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GAS CHROMATOGRAPHIC "POLARITY" OF THIN, BONDED LAYERS (MODIFIED SUPPORTS)

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SUMMARY

Modified gas chromatographic supports based on very thin, non-extractable layers of Carbowax 20M on Chromosorb W have become popular phases, and other polymer–support combinations may follow. It is therefore desirable for the practitioner of gas chromatography to know something about the "polarity" of these phases. The available polarity scales are predicated on gas–liquid partition involving heavy loads of liquid phase. Thus they are not, in principle, applicable to very thin, bonded layers. In practice, however, it is helpful to know that supports modified by polar materials such as Carbowax 20M or polyethylene glycol adipate appear much *less* polar than their regular gas–liquid chromatographic counterparts, *i.e.*, packings with heavy loads of Carbowax 20M or polyethylene glycol adipate: the retention indices for typical polar probes differ by *ca.* 100–400 units. Phases based on non-polar materials, *e.g.*, Apiezon L, can show the opposite effect.

INTRODUCTION

The task of deciding which of the many polymers available for gas–liquid chromatography (GLC) to try first on a given separation problem is often aided by consulting empirical polarity scales as those of Rohrschneider[1] and McReynolds[2]. It should be noted that, here as throughout this paper, the use of the term "polarity" conforms to the loose, descriptive meaning it has generally assumed in the GLC literature. The term does not imply a precisely defined quantity but, in its most common usage, relates to the magnitude of differences in Kováts' retention indices (ΔI values) for typical "polar" solutes as chromatographed on a particular phase and compared to a standard, "non-polar" phase.

These polarity scales, of necessity, are based on the ideal concept that the liquid phase alone effects solute retention. Thus, one would not expect them to be applicable to GC phases in which the liquid does not possess its normal bulk properties, *e.g.*, when it forms an extremely thin layer with possibly oriented polymer chains.

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This, however, is exactly the case of some "bonded" (= non-extractable) polymer layers we have studied in the past couple of years[3,4].

Because of the interesting chromatographic properties of these layers, and because apparently similar materials have become available from several GC supply houses[5], it would be advantageous to know, however approximate, how their "polarity" relates to the polarity of the same polymer in a regular (heavy load) GLC packing. Only the latter may be characterized by a polarity scale as mentioned above, since these scales are predicated on ideal gas–liquid partition, *i.e.*, the ΔI values should be independent of liquid phase load. This does not hold true for the case of modified supports with their extremely thin, bonded layers. There, retention can be effected by the solid support surface or the polymer film or both. However, the adsorption sites of the surface, at least those of a certain chemical structure, are modified by interaction with the polymer. Similarly the polymer is modified by the surface —by being bonded to it and by being forced into a particular orientation. It would be extremely difficult to distinguish among these effects or even to estimate their relative contribution to the retention observed.

Yet it is of value in the practice of gas chromatography to know if and in what direction the retention characteristics of say, Carbowax 20M on Chromosorb W change from the 6% load adequately described by polarity indices, to the 0.2% load of a modified support. While the latter is not amenable to such characterization on principle, it is still expedient to use these indices. One has to bear in mind, however, that the chromatographic properties of a modified support reflect the interaction of the solute with a particular, complex and largely undefined system of two components, namely support surface and polymer film, both of which consist of a variety of different chemical structures that interact with each other and with the solute to varying degrees.

To this conceptual precaution one should add a closely related, practical one: a bonded phase is much more difficult to produce and reproduce than a regular GLC packing, and it is much harder to define. A 6% Carbowax 20M packing made by rotary evaporation can be presumed to contain close to 6% of Carbowax 20M; besides, small differences in polymer load would not change its indices provided the liquid phase is reasonably well distributed on the support. A bonded layer, on the other hand, is obtained by exhaustive extraction of a similar heat-treated material; and the thickness of the layer is extremely difficult to determine with any degree of precision[4]. One would expect it to vary with synthesis conditions and our limited experience has borne this out. The extraction step introduces uncertainty even in regard to polymer composition. Carbowax 20M, for instance, shows a broad, bimodal distribution in gel permeation chromatography. It has never been investigated whether the bonded film still represents this distribution or whether, say, the longer chains are preferentially bonded.

