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CHARACTERISTICS OF A NOVEL GAS CHROMATOGRAPHIC PHASE

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SUMMARY

A novel gas chromatographic phase, obtained by heat-treatment and exhaustive extraction of a 6% Carbowax packing, has been characterized by various chromatographic tests of its sorption chemistry. The polymer layer remaining after extraction represents a 0.1 to 0.2% load; and it allows fast, efficient, and selective separations, which bear characteristics, and represent the more desirable features, of both gas–solid and gas–liquid chromatography.

INTRODUCTION

The determination of trace organics found in the environment and in biological systems is often quite difficult. In such work (*e.g.* ref. 1) we have made frequent use of a particularly suitable type of gas chromatographic (GC) packing, about which we know very little. What is known is that it represents essentially a silicic support coated with a thin layer of Carbowax 20M, distinguished from a regular gas–liquid chromatographic (GLC) phase by the fact that protracted extractions with various solvents such as benzene and methanol fail to remove the chromatographic properties from the inorganic particles[2].

GC on this phase is fast, efficient, well suited for polar compounds, and accompanied by little bleed[1–3]. Similar deactivated materials can be used for liquid chromatography[3]. We believe, furthermore, that non-extractable polymer layers, which act as homogeneous surfaces in chromatography, are a topic of interest beyond their analytical utility.

Just how thin these layers are is a question unresolved, owing to the uncertainty of ignition and elemental analysis operating at their lower limits. A reasonable upper estimate is 15 Å, representing the border region between GLC and gas–solid chromatography (GSC). Actual separations bear traits of both concepts[1,3,4]; inviting further study of the characteristics of the polymer layer.

We have attempted, therefore, to produce a series of comparably treated, but unextracted, phases with known polymer load —and to compare them with our exhaustively extracted materials.

Three approaches are used to this end. First, a measurement of the temperature dependence of the chromatographic separation (*i.e.* the apparent heat of sorption) as an indicator of interaction between the solute and the stationary phase. Second, a measurement of the linearity of the sorption isotherm (represented for reasons of convenience and clarity by a plot of the distribution ratio k' *vs.* solute concentration) as an indicator of surface homogeneity and as a possible criterion in a "GLC *vs.* GSC" context. Third, a measurement of the absolute and relative retention of various test compounds encompassing a wide polarity range, as an indicator of the interaction between solutes and the stationary phase. All three approaches were designed to allow placing the exhaustively extracted packings, with largely undefined layer thickness and chromatographic properties, within a system of better defined chromatographic phases.

EXPERIMENTAL

Celite 545, 100–120 mesh, was acid-washed in a Soxhlet, Kontes (Vineland, N.J.) Model 585100, until a new change of conc. HCl was free of yellow hue after several hours of operation. The support was dried, freed of fines in a stream of nitrogen, and covered by chloroform. The suspension was gently stirred by hand, and a solution of Carbowax 20M in chloroform slowly added. After standing for 1 h, the mixture was freed of solvent in vacuum, and the remaining packing heat-treated at 260° under a very slow flow of high-purity nitrogen overnight[2]. After the fines had again been removed, the phases were packed into 5 ft. × 2 mm I.D. borosilicate glass columns and tested in a Bendix (Ronceverte, W.V.) Model 2500 gas chromatograph.

Phases with (initial) liquid phase loads of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 2.5, 5, and 10% were thus made, and compared to two different batches of extracted supports named SC-1 and SC-2, prepared, as described earlier[2], from a 6% Carbowax 20M packing. This preparation is similar to the one above, but includes a final two-day extraction with refluxing methanol in Goldfish continuous extraction equipment. All columns were conditioned overnight at 220° before use.

The distribution (capacity) ratio k' was used throughout this study as an indicator of chromatographic retention, and was calculated from a measurement of the deadtime t_0 with methane, and the retention time from injection to peak apex, t_R, as $k' = (t_R - t_0)/t_0$.

