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A TAILOR-MADE C_{87} HYDROCARBON AS A POSSIBLE NON-POLAR STANDARD STATIONARY PHASE FOR GAS CHROMATOGRAPHY

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SUMMARY

A hydrocarbon of empirical formula $C_{87}H_{176}$ has been found to have advantageous properties for use as a stationary phase in gas chromatography. It is a non-polar solvent with a working temperature range from 30°C to about 280°C. Being a pure substance, it has reproducible properties. The information necessary for determining the precise position of the starting point of the chromatogram is given, and its separation properties are discussed, taking as examples the chromatographic behaviour of *n*-alkanes and other selected compounds. With the aid of these data, this hydrocarbon is compared with squalane and the methylsilicones, and proved to show most of the advantages of both of these phases.

INTRODUCTION

Alkanes are thought to be the least polar organic solvents and are therefore accepted as "non-polar" stationary phases in gas chromatography in the absence of a hypothetical, non-polar substance¹⁻³. In fact, experimental evidence shows that the retention properties of such liquids can be explained by assuming that they can interact with solutes by dispersion forces only. Hence their retention character is considered as the basis of comparison for all other stationary phases. By examining the additional retention of a series of substances on a polar phase compared with that on an alkane, the "polarity" of the polar stationary phase can be characterized in an empirical way²⁻⁴. However, the retention character of hydrocarbons as a group can be spoken of only as a first approximation, as there are differences between the solvent properties of the individual substances, with the retention data depending mainly on the molecular weight⁵⁻⁸. Solvents of higher molecular weight appear to be slightly polar if compared with squalane, a liquid repeatedly proposed and accepted as a non-polar standard^{1,3,4,9,10}.

Such a choice is prejudicial to high-temperature work as the upper temperature limit of the use of squalane is only 100-120°C. Note also that squalane is a mixture of varying amounts of diastereoisomers. Therefore, the use of methylsilicones has been advanced as a standard or as one of a set of "preferred phases"^{11,12}, as they are almost non-polar and stable up to 300°C. This choice may also be criticised for several

reasons. Firstly, they are polymers and as such their molecular weight changes from batch to batch, thus affecting retention data. Secondly, sp^3 -hybridized silicon atoms are Lewis acids capable of forming weak complexes by $\pi(p,d)$ -bonds with bases such as ethers and alcohols. Finally, methylsilicones are always altered during the preparation of the column packing. During conditioning, the column is heated to higher temperatures for a given period of time in order to allow the methylsilicone chains to substitute the surface hydroxyl groups of the support¹³. Volatiles formed in these reactions and those present in the original polymer evaporate, resulting in a serious loss of weight of the applied polymer. Such a liquid cannot be accepted as a standard if well defined experimental conditions and reproducibility of retention data are required¹⁴.

In this paper, we describe the properties of a "tailor-made" hydrocarbon that combines most of the advantages of the two above-mentioned liquids. It has nearly optimal properties if it is accepted that the following, partly contradictory, conditions have to be fulfilled: (1) the hydrocarbon should be a pure substance with no chiral centres; (2) its melting point should be as low as possible; (3) it should be of low viscosity; (4) the upper temperature limit of its use should be determined by its pyrolytic stability and not by volatility; and (5) the price of the substance should not be prohibitive for its use as a stationary phase.

Obviously, points (2) and (3) imply a hydrocarbon of low molecular weight, consequently too volatile to be used as a stationary phase. Therefore, the lowest admissible molecular weight to satisfy condition (4) had to be estimated. For this purpose, a series of 1,1,6,6-tetraalkylhexanes of general formula I, where R = alkyl, ranging from $C_{30}H_{62}$ to $C_{78}H_{158}$ have been synthesized in our laboratory. By investigating their thermal behaviour, we concluded that for a hydrocarbon to be non-volatile up to 300°C , a minimum molecular weight (M) of about 1200 is required⁷.

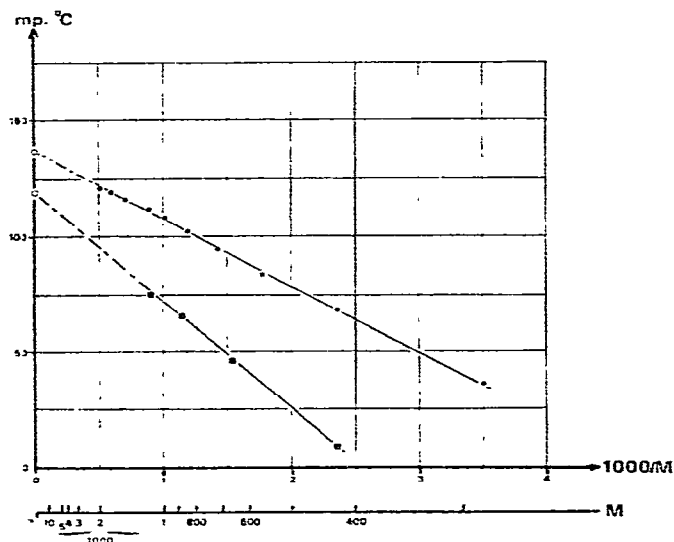


Fig. 1. Melting points of n -alkanes and branched hydrocarbons of structure I as a function of the reciprocal of the molecular weight (from ref. 15). For the melting points of n -alkanes of higher molecular weight, see ref. 16.

Fig. 1 shows that an *n*-alkane of the same molecular weight melts at about 112°C and that even the melting point of a branched alkane of structure I would be too high (80°C)¹⁵. Therefore, the synthesis of the hydrocarbon of structure II (C₈₇H₁₇₆, 24,24-diethyl-19,29-dioctadecylheptatetracontane; mol. wt. = 1222.37) was undertaken, assuming that it has the necessary degree of branching to bring about the desired melting point¹⁷. Its physical properties are summarized in Table I.