The measurement of a ΔI value is simple, but the precision obtained with a particular column may be deluding. First, the linear range of the distribution isotherms is generally shorter for the modified support than for a regular GLC packing using the same polymer. Thus the constancy of indices needs to be ascertained with varying amounts of solute. Second, modified supports, because of their extremely thin polymer layer, are much more susceptible to chemical changes with time and usage than a regular GLC phase. This paper will therefore refrain from reporting a large number

of largely meaningless indices, but rather describe their trends and approximate magnitudes. The general direction of this trend was clear from early work on bonded phases and, indeed, from some of the earliest literature in gas chromatography.

Several years ago we attempted to establish the thickness of bonded Carbowax 20M layers by comparing them to layers of known thickness. This approach was based on solute pairs of polar and non-polar compounds, whose retention behaviour was followed from 0 to 10% liquid phase load. In this way the behaviour of bonded phases was shown to correspond approximately to the minimum in the k' (polar)/k' (non-polar) ratio[4]. Fig. 1 shows a graph from the publication, reproduced here to illustrate the changes in polarity over a wide load range. It is obvious that the retention index of the alcohol (the polarity of the phase) is high for both the bare surface and the regular GLC packing, while it is low for the intermediate area with the minimum correlating roughly to that of a typical modified support. The behaviour of the alcohol is paralleled by that of other polar probes. Thus, the bonded layer of a polar polymer will appear to behave less polar than the same polymer in bulk form. While the cited study[4] dealt only with Carbowax 20M, one would expect other polar polymers to behave likewise and suspect that non-polar polymers may perhaps reverse the trend. In any case, a more detailed picture of what "polarity" to expect from the same polymer in thick *versus* thin layer form was clearly desirable. This study was therefore designed to compare the chromatographic polarity of three regular 5% GLC phases with that of supports carrying the same polymer as thin, bonded layers.

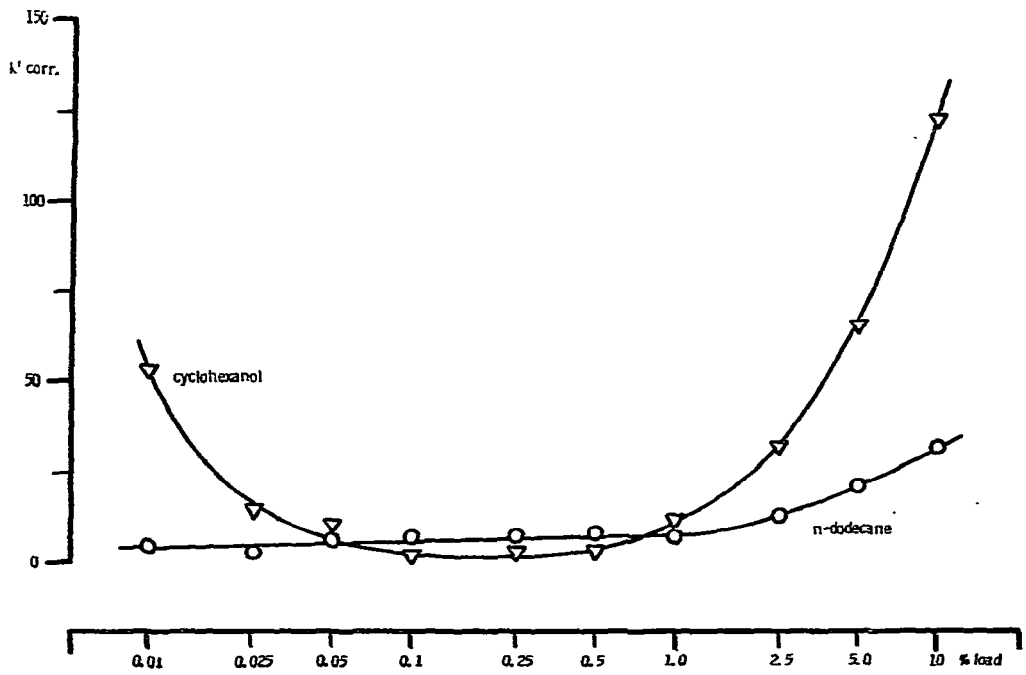

Fig. 1. Retention of an alcohol and a hydrocarbon on various loads of Carbowax 20M on Chromosorb W. Conditions as given in ref. 4.