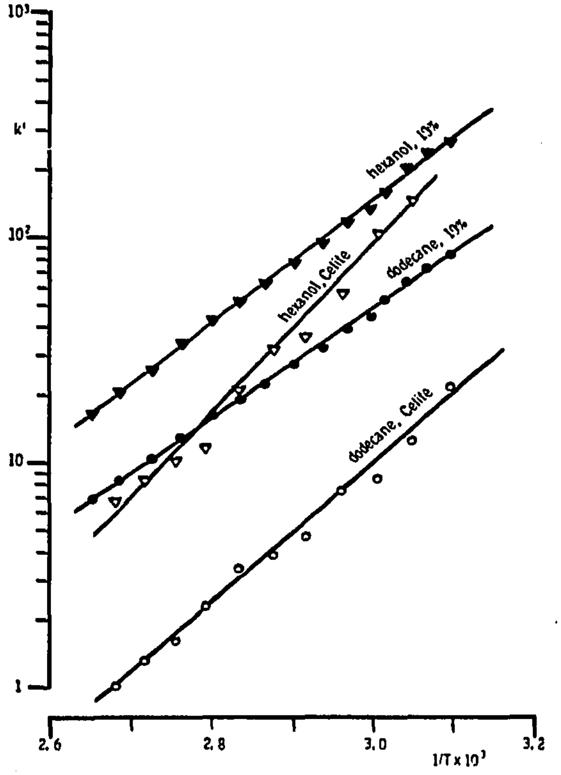
The test compounds included *n*-dodecane, *n*-tetradecane, naphthalene, acetophenone, aniline, phenol, cyclohexanol, and *n*-hexanol, and also, to a minor extent, *n*-hexadecane, nitrobenzene, cyclohexanone, cyclohexylamine, and cyclohexyl acetate. Selected results are presented in the following section.

RESULTS AND DISCUSSION

Figs. 1 and 2 and Table I suggest, in conjunction with Fig. 6, the following picture: The interaction of alkanes with the silicic surface is influenced little by the Carbowax layer until the latter reaches a considerable thickness (1% load); *i.e.* the retentions (and the measured heats of sorption) do not vary appreciably from 0 to 1% Carbowax 20M. As is well known, alkanes interact less with either the Celite surface or the polyethylene glycol bulk liquid than do alcohols, and this is borne out by the data in Table I. (Chromatographic efficiency, though, improves markedly in the 0–1%

load range; and the extracted packings have HETP values as good as any of the heavy-load packings.)

The interaction of the surface with alcohols (in contrast to hydrocarbons) proceeds, most probably, through its silanol groups. These are the very groups, of



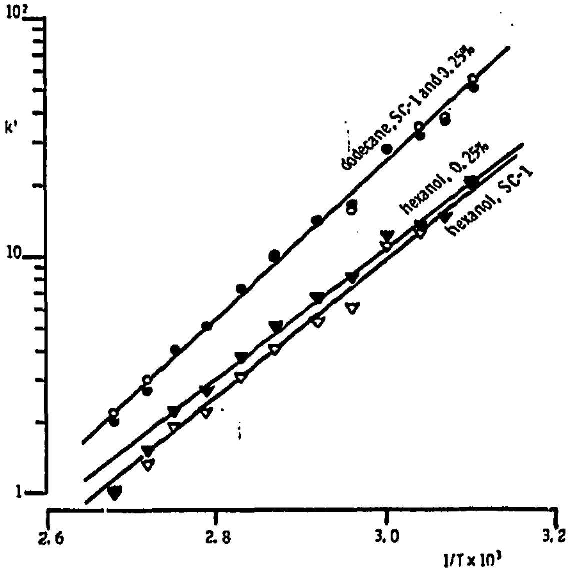


Fig. 1. Temperature dependence of the (uncorrected) distribution ratio of dodecane (circles) and hexanol (triangles) on 10% Carbowax 20M on Celite (full symbols) and Celite (empty symbols). All injections *ca.* 1 μg. Deadtimes as shown in Table I.

Fig. 2. Temperature dependence plot similar to Fig. 1, for alcohol and hydrocarbon chromatographies on 0.25% Carbowax 20M on Celite (full symbols), and an extracted packing (SC-1; empty symbols).