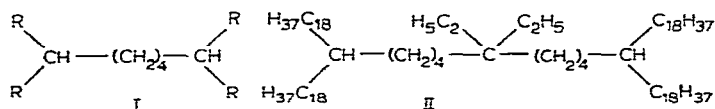


TABLE I

PHYSICAL PROPERTIES OF HYDROCARBON II, C₈₇H₁₇₆

For the determination of the melting points, see Fig. 2. Sample P, dissolved and precipitated substance; sample M, crystallized from the melt at 21–22 °C. Confidence limits at the 95% significance level.

Property	Sample	Value
Melting point	P	33.3 ± 0.6 °C
	M	28.3 ± 0.3 °C
Enthalpy of fusion	P	28.7 ± 0.4 cal·g ⁻¹
	M	23.3 ± 1.2 cal·g ⁻¹
Density at 130 °C		0.776 ± 0.001 g·cm ⁻³
Specific volume at 130 °C		1.289 ± 0.002 cm ³ ·g ⁻¹
Coefficient of cubic thermal expansion		(0.746 ± 0.007) 10 ⁻³ °C ⁻¹
Molecular weight		1222.37 g·mole ⁻¹
Molecular weight by vapour osmometry		1217 ± 30 g·mole ⁻¹
Lower temperature limit of use as stationary phase		30 °C
Higher temperature limit of use as stationary phase (estimated)		280–300 °C

In Fig. 2, two melting curves of the same sample of hydrocarbon II are depicted. Trace P refers to the substance obtained in the last purification step. The hydrocarbon was dissolved in *n*-hexane and precipitated at 0°C by the addition of propanol-1. The white powder obtained by this procedure showed a shoulder of widely varying area on the melting curve at about 31° and a sharper peak at 33.3 ± 0.6°C. The previous handling largely determines the magnitude of the pre-melting effect, which might be due to structural defects introduced by mechanical shearing in the course of handling. By cooling the molten substance at different cooling rates, it always solidified at 21–22°. Trace M in Fig. 2 is the melting curve of such a solidified sample, whereby transitions were observed at *ca.* 25.6 (shoulder, sometimes missing), 26.6 ± 0.2 and 28.3 ± 0.3°C with varying areas under the individual peaks. It is interesting to note that substances once molten never again showed the high melting point of the precipitated substance.

The hydrocarbon has been used as the stationary phase in two packed columns for 8 months. During this period, about 500 chromatograms have been measured on each of them, the columns having also been heated overnight at 30–250°C. Subse-

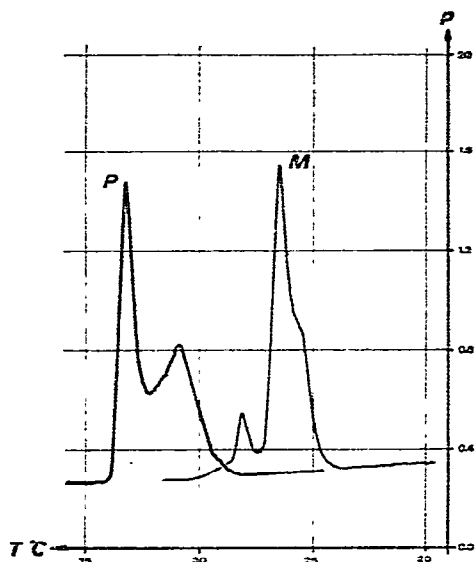


Fig. 2. Melting curves of a sample of the hydrocarbon II (4.52 mg) in a differential scanning calorimeter. Curve P, substance precipitated from its solution in *n*-hexane with propanol-1 at 0 °C; curve M, after crystallisation in the calorimeter at a cooling rate of 1–2 °C·min⁻¹ at 21–22 °C. The power, *p*, is in mcal·sec⁻¹.

quently, the unchanged hydrocarbon was recovered from the column packing by extraction in nearly quantitative yield.

In conclusion, we felt that this substance can be proposed as a standard stationary phase, and its gas chromatographic properties were therefore investigated. The results are reported below.

EXPERIMENTAL

The substances used as solutes were obtained from Fluka (Buchs, Switzerland), and the rare gases and light hydrocarbons were products of Air Liquide (Paris, France).

The chromatographic data were measured with a Packard-Becker (Delft, The Netherlands) Model 419 apparatus, the thermostated oven of which was slightly modified. By inserting an additional box of aluminium plates to regulate the circulation of the hot air, the temperature gradient, originally 1.5°C between extreme points, could be reduced to 0.3–0.5°C for isothermal work. The flow-rate of the helium carrier gas was regulated by a thermostated ($25 \pm 0.5^\circ\text{C}$) Brooks (Hatfield, Pa., U.S.A.) valve. The temperature of the column oven was constant to within $\pm 0.1^\circ\text{C}$ over 8 h. The flow-rate was determined twice daily with a soap-film device and controlled continuously with the aid of a precision flow meter¹⁸. The support was prepared from Chromosorb G (Johns-Manville, Denver, Colo., U.S.A.), which was made to react with trimethylsilanol in the presence of ammonia vapour at 100°C for 24 h in three successive treatments¹³. Two column packings were prepared by wetting the silanized support (particle diameter 180–220 μm) with a solution of hydrocarbon II in *n*-hexane and evaporating the solvent. The columns were Pyrex tubes (length 240

cm, I.D. 0.4 cm). Column A contained 2.583 g of stationary phase (column packing ratio, Chromosorb:hydrocarbon \approx 90:10, w/w) and column B contained 4.017 g of stationary phase (packing ratio \approx 86:14, w/w).

The melting curves of hydrocarbon II were recorded on a Perkin-Elmer Model DSC-1B differential scanning calorimeter. The measurements were made on samples of 1–4 mg in a nitrogen atmosphere at a heating rate of $1^\circ\text{C}\cdot\text{min}^{-1}$. The molecular weight was determined with a Knauer (Berlin, G.F.R.) vapour-pressure osmometer in toluene solution (standard: benzil).