EXPERIMENTAL

The three tested liquid phases were PEGA (polyethylene glycol adipate), Carbowax 20M and Apiezon L; the latter purified by column chromatography on silica gel with hexane. Regular 5% packings were made by conventional rotary evaporation; bonded layers (modified supports) were synthesized as previously described[6], using, as coating and extracting solvents, respectively, dodecane and methanol for PEGA, hexadecane and methanol for Carbowax 20M, and octadecane and hexane for Apiezon L, all at boiling point temperatures. A specially purified Chromosorb W (100–120 mesh)[7] served as support in each case.

The materials were filled into 1 m × 1.8–2.0 mm I.D. glass columns, and tested in a Shimadzu 4B gas chromatograph with flame ionization detection. Test mixtures included homologous series of normal hydrocarbons, primary alcohols and fatty acid methyl esters (including methyl oleate and linoleate), as well as two mixtures containing a variety of compounds with different functional groups. The amounts of compounds were comparable but not equal; a feature designed to facilitate peak identification.

RESULTS AND DISCUSSION

Fig. 2 shows the two test mixtures on both thin and thick layers of Carbowax 20M. Polar compounds elute on the former some 20–50° lower in the temperature program, while hydrocarbons show approximately the same retention temperature in both systems. For instance, indole, nitronaphthalene, diphenylamine, benzophenone and phenanthrene all elute *before* docosane on the modified support but *after* docosane on the regular 5% GLC phase. Diphenyl ether elutes before *hexa*decane on the former but after *octa*decane on the latter. Thus, the modified support is considerably less polar than the regular GLC phase, with differences in the range of 100–400 Kováts' index units for the polar probes shown in Fig. 2. PEGA behaves generally similar to Carbowax 20M, with differences being somewhat more pronounced.

This decrease in polarity is also illustrated by Fig. 3, which contrasts the retention behaviour of alcohols and hydrocarbons on Carbowax 20M. The alcohols elute some 20° earlier from the modified surface while the difference in hydrocarbons is hardly noticeable.

The picture changes, as shown in Fig. 4, when the liquid phase is not a polyethylene glycol but a mixture of branched hydrocarbons. The differences in retention temperatures of normal hydrocarbons on the two packings made with purified Apiezon L are pronounced and increase with molecular weight: octacontane, $C_{38}H_{78}$, elutes at about the same temperature from the modified support as tetracosane, $C_{24}H_{50}$, from the 5% GLC phase.

Alcohols and other polar compounds are not commonly chromatographed on Apiezon L, and the adsorption isotherm on the modified support is highly non-linear. Thus a plot of retention temperatures would be strongly dependent on solute concentration and consequently of little value. Whether the modified support or the regular GLC phase appears more "polar" depends on the nature of the solute probe and the amount injected. Using the two test mixtures shown in Fig. 2, the modified support was about as "polar" as the regular GLC phase. The modified support would have appeared more polar when tested with a diluted, less polar when tested with a concentrated probe mixture.