TABLE I

TEMPERATURE DEPENDENCE OF ALCOHOL AND HYDROCARBON CHROMATOGRAPHIES

Apparent heats of sorption from original log k' *vs.* $1/T$ plots (kcal/mole). In parentheses: t_0 (sec).

Solute	*Blank Celite*	*SC-1*	*0.25% Carbowax 20 M*	*10% Carbowax 20 M*
n-Hexanol	17.8 (8)	13.5 (21)	12.5 (22)	12.4 (10)
n-Dodecane	14.5 (22)	15.2 (21)	15.2 (22)	11.4 (10)

course, which could be expected to hydrogen-bond to the ether oxygens of Carbowax 20M (Ref. 5). Consequently, alcohol interaction with the surface, as well as retention and peak spreading, drop sharply as minute amounts of liquid phase are added. This phenomenon is, of course, well known from the literature (*e.g.* refs. 6 and 7), but it is noteworthy that the heat of sorption for the alcohol falls below that for the hydrocarbon, and that the exhaustively extracted phase SC-1 falls into a (chromatographically) very desirable range. Its load, as judged from the data in Table I, is smaller than 0.25% of Carbowax 20M.

The measurements shown in Figs. 3, 4, and 5 test the linearity of the sorption isotherms of various model compounds. Between the straight lines of the partition isotherms, characteristic of GLC as shown in Fig. 3, and the (conventionally) convex adsorption isotherms, characteristic of GSC as shown in Fig. 4, there lies the intermediate yet unique area represented by Fig. 5. This form of representation, as compared to the use of conventional adsorption isotherms, is particularly sensitive to small changes in thin layers, and slight differences in packings can be expected to show up.

Both cyclohexanol and tetradecane have linear ranges only slightly smaller than those on 10% Carbowax 20M. The deviation of phenol is more pronounced —in conventional representation, it would have a very slightly convex adsorption isotherm— and one could probably attribute this effect to its aromatic ring structure.

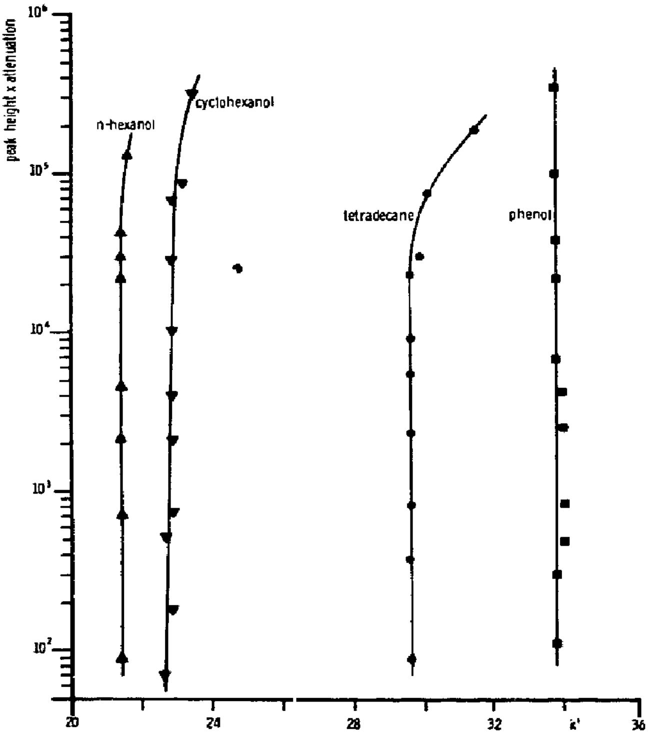


Fig. 3. Constancy of chromatographic distribution ratios at various solute concentrations (representing the linearity of the sorption isotherm). Column temp., 170° (phenol) and 110° (all others). Injected amounts range from 10 ng to 30 μg for all compounds. Deadtime $t_0 = 8.5$ sec. Injection port temp., 220°; flame ionization detector temp., 240°. Packing, 10% Carbowax 20M on Celite.