The specific volume and thermal dilatation of the hydrocarbon were determined in a home-made pycnometer on three samples of 800 mg each at different temperatures between 30 and 190°C . With the experimental specific volumes, v , (corrected for vacuum) the coefficients of the equation $\ln v = \ln v(T^\dagger) + \kappa(T - T^\dagger)$, where T is the temperature and $T^\dagger = 130^\circ\text{C}$, were determined by linear regression. For the values of the specific volume at 130° [$v(T^\dagger)$] and the coefficient of thermal expansion, κ , see Table I.

All of the necessary calculations were made on a Control Data Model Cyber 7326 computer at the École Polytechnique Fédérale de Lausanne. The programs were written in Fortran. The coefficients of the various equations were determined by the least-squares method, using the routines CARLIN, IMG, LSQ1Z, LSQ2Z and PSQ3Z of the numerical analysis library POLYFTN, developed in the Department of Mathematics (under the responsibility of Prof. J. Descloux). Prior to calculations, some of the experimental results were first rejected by means of adequate statistical tests.

RESULTS AND DISCUSSION

The starting point of the chromatogram

For the determination of chromatographic data, the retention property X (distance on the chart, time, volume) of a hypothetical, non-retained substance is necessary. By working with a thermal conductivity detector, nitrogen is accepted as a substitute for such a substance. If a flame-ionization detector is used, methane is commonly assumed to approximate to the ideal properties, which is certainly an unsatisfactory assumption for precision work. The true zero can easily be determined if the relative retentions of a pair of substances are known with the necessary precision.

Let us choose one of the solutes to be methane, as it appears near to the true zero and it is detected by currently used detectors. Let us further assume that it is injected together with a second substance, A, (see Fig. 3) which is sufficiently separated from methane. The relative retention of A with respect to methane is then given by

$$r_{A/\text{CH}_4} = \frac{X'_R(A)}{X'_R(\text{CH}_4)} = \frac{X_R(A) - X_m}{X_R(\text{CH}_4) - X_m} \quad (1)$$

where X is the retention property of the solute (distance, d ; time, t ; volume, V) and X'_R , X_R and X_m represent the gross, corrected (net) and dead retention properties, respectively. Eqn. 1 gives, after the necessary transformations:

$$X_m = X_R(\text{CH}_4) - \frac{X_R(A) - X_R(\text{CH}_4)}{r_{A/\text{CH}_4} - 1} = X_R(\text{CH}_4) - \delta \quad (2)$$

TABLE II

GROSS RETENTION VOLUMES OF NEON AND NET RETENTION VOLUMES OF PERMANENT GASES AND LIGHT HYDROCARBONS
 All volumes in millilitres, referred to mean column conditions (mean pressure and column temperature). Net retentions calculated with neon as non-retained substance. Column B with 4.017 g of stationary phase; thermal conductivity detector; helium carrier gas. Data for neon, averages of 4-6 experiments; all other data, averages of 3-4 determinations. In italics: values for neon calculated with the aid of the coefficients of a linear regression; for the other substances, values calculated with the data listed in Table IV.

Compound	Temperature (°C)										
	30	50	70	90	110	130	150	170	190	210	230
Neon	26.49	26.54	26.13	26.33	26.31	26.14	26.09	26.09	26.11	25.97	25.67
Nitrogen	26.49	26.43	26.37	26.30	26.24	26.17	26.11	26.04	25.98	25.92	25.85
	0.15	0.07	0.06	0.10	0.11	0.18	0.08	0.14	0.15	0.05	0.19
Hydrogen	0.10	0.10	0.10	0.10	0.10	0.11	0.11	0.12	0.12	0.12	0.13
	0.33	0.19	0.14	0.18	0.13	0.19	0.18	0.22	0.35	0.35	0.36
Argon	0.27	0.20	0.17	0.16	0.16	0.17	0.19	0.22	0.27	0.33	0.43
	0.42	0.51	0.43	0.44	0.45	0.49	0.47	0.58	0.47	0.47	0.58
Krypton	0.45	0.45	0.45	0.46	0.47	0.47	0.48	0.50	0.51	0.52	0.54
	2.33	1.80	1.62	1.61	1.45	1.52	1.39	1.44	1.43	1.38	1.49
Xenon	1.96	1.77	1.65	1.56	1.50	1.46	1.43	1.43	1.43	1.43	1.45
	8.89	7.60	6.47	5.84	5.13	4.83	4.35	4.09	3.71	3.57	3.54
Methane	8.96	7.55	6.53	5.76	5.18	4.72	4.35	4.06	3.82	3.62	3.46
	1.15	1.14	1.07	1.04	1.00	1.00	0.94	0.91	0.98	0.96	1.00
Ethane	1.20	1.12	1.06	1.02	0.99	0.97	0.96	0.96	0.96	0.97	0.98
	9.04	7.13	6.40	5.36	4.69	4.27	3.71	3.50	3.23	3.02	—
Propane	8.98	7.36	6.21	5.35	4.71	4.21	3.81	3.49	3.23	3.01	2.83
	29.60	21.48	16.90	13.33	10.84	9.16	7.74	6.88	6.04	5.47	—
Butane	29.57	21.74	16.69	13.27	10.87	9.13	7.83	6.84	6.07	5.45	4.96
	103.81	66.19	45.73	33.25	25.06	19.85	15.95	13.32	11.34	9.77	—
Neopentane	103.16	66.61	45.83	33.22	25.15	19.74	15.99	13.29	11.30	9.81	8.65
	107.91	70.10	48.73	35.69	26.79	21.07	17.35	14.20	12.21	10.42	—
Tetramethylsilane	107.77	70.32	48.74	35.50	26.96	21.20	17.17	14.26	12.11	10.48	9.21
	148.21	90.92	60.15	42.92	31.53	23.95	19.27	15.65	13.00	11.15	—
	147.24	91.34	60.69	42.68	31.45	24.12	19.12	15.61	13.05	11.15	9.71

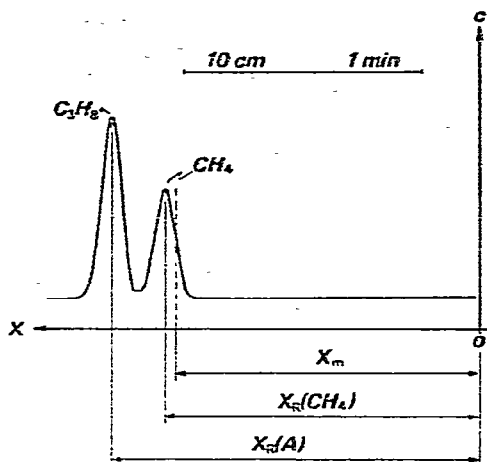


Fig. 3. Chromatogram of a mixture of methane and propane. Column B with 4.017 g of the hydrocarbon II; 210 °C; helium carrier gas. Concentration, c , in arbitrary units.