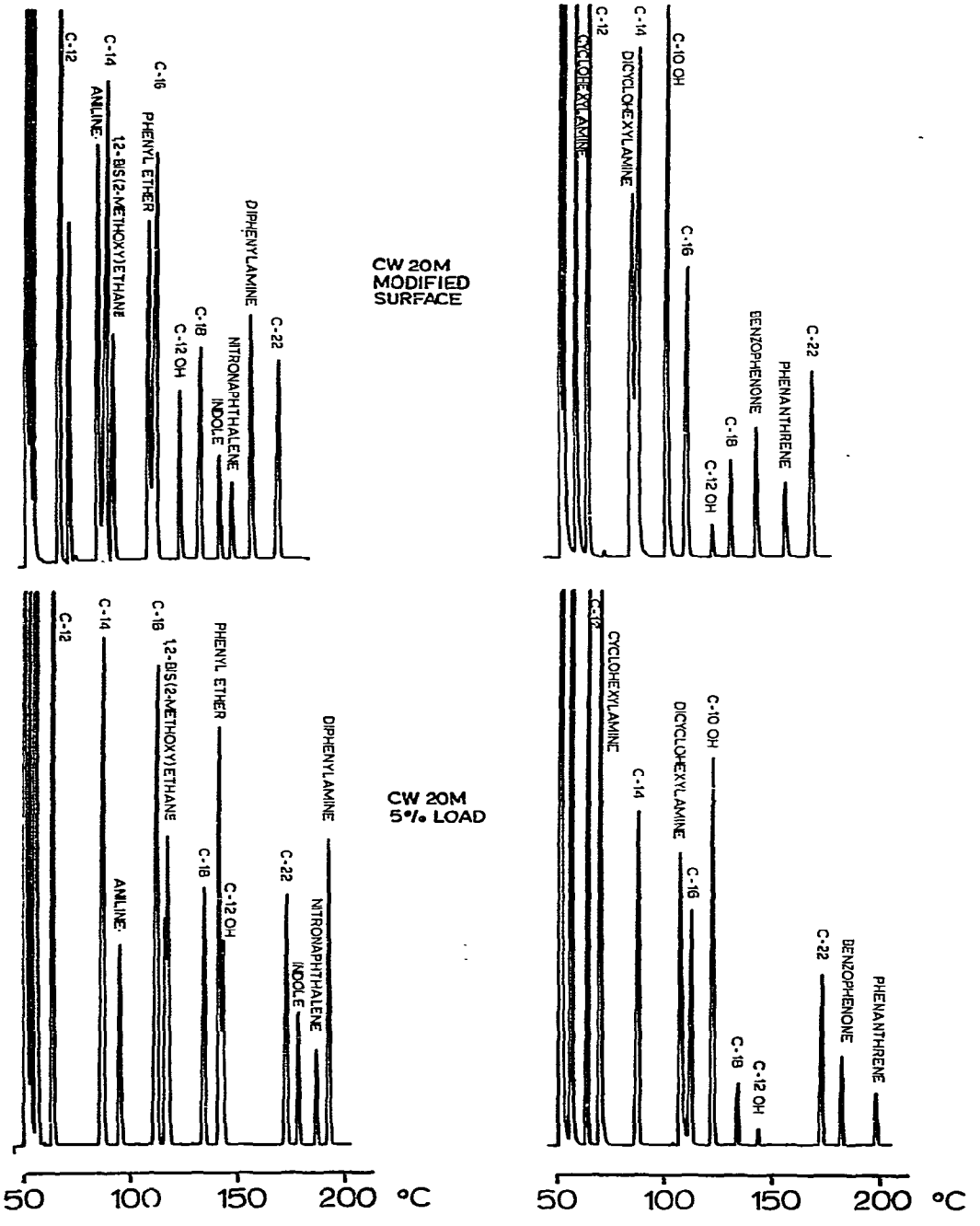

Fig. 2. Temperature-programmed gas chromatography of two test mixtures containing *n*-hydrocarbons and straight-chain primary alcohols listed by carbon numbers, and a variety of polar compounds as indicated, on a modified support and a 5% phase of Carbowax 20M on Chromosorb W (100–120 mesh). Shimadzu 4B, 1 m × 1.8–2 mm I.D. glass columns; nitrogen flow-rate, 30 ml/min; temperature program, 6°/min; FID.

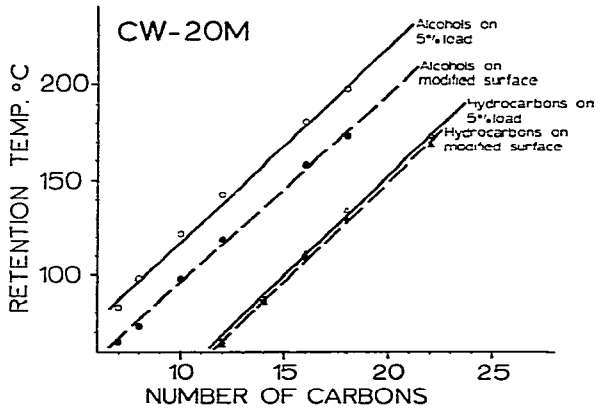

Fig. 3. Retention temperatures of homologous series of primary alcohols and *n*-hydrocarbons on a modified support and a 5% phase of Carbowax 20M. Other conditions as in Fig. 2.