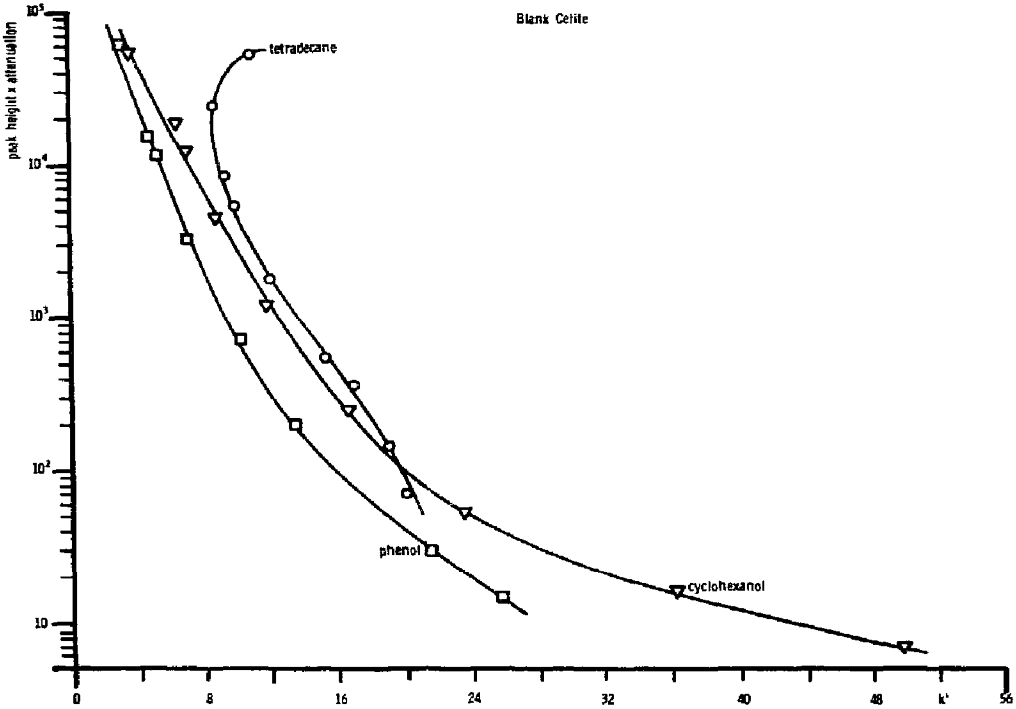


Fig. 4. Distribution ratio plot similar to Fig. 3. Column temp., 85°. Deadtime $t_0 = 15.0$ sec. Injected amounts range from *ca.* 50 ng to 30 μg. Stationary phase, blank Celite.