For calculation of the value of δ , a precise knowledge of the relative retention r_{A/CH_4} is necessary. To provide this, we equipped the chromatograph with a thermal conductivity detector, and on column B, containing 4.017 g of hydrocarbon II, we determined the gross retention volume of a series of permanent gases and light hydrocarbons. The results, summarized in Table II, show that neon has the smallest gross retention volume. We accepted tentatively that this value corresponds to the dead volume of the column, which implies that neon is supposed to be insoluble in the stationary phase, which is obviously not true. The systematic error introduced by this assumption at 25°C can be estimated as follows. From Henry's coefficient, h , reported in the literature for permanent gases and methane in several n -alkanes for 25°C¹⁹⁻²⁵, Henry's molal coefficient, $g^{(m)}$, was calculated as

$$g^{(m)} = M h / 1000 \quad (3)$$

where M is the molecular weight of the solvent. The coefficients h and $g^{(m)}$ are defined by

$$p = h x = g^{(m)} m \quad (4)$$

where p is the partial pressure of the solute over the solution, x is its mole fraction and m is its concentration in the solvent expressed in molality (moles of substance per kilogram of solvent). From Henry's molal coefficient, the related standard chemical potential was calculated, given by

$$\Delta\mu^{(m)} = RT \ln g^{(m)} \quad (5)$$

where Δ is the difference between the ideally dilute solution and the ideal gaseous state. Finally, by using the equation

$$V_a = \frac{RT_c}{1000 g^{(m)}} \quad (6)$$

the specific retention volume of the solute can be calculated by assuming that the solvent in question is used as the stationary phase.

It has been shown^{6,7} that, in agreement with the Flory²⁶ and Huggins²⁷ theory for mixtures of molecules of unequal size, the dependence of a quantity such as $\Delta\mu^{(m)}$ on the reciprocal of the molecular weight of the solvent is linear, to a first approximation. The data plotted in Fig. 4 confirm this linear relationship. Extrapolation to the molecular weight of hydrocarbon II shows that our values are of the right order of magnitude and, further, that neon might have a specific retention volume of about 0.02 ml at 25°C. In Table III, this value is compared with those of the permanent gases and of methane measured from neon as zero. If the estimated value of the retention volume of neon is correct, its neglect would introduce an error of about 7% in the specific retention volume of methane. Other permanent gases such as hydrogen and nitrogen have even higher retentions than neon.

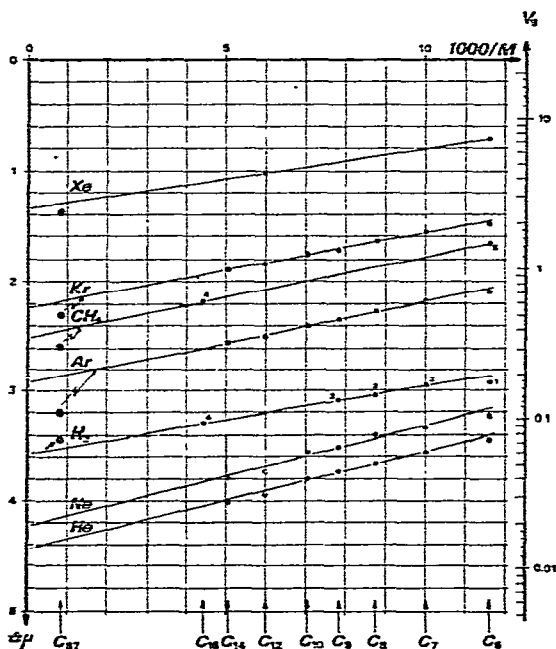


Fig. 4. Chemical potential related to Henry's molal coefficient, $\Delta\mu$, of several gases in *n*-alkanes and in hydrocarbon II. The logarithmic scale of the specific retention volume ($\text{ml}\cdot\text{g}^{-1}$) is also shown. Data for xenon, see ref. 19; for krypton, argon, neon and helium, see ref. 20; for hydrogen and methane point marked by 1, see ref. 21, by 2 see ref. 22, by 3 see ref. 23, by 4 see ref. 24 and by 5 see ref. 25. Data on hydrocarbon II were extrapolated to 25°C with the aid of the regression coefficients listed in Table IV.

Unfortunately, we cannot use the value of $0.02 \text{ ml}\cdot\text{g}^{-1}$ for neon as a correction for the whole temperature range. A substance with a positive free enthalpy difference will be more soluble at higher temperatures, and the correction will therefore be greater. Obviously, static measurements of the solubility of neon in the presence of helium would permit the calculation of the precise value of this correction and thus enhance the precision.

TABLE III

SPECIFIC RETENTION VOLUMES ON HYDROCARBON II

Values (ml·g⁻¹) extrapolated to 25 °C by using the coefficients in Table IV. For details, see text.

Estimated from Fig. 3 Ne	Measured from neon as starting point						
	Ne	Ar	Kr	Xe	H ₂	N ₂	CH ₄
0.02	0	0.12	0.50	2.33	0.074	0.024	0.304

In the absence of such data, we compared the temperature dependence of the dead volume of the column measured for neon with that calculated from the thermal expansion of the stationary phase. The dead volume of the column obviously changes with temperature because of the thermal expansion of the stationary phase as

$$V_m = V_m(T^\dagger) + V_{sp}(T^\dagger) [1 - e^{\kappa(T - T^\dagger)}] \quad (7)$$

where T^\dagger is a chosen temperature, κ the coefficient of cubic thermal expansion of the stationary phase and $V_{sp}(T^\dagger)$ the volume of the stationary phase at the temperature T^\dagger . In Fig. 5, the experimental gross retention volumes of neon are plotted as a function of the column temperature. The broken line is the linear regression calculated from the experimental data, while the full line was calculated from eqn. 7 by using the data in Table I. The agreement is very satisfactory.