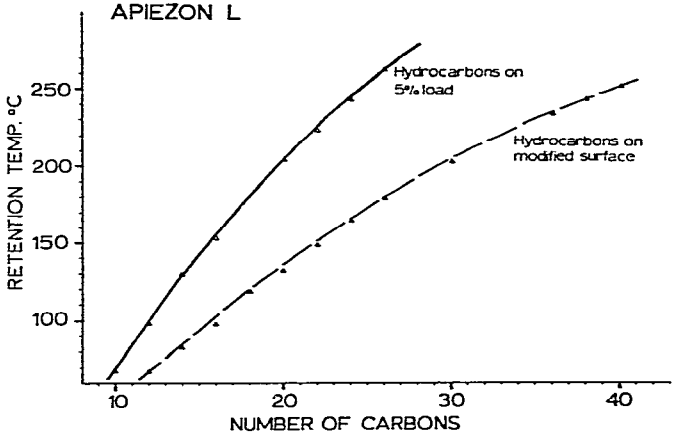

Fig. 4. Retention temperatures of normal hydrocarbons on a modified support and a 5% phase of purified Apiezon L. Other conditions as in Fig. 2.

Too little is known about the interactions occurring on surfaces to attempt to rationalize the observed behaviour in molecular terms in all but a few selected cases, for instance the chromatography of alcohols on Carbowax 20M based phases. Carbowax 20M is essentially a polyethylene glycol and its interaction with polar compounds, *e.g.*, alcohols, is much stronger than that with hydrocarbons. Presumably the very same groups (the ether oxygens of the thin layer) that interact with the solute alcohol are also responsible for interaction with the surface silanols. The solute alcohol, then, encounters less interaction with both the (deactivated) surface and the thin (bonded) polymer layer than it would have encountered with either a bare surface or a thick (bulk) polymer layer.

On the other hand, hydrocarbons are very little retained by Carbowax 20M, *viz.*, there is little difference in retention among a bare Chromosorb W and a 0.1% or a 1% load of Carbowax 20M on that support. Neither does Carbowax 20M appreciably deactivate the support against interaction with hydrocarbons, as demon-

strated by Figs. 1 and 3. As hydrocarbons are the standards upon which all measurements of retention indices of polar probes are based, the difference in polarity between a modified support and a regular GLC phase becomes obvious.

Apiezon L deactivates the support surface somewhat more efficiently against hydrocarbons, presumably by bonding to the same sites a hydrocarbon solute would occupy. Hydrocarbons also interact very strongly with a thick Apiezon L load and the difference between the modified support and the regular phase as seen in Fig. 4 is much larger than the respective, almost negligible difference for Carbowax 20M seen in Fig. 3.

The polar and non-polar *bulk* liquid phases behave very differently towards hydrocarbons, and this difference, at least on formal grounds, seems to be a major effect in determining polarity. To overemphasize the point: it is the behaviour of the *n*-hydrocarbon standard (as well as, or perhaps even more than, the behaviour of the polar probe) that decides the outcome of the polarity measurement.

It is also interesting to look at the situation from the viewpoint of retention temperatures. In terms of surface deactivation only, one would expect Carbowax 20M to be more efficient than Apiezon L. Yet, under the conditions we used and with the polar probes as listed in Fig. 2, these compounds eluted considerably earlier from the modified support based on Apiezon L than from the one based on Carbowax 20M. The average of retention temperatures for the 5% Apiezon L phase was, in fact, comparable to that of the support modified by Carbowax 20M. Comparing packings using the *same* polymer, an average 40° difference in retention temperature between the 5% GLC phase and the corresponding modified support was found for the polar probes. This applies to Carbowax 20M as well as PEGA and Apiezon L.

Not too much can obviously be made of these data and, as stated earlier, the use of Apiezon L in this study simply served to include a non-polar phase; its application with polar solutes would be a poor choice indeed in any practical situation. The supports modified by polar polymers are clearly much more important.