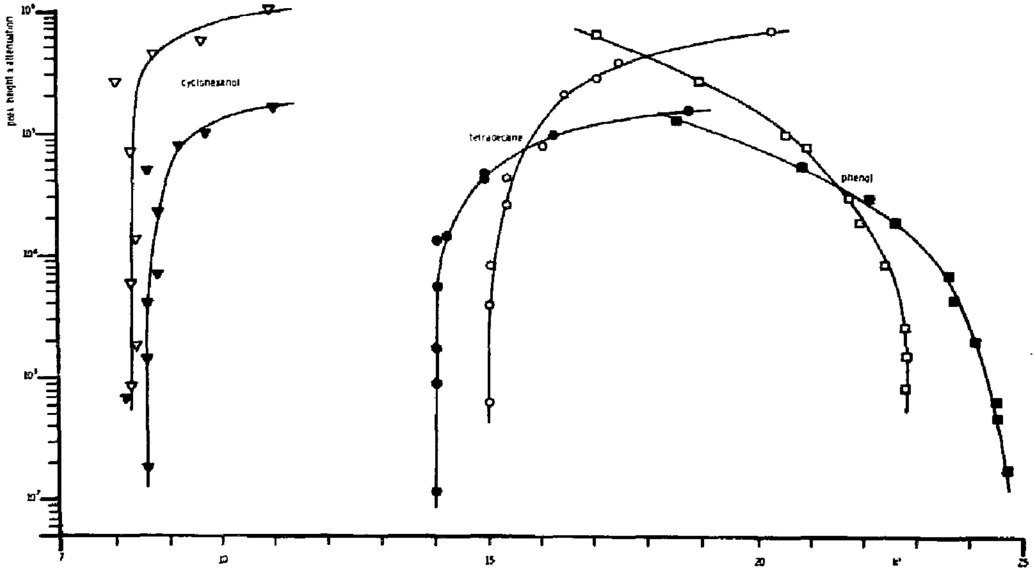


Fig. 5. Distribution ratio plot similar to Fig. 3. Column temp., 89° (tetradecane and phenol) and 50° (cyclohexanol). Deadtime t_0 values between 12.3 and 13.0 sec. Injected amounts range from *ca.* 10 ng to 30 μg. Stationary phase: 0.25 Carbowax 20M on Celite (full symbols), and an extracted packing (SC-1; empty symbols).

Still, chromatography in the lower concentration ranges hardly suffers. Its attributes mimic GLC, even though there is no bulk liquid phase available. (The only traits attributable to GLC are the peculiar Van Deemter plot[4] and the propensity of the extracted phase to separate closely related compounds[3].)

Fig. 6 shows the retention of two model compounds through the entire load range from 0 to 10% Carbowax 20M. Their contrasting behavior, and the well-known minimum of retention for polar compounds, can be clearly observed. Similar data have been used in this study to define the thickness of the polymer layer remaining after exhaustive extraction, *viz.* by comparing relative retention times. This measurement should be preciser than one based on absolute retention times; but, here as in prior comparisons, arguments rest on the premise that the thin polymer layers remaining after exhaustive extraction of a 6% intial load are, in fact, comparable to those applied a priori as thin layers.

This premise has some experimental support, *i.e.* a good SC-type packing can also be made from very low initial loads, and the heat-treatment can be expected to yield uniform polymer distributions. Yet, one needs to be aware that the two types of supports might not be entirely comparable.

Setting this caution aside, one can measure relative retention data for selected pairs of substances and deduce, as shown in Fig. 7, the unknown loads of the SC-phases. There are two possible results for each SC-measurement (marked by shaded circles). One could probably eliminate the two lowest possibilities —located on the naphthalene/*n*-tetradecane and acetophenone/*n*-tetradecane curves— by the argument that, were they the correct choice, the *k'* ratio of the cyclohexanol/*n*-dodecane pair