In conclusion, the bias of the net retention volumes shown in Table II can be considered to be not too serious; even for a value of 0.8 ml (corresponding to a specific retention volume of 0.20 ml·g⁻¹) it is not more than 10%.

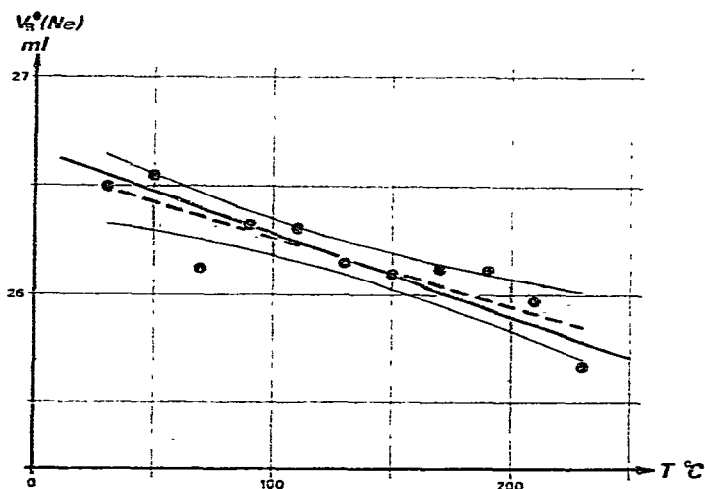


Fig. 5. The dead volume of column B (4.017 g of stationary phase) as measured by the gross retention volume of neon versus column temperature. Broken line, linear regression $V_m = V_m(T^\dagger) + b(T - T^\dagger)$ with slope of 0.0032 ± 0.0013 ml·°K⁻¹; solid line, trace of eqn. 7, where the value of $V_m(T^\dagger)$ was taken from the linear regression; its slope at 130 °C is 0.00386 ml·°K⁻¹. $T^\dagger = 130$ °C. The shaded area shows the confidence limits of the linear regression at the 95% confidence level.

Neglecting this bias, the chemical potential related to Henry's molal coefficient was calculated by the least-squares method using eqns. 6 and 8:

$$RT \ln g_j^{(m)} = \Delta\mu_j^{(m)} = \Delta H_j(T^\dagger) - T\Delta S_j(T^\dagger) + \Delta C_{p,j} \left(T - T^\dagger - T \ln \frac{T}{T^\dagger} \right) \quad (8)$$

$T^\dagger = 403.15^\circ\text{K}$ ($= 130^\circ\text{C}$), where T is the absolute temperature, $\Delta H_j(T^\dagger)$ the molar enthalpy difference, $\Delta S_j(T^\dagger)$ the molar entropy difference of the solute, j , between the ideal dilute solution and the perfect gaseous state at 130°C ; $\Delta C_{p,j}$ is the difference of the molar specific heat in these two states and is assumed to be constant over the whole temperature range (Kirchoff's method). The results are shown in Table IV.

TABLE IV

DIFFERENCES IN MOLAR ENTHALPY, ΔH_j , MOLAR ENTROPY, ΔS_j , BETWEEN IDEAL DILUTE SOLUTION AND PERFECT GASEOUS STATE AT 130°C AND DIFFERENCE IN MOLAR SPECIFIC HEAT, $\Delta C_{p,j}$

Calculated with eqn. 8 and the retention volumes shown in Table II, by taking neon as non-retained substance.

Compound	$\Delta H_j (T^\dagger)$ (<i>kcal</i> · <i>mole</i> ⁻¹)	$\Delta S_j (T^\dagger)$ (<i>cal</i> · <i>mole</i> · <i>°K</i> ⁻¹)	$\Delta C_{p,j}$ (<i>cal</i> · <i>mole</i> ⁻¹ · <i>°K</i> ⁻¹)
Nitrogen*	-0.214	-14.69	+3.75
Hydrogen*	+0.669	-22.57	+45.75
Argon*	-0.555	-12.33	+1.78
Krypton	-1.139	-11.79	+4.93
Xenon	-2.192	-12.07	+1.06
Methane	-1.018	-12.29	+3.22
Ethane	-2.509	-13.08	+0.47
Propane	-3.441	-13.86	+1.92
Butane	-4.444	-14.81	+4.82
Neopentane	-4.430	-14.64	+3.85
Tetramethylsilane	-4.803	-15.30	+5.17

* Probably with heavy bias.

With the aid of the regression coefficients [$\Delta H_j(T^\dagger)$, $\Delta S_j(T^\dagger)$ and $\Delta C_{p,j}$], the relative retentions of ethane, propane and butane were re-calculated with respect to methane. The results (Fig. 6) give the necessary information for the determination of the starting point of the chromatogram by the method summarized in eqn. 2.

As an example, the chromatogram of a mixture of methane and propane at 210°C is shown in Fig. 3 (column B). We measured 15.4 and 13.2 cm for the gross retention distances of propane and methane, respectively. From Fig. 6, we read off 5.7 as the relative retention of the propane, and so we calculate

$$d_m = 13.2 - \frac{15.4 - 13.2}{5.7 - 1} = 13.2 - 0.47 = 12.7 \text{ cm} \quad (9)$$

for the distance corresponding to the dead volume of the column.