For these, the chromatographer can expect to find his modified support a significantly less polar phase than the position of this polymer on a polarity scale would indicate. Taking the average of our probes, the modified support based on Carbowax 20M was some 200 index units less polar than the 5% phase (and some 400 units more polar than the modified support based on Apiezon L). Fig. 5 illustrates this by the separation of the methyl esters of stearic, oleic and linoleic acids which is sometimes considered a measure of phase polarity. While both PEGA and Carbowax 20M regular phases show some separation, the modified supports based on these polymers do not —and it would have been unwise to attempt to use them for such a purpose. Apiezon L has been included merely for comparison; no apparent change in polarity occurs.

It is a well known chromatographic practice to deactivate troublesome surface sites by adding polar, empirically chosen substances ("tail-reducers"). In one sense, the ultrathin polymer layers of the modified supports act in a similar way, except that they are non-extractable, *i.e.*, "bonded". Two considerations are perhaps important in designing a chromatographically useful bonded layer. First, there are certain combinations of adsorbent and chemisorbate, *i.e.*, support and liquid phase, that work well, presumably because of a chemical and perhaps geometrical "fit" Too few combinations have been experimentally tested to attempt a classification, and

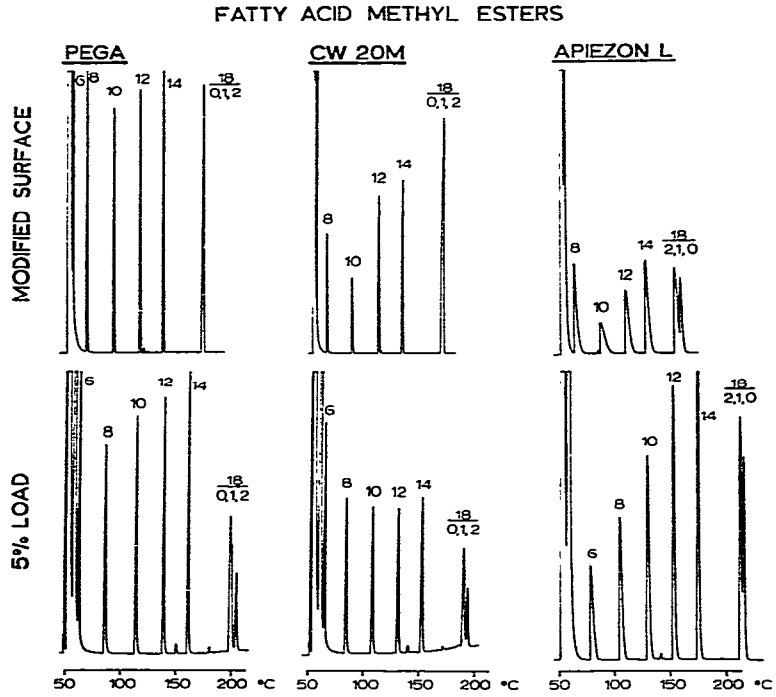

Fig. 5. Chromatographies of fatty acid methyl esters on modified supports and 5% GLC phases of PEGA, Carbowax 20M and Apiezon L. Other conditions as in Fig. 2.

chemisorption data are helpful but not always applicable. This is so because chromatographic parameters such as retention (including relative retention of a polar/non-polar pair) and peak shape are extremely sensitive, though not always easily interpreted, indicators of surface condition. Furthermore, the production of a bonded layer usually requires clean-up, heat treatment and extraction steps —all manipulations not commonly applied to materials used for physicochemical measurements. From an empirical viewpoint based on the silicic surfaces of diatomaceous earth or silica gel, polyethylene oxide structures work well as do hydrocarbon structures, perhaps utilizing different sorption sites. The molecular weight of the polymer has to be large enough to produce the desired effect. Attempts at bonding aromatic structures by similar means have not proved successful so far (possibly because of their rigid structure); some silicones, however, provided an occasional worthwhile chromatographic performance.

Second, in order to "deactivate" a support, the polymer has to be capable of interacting with the sites that retain the solute —an obvious but perhaps not always fully realized condition. Our knowledge of surfaces in general and silicic surfaces in particular is fragmentary (*e.g.*, ref. 8), and when precise knowledge is lacking on surface sites, and their interaction with polymer structures on one hand and solute structures on the other, it may be well to fall back on the simplest of all chemical approaches, *i.e.*, looking for chemical similarity between polymer and solute.

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