_2Si, not R_2SiO, from R_2SiCl_2. The nominal layer thickness d, in Ångstroms, is then given by

$$d = \frac{\% \text{ org.} \times 10^4}{(100 - \% \text{ org.}) \times S} \text{Å} \qquad (1)$$

where % org. is percent organic matter, calculated from % C data without correction for blank values; and S is the BET surface area in m^2/g of the bare support, as given by the supplier (note, however, that Gilpin and Burke's raw data, which are treated here in the same manner, have been corrected by the authors for blank values.)

For calculation of α_{exp}, the micromoles of bonded reagent per square metre of support, the same approach was used:

$$\alpha_{exp} = \frac{\% \text{ org.} \times 10^6}{\text{MW org.} \times S \times (100 - \% \text{ org.})} \mu mol/m^2 \tag{2}$$

where MW org. is the gram molecular weight of the silyl portion of the reagent regardless of the number of functional groups, e.g. $C_{18}H_{37}Si$ from $C_{18}H_{37}Si(OC_2H_5)_3$, or $(C_6H_5)_2Si$ from $(C_6H_5)_2SiCl_2$.

RESULTS AND DISCUSSION

If one believes in the stoichiometry of bonded phases, the number of silanol groups available on a surface is obviously of great importance. It defines the maximum extent of reaction if the phase is "monomeric". Furthermore, unreacted silanol groups can contribute significantly to retention[10].

In our case, the number of silanol groups and the water content of the support was likely determined by keeping the phase in refluxing hexadecane (i.e. at 287°C) for 2 h with a stream of arid nitrogen flushing through. In comparison, treating a silicic surface at the same temperature in a desiccator would still be considered compatible with keeping intact a number of silanol groups close to the frequently assumed maximum; i.e. roughly five OH groups per 100 $Å^2$ or 8 μmole per m^2 (ref. 11).

The number and type of silanol groups on a silicic surface is, of course, a controversial subject. According to Boehm et al.[12], for instance, silica gel contains one strongly adsorbed water molecule per two silanol groups between 100° and 350°C in high vacuum, and the presence of adsorbed water continues even beyond that temperature. One may note that for the "bonding" of Carbowax 20M (ref. 8) —a reaction that is dependent on the presence of silanol groups[13]— refluxing hexadecane turned out to be the best reaction medium.

A reaction temperature of 287°C, however, might be considered by some as excessively high. On the other hand, it has been observed that the highest possible temperatures and longest reaction times give the best surface coverages (e.g. ref. 14). To us, condensation of reactive silanol groups at 287°C would not be as great a concern as, for instance, possible rearrangement reactions of the silicone monomers. However, we have not made any measurements of the integrity of the reagents under synthesis conditions. To make up for that, at least in part, two reactions were repeated in refluxing octane (126°C). As will be seen later, this leads to an approximate halving of the carbon content, but preserves, roughly, the ratio of layer thicknesses obtained from mono- versus difunctional monomers. This would tend to support the viewpoint of Unger et al.[14]. For a different viewpoint, however, see the paper by Little et al.[15].

Be that as it may, our main interest was to find out whether or not pore size

played a role in determining the layer thickness of bonded phases. Shown in Table I are data obtained by using two monofunctional, three difunctional and one trifunctional reagent on silica gel 62 and Chromosorb W (which have surface areas of approximately 300 and 1 m^2/g, respectively). The layer thicknesses turn out to be significantly higher in each case on the low-surface support.

TABLE I

BONDED LAYER THICKNESSES ON TWO SUPPORTS

Silane reagent	Nominal layer thickness ($\mathring{A}$)	
	On Chromosorb W ($S \approx 1$ m^2/g)	On silica gel 62 ($S \approx 300$ m^2/g)
In refluxing hexadecane		
Diphenyldiethoxy-	8.9	3.1
Triphenylethoxy-	8.4	3.1
Octadecyltriethoxy-	23.5	7.8
Octadecylmethyldiethoxy-	32.6	6.4
Octadecylmethyldichloro-	30.0	7.6
Octadecyldimethylchloro-	24.8	5.9
In refluxing octane		
Octadecylmethyldichloro-		3.6
Octadecyldimethylchloro-		2.6

However, one may dispute the validity of this comparison. First, Chromosorb, as a "natural" material, has a pore structure visibly different (by scanning electron microscopy) from that of silica gel. Second, and perhaps more important, carbon analyses of low-surface phases are stretching this technique to its limits and can be expected to err on the high side. "Blank" silicic surfaces show often small and changing carbon content, presumably from organic contamination, and it is not clear whether and, if yes, to what extent this influences the analytical data: would one expect a bonded phase to pick up contaminants in the same manner as the bare silicagel does?