Retention behaviour of *n*-alkanes

During an 8-month period, about 1500 retention values of *n*-alkanes from pentane to pentadecane were determined on columns A and B between 30 and 250°C . The net retention volumes did not change with time, and the relative error of a single determination amounted to about $\pm 1\%$. The specific retention volumes calculated

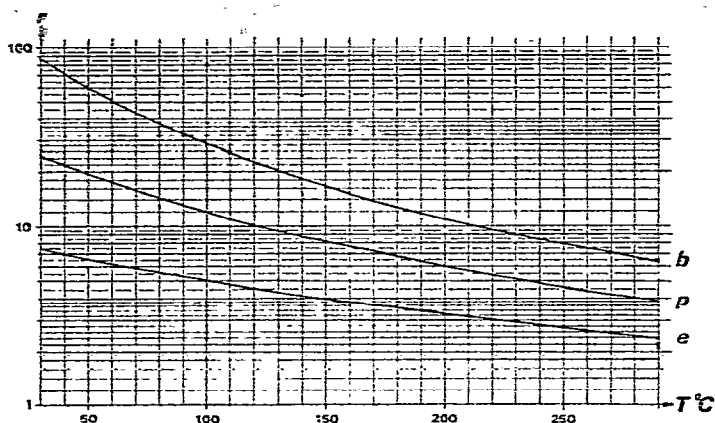


Fig. 6. Relative retention of ethane (e), propane (p) and butane (b) with respect to methane as a function of temperature. For details, see text. Values over 230 °C are extrapolated.

from the results showed a systematic difference of *ca.* 3%, the values being smaller on column B, which could be due to the error in the determination of the weight of the stationary phase. Therefore, the parameters of eqn. 8 were calculated with the average of the specific retention volumes. The regression coefficients of the higher homologues showed a systematic variation. By fitting the equation

$$\Delta\mu_z^{(m)} = (\alpha_0 + \alpha_1 z + \alpha_2(z^2 - z)/2) - T(\beta_0 + \beta_1 z) + \left(T - T^\dagger - T \ln \frac{T}{T^\dagger}\right) (\gamma_0 + \gamma_1 z) \quad (10)$$

where z (≥ 8) is the carbon number of the n -alkane C_2H_{2z+2} , to the experimental points for the n -alkanes from octane to pentadecane, the deviations of the experimental points (averages) were of the order of 0.6% [$\Delta_{rel}(95\%) = \pm 1.3\%$]. This regression permits extrapolation to a few higher homologues. The results listed in Table V are

TABLE V

SOLUBILITY PARAMETERS OF n -ALKANES

Experiments in the temperature range indicated; m = number of experimental points. For details see Table IV and text. $T^\dagger = 403.15$ °K (= 130.0 °C).

Compound	Temperature range (°C)	m	$\Delta H_j(T^\dagger)$ (kcal·mole ⁻¹)	$\Delta S_j(T^\dagger)$ (cal·mole ⁻¹ ·°K ⁻¹)	$\Delta C_{p,j}$ (cal·mole ⁻¹ ·°K ⁻¹)
Pentane	50–250	257	-5.418	-15.78	+7.02
Hexane	50–250	271	-6.438	-16.99	+9.16
Heptane	50–250	245	-7.445	-18.20	+10.58
Octane	90–250	223	$\alpha_0 + \alpha_1 z +$ $\alpha_2(z^2 - z)/2$ with $\alpha_0 = -0.143$ $\alpha_1 = -1.0444$ $\alpha_2 = +0.00282$	$\beta_0 + \beta_1 z$ with $\beta_0 = -9.12$ $\beta_1 = -1.277$	$\gamma_0 + \gamma_1 z$ with $\gamma_0 = -1.79$ $\gamma_1 = +1.632$
Nonane	90–250	188			
Decane	130–250	143			
Undecane	130–250	121			
Dodecane	190–250	63			
Tridecane	190–250	63			
Tetra- decane	210–250	39			
Penta- decane	230–250	17			

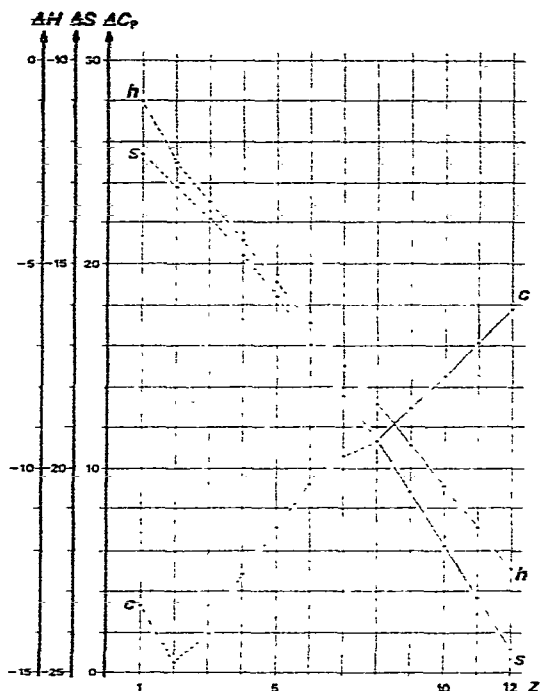


Fig. 7. Solubility parameters for n -alkanes as a function of the carbon number, z . Values for methane to heptane are calculated for each hydrocarbon by using eqn. 7. ΔH (trace h-h) in kcal·mole⁻¹, ΔS (trace s-s) and ΔC_p (trace c-c) in cal·mole⁻¹·°K⁻¹.

plotted in Fig. 7 together with the results for the light hydrocarbons (see Table IV) as a function of the carbon number of the n -alkane:

Note that this plot is not linear. Therefore, the determination of the starting point of the chromatogram is not justified by linearization of the logarithms of the retention data of n -alkanes, as suggested repeatedly (for the same criticism, see also ref. 28).

In order to facilitate the conversion of retention indices, the recalculated specific retention volumes, obtained by using the regression coefficients, are given in Fig. 8.

The data summarized in Table VI give a rough comparison of hydrocarbon II with a methylsilicone and an alkane with a carbon number of C₃₀ (e.g., squalane). The relative retention of two consecutive n -alkanes is a measure of the separation efficiency of the phase for hydrocarbons. On two similar columns (with the same phase ratio and same number of theoretical plates but different stationary phases), the separation efficiency obviously decreases if the relative retentions are smaller.