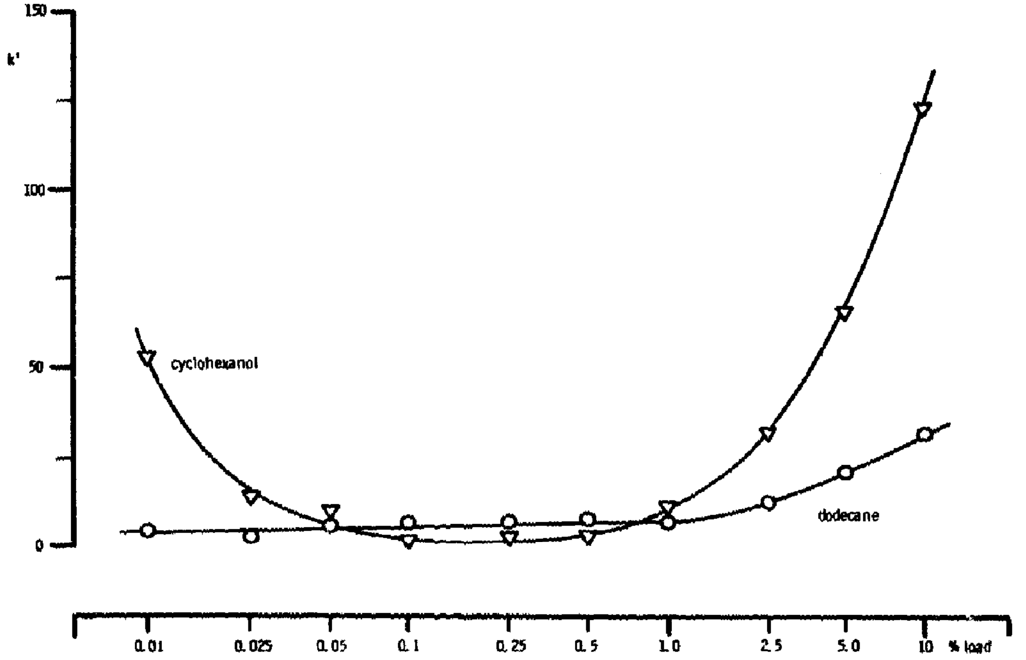


Fig. 6. Distribution ratios measured at 70°, with 1-μg injections of cyclohexanol and dodecane on Carbowax 20M on Celite, varying in load from 0.01% to 10%. Corresponding t_0 values: 9.4, 16.0, 12.3, 24, 28, 28, 27, 15.3, 12.4, and 4.9 sec.

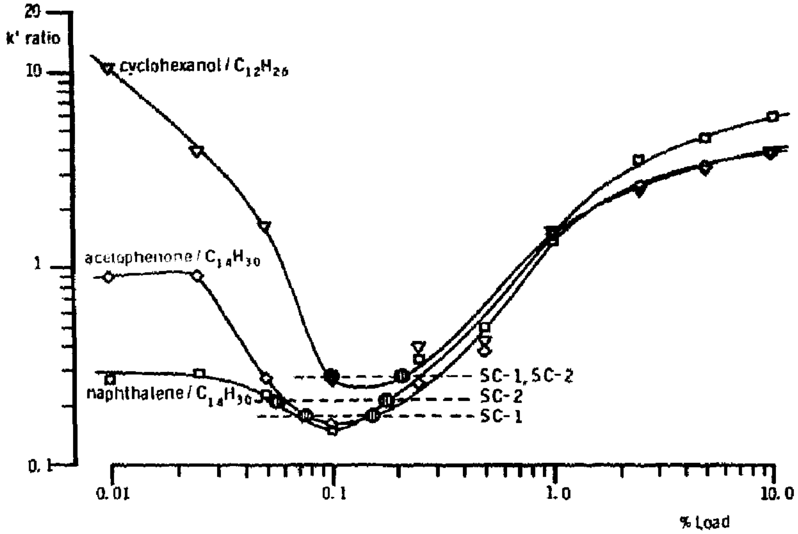


Fig. 7. Relative retention of paired solutes on Carbowax 20M on Celite, varying in load from 0.01% to 10%. Column temp., 90° (acetophenone/tetradecane and naphthalene/tetradecane), and 70° (cyclohexanol/dodecane). Superimposed values (dashed lines, and circles at intersections) from extracted packings SC-1 and SC-2 at similar conditions. As in Fig. 6, t_0 values were chosen for chromatographic expediency and varied between 5 and 46 sec.

would have to be much higher. That leaves four other possible values, all in the 0.1 to 0.2% load range.

This range would be consistent with other data in this and earlier studies[2]. It implies a film somewhat thicker than a monolayer[6], but still within the reach of surface forces.

In the context of analyzing polar compounds of higher molecular weight by GC (when thermal decomposition and column bleed can play decisive roles), the exhaustively extracted phases fall precisely into the desired load range, where elution time (or temperature) is at a minimum, chromatographic efficiency is high, and the support surface is well deactivated.

There is little doubt that the surface contributes substantially to the characteristics of solute retention and, in this sense, one may speak of GSC on a modified, probably close to 'ideal', surface. The extremely thin layer and the capacity of this phase for isomer separations support this view. On the other hand, the visual appearance of chromatograms, the low heats of sorption, and the good linear range, all are strongly reminiscent of GLC. In all probability, the liquid film does interact with the solute molecules to some degree, aside its moderating influence on surface activity. Equally probable is that so thin a film does not exactly reflect properties of the bulk liquid phase[6]. Furthermore, one would expect different types of molecules to interact to different degrees with the surface and the liquid phase; in fact, these contributions can be fairly closely defined in favorable cases.

Thus, it may prove a futile attempt to categorize chromatography on the extracted phases as either adsorption or partition type. It belongs, obviously, into the border region between the two concepts —and, fortunately, it bears the more desirable characteristics of both GLC and GSC.

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