To cope with this problem, a series of syntheses was carried out with chromatographic supports (Porasils) whose surface areas varied over a wide range. The reagents were conventional: the monofunctional octadecyldimethylchlorosilane and the difunctional octadecylmethyldichlorosilane. Also used was Chromosorb P as a diatomaceous support of larger surface area. Interestingly, this non-calcined material behaved quite different from Chromosorb W; one may speculate that natural micropores were perhaps present in the former but not in the latter, or that the purification of Chromosorb P by HCl at ≈ 850°C (ref. 7) brought about changes in the physical or chemical nature of the surface.

The experimental results are plotted in Fig. 1. They show clearly that layer thickness does indeed vary with pore size. Furthermore, that the difunctional reagent behaves exactly like the monofunctional one in this regard.

These two are represented in Fig. 1 by lines A and B, respectively. Whether the lines are really straight in a log/log plot is unclear because of the rather large experimental variation. A similar statement could be made about lines C, D and E, which are included here for purpose of comparison.
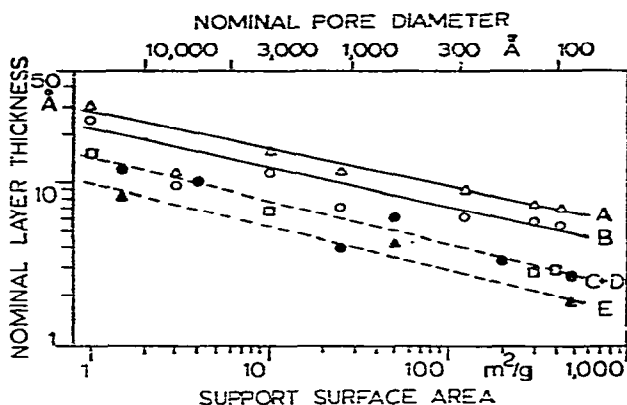
Fig. 1. Correlation of nominal layer thickness, calculated as described in text, and surface area, as given by manufacturer. Nominal pore size according to Halpaap[6]. Line A, △: octadecylmethylsilyl-; line B, ○: octadecyldimethylsilyl-; line C, □: diphenylsilyl-; line D, ●: trimethylsilyl-; line E, ▲: dimethylsilyl-; lines D and E after data from Gilpin and Burke[17].

Line C connects four measurements of a bonded phase based on the diphenyl-silyl unit[16], on Chromosorb W, Porasil F, silica gel 62, and LiChrosorb Si-100. It is interesting to note that the difference in particle diameter (LiChrosorb at a nominal 10 μm and the other materials above 100 μm) does not seem to make any difference, thereby denying, for this case, a possible differentiation between exterior (easily accessible) and interior particle surfaces.

Lines D and E represent Porasils with bonded layers derived from trimethyl-chlorosilane and dimethyldichlorosilane, respectively. The points are calculated from data taken from the work of Gilpin and Burke[17]. Why these authors have carried out such reactions and how they have accounted for the amounts of bonded carbon, differs drastically from our motivation and interpretation. It is interesting to see, however, how well their measurements fit into the plot of Fig. 1. One may also note that their monofunctional reagent TMCS (line D) produces nominally thicker layers than their difunctional DMCS (line E). With the reagents we used, the roles are reversed. Such comparisons, however, may not be too meaningful in the absence of detailed information on how "bonding" takes place.

If one considers lines A through E to be straight, one way of expressing the relationship shown in Fig. 1 is this: When the nominal pore diameter[6] doubles, the thickness of the layer increases by about 15 to 20%. This is certainly not a very large increase and it appears to be less than the respective increase measured with polymers[5]. It is, however, significant by all evidence.