TABLE VI

APPROXIMATE RELATIVE RETENTION OF TWO SUCCESSIVE n -ALKANES AT 120 °C AND THE SPECIFIC RETENTION VOLUME OF n -OCTANE AT 100 °C ON A FEW STATIONARY PHASES

Stationary phase	$r_{(z+1)/z}$ at 120 °C	V_g (octane) (ml·g ⁻¹) at 100 °C
C ₃₀ hydrocarbon	1.979 (ref. 7), 1.95 (ref. 4)	230–250 (ref. 7)
Methylsilicone	1.77 (ref. 4)	≈ 100 (ref. 29)
Hydrocarbon II	1.95–1.90	157.7

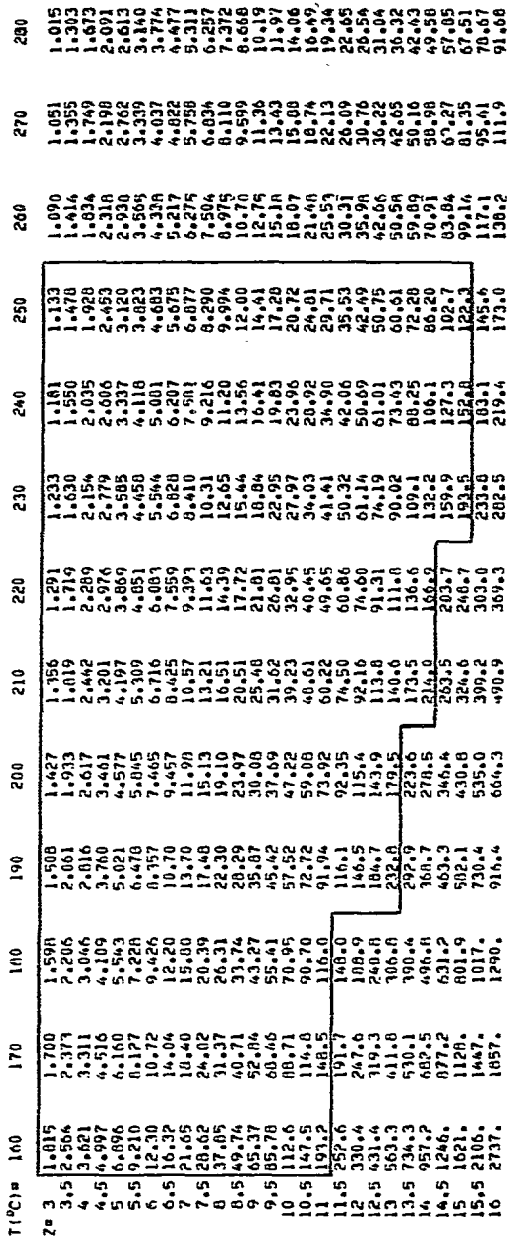
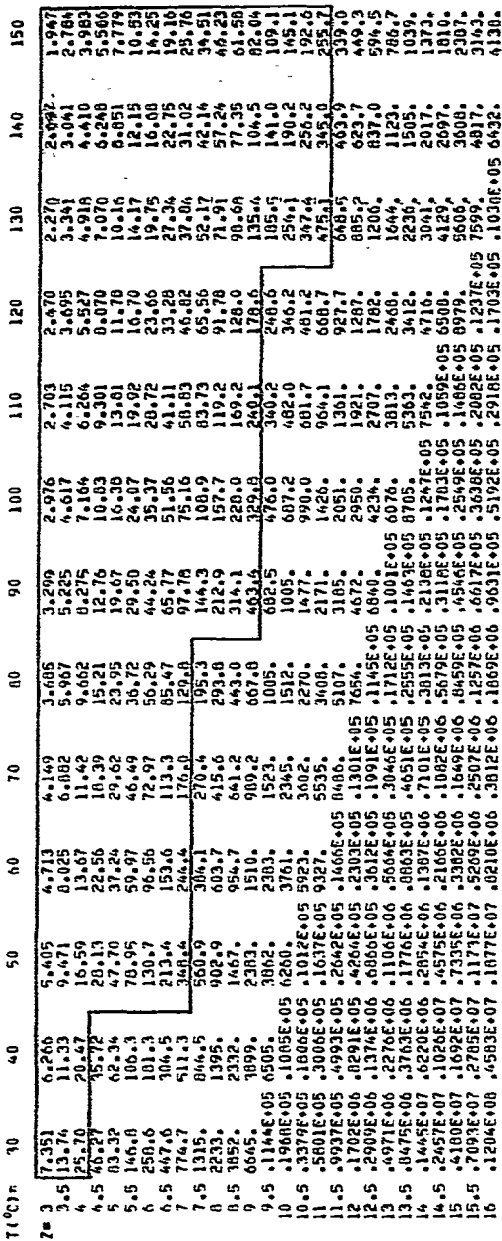


Fig. 8. Specific retention volumes of *n*-alkanes calculated with regression coefficients. Hypothetical *n*-alkanes with half carbon numbers are also listed in order to facilitate interpolation. Experimental values are limited to within the marked frames.

We observed that this number is about the same on hydrocarbon II and on the C₃₀ alkane but it is smaller on methylsilicones.

Methylsilicones are often spoken of as "rapid" stationary phases, meaning that the chromatograms on them are shorter in comparison with, for instance, squalane. On the one example of the retention volume of *n*-octane at 100°C, we observed that hydrocarbon II resembles the methylsilicone more than squalane in this respect.

Retention data of selected compounds

The retention indices of about 150 compounds were measured between 50 and 250°C. Statistical analysis showed that there was no significant difference between columns A and B, and therefore all results were evaluated together. The variance of a single determination is of the order of 1–2 units, except for the pyridines. These substances had to be injected in larger amounts as small samples gave peaks with serious tailing and widely varying retention indices.