How does it come about? Even outright speculation cannot provide a fully satisfactory picture. One of the obvious avenues of explanation is to assume the presence of pores accessible only to the BET test gas, but not to the derivatizing reagent. After all, so-called micropores are assumed to exist in many types of silica. But this explanation runs into two difficulties. If micropores are responsible for the effect, one would expect the size of the reagent to play a dominant role (small molecules being *strongly* favored over large ones) and one would also expect to notice the effect particularly well with narrow-pore (large-surface-area) supports. Fig. 1, however, just does not show that. The large molecules (as well as the polymers of ref.

5, incidentally) do not appear to be subjected to much steric discrimination when compared to the small molecules. (One needs to realize, though, that this comparison is not entirely fair: Different synthesis conditions of the bonded phases are involved.) And then, the change in layer thickness, on a "per-surface-unit" basis, is much larger on the wide-pore, small-surface-area supports, where one would not expect much influence from micropores to prevail (although, of course, this again remains speculation in the absence of appropriate measurements). Furthermore, the experiments involved three different types of silicic material with completely different methods of production —yet, with the exception of those from Chromosorb P, the data fall into a reasonably coherent pattern.

Another steric consideration involves the available pore volume. An approximate calculation carried out for the support with the highest carbon load (line A in Fig. 1) shows that an average pore diameter of 100 Å is reduced by ≈ 15%, but a diameter of 10,000 Å only by ≈ 0.5%. While the organic phase fills about one quarter of the pore volume in the former case (a silica gel with about 400 m²/g) it fills only one hundredth in the latter (a material of ca. 2.5 m²/g). If pore capacity were at stake here, one would again expect to see a particularly strong effect with high-surface-area materials, an expectation not borne out by Fig. 1.

One may also question the validity of the measurements of surface area and carbon content. As regards systematic errors in area data, we shall adopt the comment made by Gilpin and Burke (though in a different context) that, "since all arguments presented in this paper are relative, this will not affect the interpretations. All data would be merely shifted with trends remaining unchanged."[17] In regard to carbon content measurement, the critical cases involve the low-surface-area materials. Since their loads are very low, a minor organic contamination can result in a large error. What's more, that error would produce an upswing of apparent layer thickness similar to the one observed. Against this disturbing possibility speaks, however, that the trend is observable throughout the range of surface areas, and that the measurements of Gilpin and Burke, who apparently used painstaking caution in their sample preparation, roughly parallel ours. (Some of their deviations are most likely due to the fact that batches of Porasil can vary quite widely in surface area from the one cited for a particular category. We were fortunate to obtain from Waters Assoc. surface area measurements for most of our batches of Porasil.)

Thus we have no comprehensive explanation to offer for the observed effect, just the experimental evidence that it exists (and exists with all kinds of bonded phases). That, however, may be quite important whenever supports of different surface areas are compared.

The bonded-phase load can also be expressed in terms of α_{exp} (μmol bonded reagent per m²) (ref. 14). This is a number often used to define the extent of reaction. As we have just seen, it depends, among other things, on the surface area of the support. Still it is interesting to compare our values with some reported in the literature for similar reagents. As noted, for instance, by Colin and Guiochon[3], seemingly contradictory results can be found in the literature. For instance, Karch et al.[18] obtained α values of 8.7 and 2.6* on LiChrosorb Si-100 for reactions with

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* Calculated from the data in ref. 18 via eqn. 2; however, these much-quoted numbers change to 4.3. and 3.6, respectively.

dimethyldichlorosilane and octadecylmethyldichlorosilane, respectively; whereas Kirkland[19] obtained larger values with octadecyltrichlorosilane (3.1) than with trimethylchlorosilane (2.5) or dimethylbenzylchlorosilane (2.5) on Spherosil X0A 400. Our values for octadecylmethyldichlorosilane on Porasil E (4.0) or Porasil F (5.3) are larger than any of the values reported in the literature for ODS-silanes. This does not imply, however, that ours is a superior or even a very different method. Rather, it reflects mainly the difference between the high-surface-area materials commonly used in liquid chromatography and the low-surface-area Porasils E and F quoted in comparison.

The variation of α_{exp} with surface area or nominal pore size is shown in Fig. 2. Obviously, this variation must be the same as that of the layer thickness. But re-expressing the data by use of this parameter serves three purposes. First, it conforms to current practice and thus facilitates comparison. Second, it calls attention to the fact that α_{exp} or similar expressions, which are often used to characterize surfaces, are independent of surface area only in theory and, one might add, in the premises of most authors. Third, it reflects better the stoichiometry of the synthesis reaction. This consequence of comparison on a molar basis regroups lines A to C, which represent larger molecules, *versus* lines D and E, which represent smaller ones. (We have also included, connected by line F, two data points from a recent study of inorganic layers: The crosses represent Chromosorb W and silica gel 62 covered by three layers of chromia synthesized from CrO_2Cl_2 (ref. 20)).
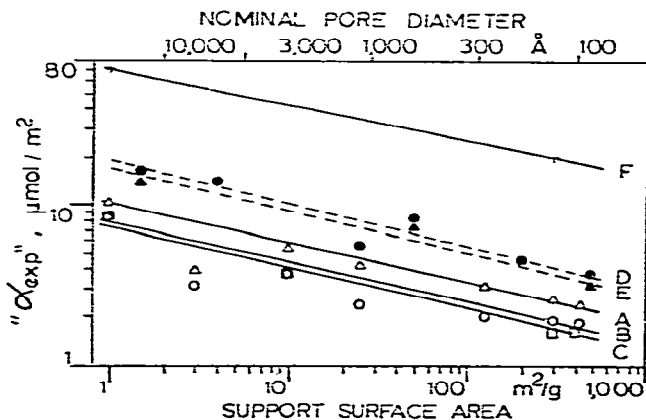

Fig. 2. Correlation of α_{exp} and surface area. Data and symbols as in Fig. 1. Additional line F, +: chromia, three layers[20]; where α_{exp} = μmol Cr/m^2.

If one chooses to accept five silanol groups per 100 $\mathring{A}^2$ as the maximum value (and values almost double that have been quoted in the literature) then the maximum value of α_{exp} is 8 μmoles/m^2. Our highest values, on Chromosorb W, are 7.9 and 10.1 for the mono- and difunctional ODS reagents. This is reasonable, especially since these values, owing to the problems of carbon analysis, may be on the high side.

In comparison, the data of Gilpin and Burke (who, however, used a totally different interpretation[17]) yield a value of 16.7 for TMCS on Porasil F. This value may

appear high, but one needs to realize that such a number depends crucially on the surface area used in calculation (in analogy to our own data, we have taken manufacturer's data quoted by Gilpin and Burke to arrive at this figure). It is interesting, however, to note how well, given the different conditions and difficult correlations, the two data sets fit together in Fig. 2. That, and not absolute values, was to be demonstrated.

This little exercise points out, however, the caution with which seemingly secure data such as α_{exp} values have to be treated. One may add further, more speculative considerations.

Silanizing reagents can react with silanol groups or with water. Silanol groups and adsorbed water stand in a dynamic relationship (whose time frame, however, varies strongly with conditions).

The immediate ratio of silanol groups to water molecules[12] is generally unknown, and the distinction between the two is experimentally difficult and literature-wise controversial. It is uncertain, for instance, how a procedure such as ours (boiling the support in hexadecane with very dry nitrogen bubbling through) has influenced this ratio.

Given a certain ratio, one may expect a *mono*functional reagent to yield "bonded" layers with silanol groups, but "non-bonded" compounds with water (provided, of course, that the reagent is of high purity and does not disproportionate under reaction conditions). Yet, among other considerations, "bonded" and "non-bonded" are really experimental synonyms for "non-extractable" and "extractable". Thus it can happen that the efficiency of extraction affects parameters chosen to characterize the efficiency of reaction.

Some additional effects can threaten the validity of structural data when *di-* or *tri*functional reagents are involved. For instance, it is difficult, though theoretically possible, to distinguish between separate monomer units each attached to its own silanol, and the same number of monomer units assembled into short chains, which are then bonded to much fewer surface anchor groups.

Clearly there is lots of room left for speculation. It is interesting, however, that there seems to be little difference between mono-, di- and trifunctional reagents. It may even be that the chromatographic behavior of bonded phases could parallel that experience.

ACKNOWLEDGEMENTS

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