Examination of the results listed in Table VII would suggest that this stationary

TABLE VII
RETENTION INDICES OF SELECTED COMPOUNDS ON THE HYDROCARBON II

Under the heading *m* the number of determinations is given in the temperature range shown in the fourth column. *V* is the variance around the linear regression with *m* – 2 degrees of freedom. The constants of the linear regression, *I*₁₃₀ and the temperature dependence for a 10 °C interval, 10(∂*I*/∂*T*), are listed in the last four columns. For convenience, the indices at 70 and 190 °C are also given. Experimental conditions: values on two columns A and B with 2.583 and 4.018 g of hydrocarbon; determination at intervals of 20 °C; injection of about 0.05 mg per component with the exception of pyridines, where larger amounts were applied (ca. 0.2 mg); flame-ionization detector.

Type of compounds	Compounds	<i>m</i>	Temperature range (°C)	<i>I</i>			10(∂ <i>I</i> /∂ <i>T</i>)		
				70 °C	130 °C	190 °C			
Hydrocarbons	<i>Isoalkanes</i>								
	Neopentane*		30–230	406.4	409.0	411.6	0.44		
	2,2-Dimethylbutane	22	50–150	0.76	535.1	541.2	1.01		
	2,3-Dimethylbutane	14	50–150	0.51	567.9	573.2	0.89		
	2,2-Dimethylpentane	15	70–190	0.79	624.2	627.7	631.2	0.58	
	2,3-Dimethylpentane	15	50–170	0.85	674.3	679.9	685.5	0.94	
	2,4-Dimethylpentane	29	50–210	1.11	626.9	629.5	632.1	0.44	
	2,2,3-Trimethylbutane	16	50–150	1.28	641.5	653.1	664.7	1.93	
	2,2-Dimethylhexane	12	70–210	0.24	715.8	719.6	723.4	0.64	
	2,3-Dimethylhexane	12	90–210	0.13	761.0	766.0	771.0	0.84	
	2,4-Dimethylhexane	18	90–210	0.61	729.6	733.4	737.2	0.63	
	3,4-Dimethylhexane	13	90–190	0.71	774.0	780.4	786.8	1.06	
	2,3,4-Trimethylpentane	15	90–210	0.42	755.5	765.6	775.7	1.68	
	2,2,4-Trimethylpentane	13	90–210	0.33	788.6	694.8	701.0	1.68	
	2,2-Dimethylheptane	17	90–210	0.70	811.6	815.8	820.0	0.70	
	2,2,4,6,6-Pentamethylheptane	11	130–250	2.10		990.5	1002.9	2.07	
		<i>Alkenes</i>							
		1-Pentene	9	50–150	0.51	482.5	483.9		0.27
		1-Hexene	14	50–190	0.74	584.5	585.3	586.1	0.14
		1-Heptene	16	50–230	1.23	683.6	685.2	686.8	0.26
		1-Octene	19	110–250	1.92	783.7	784.7	785.9	0.19
		1-Nonene	21	110–250	1.52	883.4	885.0	886.6	0.26
	1-Decene	22	130–250	0.76		984.6	986.6	0.34	
	1-Undecene	18	130–250	0.99		1084.3	1086.6	0.38	
	1-Dodecene	14	170–250	0.53		1184.3	1186.6	0.38	
	1-Tridecene	8	190–250	1.39		1284.4	1286.9	0.42	

TABLE VII (continued)

Type of compounds	Compounds	m	Temperature range (°C)	V			10 (∂I/∂T)
				I	70 °C	130 °C	
<i>Alkynes</i>							
	1-Pentyne	13	50-130	1.02	484.5	484.9	-0.06
	1-Hexyne	14	50-190	0.95	587.3	587.6	587.9
	1-Heptyne	18	50-230	1.49	687.1	688.4	689.7
	1-Octyne	27	90-250	3.06	785.8	788.3	790.8
	1-Nonyne	18	110-250	1.78	885.3	888.0	890.7
	1-Decyne	16	130-250	1.97		986.7	990.6
<i>Monocyclic hydrocarbons</i>							
	Cyclopentane	15	50-130	0.59	575.9	588.3	2.06
	Cyclohexane	22	50-210	0.99	675.6	694.5	713.4
	Cycloheptane	18	90-190	1.99	811.6	838.8	866.0
	Cyclooctane	16	130-230	0.50		966.9	999.2
	Cyclodecane	8	190-250	0.61		1180.0	1223.1
	Cyclododecane	8	190-250	0.40		1362.7	1412.6
<i>Bicyclic hydrocarbons</i>							
	<i>cis</i> -Hydrindane	19	130-250	1.29		1034.9	1072.8
	<i>trans</i> -Hydrindane	11	130-250	2.11		1000.3	1035.3
	<i>cis</i> -Decalin	12	170-250	0.53		1153.9	1198.7
	<i>trans</i> -Decalin	12	170-250	0.47		1112.2	1153.4
<i>Alkylbenzenes</i>							
	Benzene	24	50-230	2.47	659.2	678.8	698.4
	Toluene	25	70-250	2.22	766.8	786.5	806.2
	Ethylbenzene	24	90-250	1.57	855.2	875.9	896.6
	Propylbenzene	21	130-250	2.03	943.0	965.0	987.0
	Butylbenzene	18	150-250	0.78		1064.8	1087.0
	Pentylbenzene	16	170-250	2.85		1162.0	1183.9
	Hexylbenzene	13	190-250	1.35		1257.7	1281.2
<i>Others</i>							
	Adamantane	14	170-250	0.38		1137.6	1189.5
	Tetrahydronaphthalene	11	190-250	1.25		1189.7	1231.1
	Naphthalene	12	190-250	0.93		1215.4	1264.8
	Azulene	6	190-250	0.04		1351.2	1388.9
<i>Alkane derivatives</i>							
<i>1-Chloroalkanes</i>							
	1-Chloropropane	12	50-170	0.82	526.9	536.4	545.9
	1-Chlorobutane	19	50-190	1.51	630.4	641.4	652.4
	1-Chloropentane	19	90-230	0.89	732.2	743.3	754.4
	1-Chlorohexane	17	110-230	0.93	833.3	844.8	856.3
	1-Chloroheptane	14	130-230	1.28	934.5	946.3	958.1
	1-Chlorooctane	12	150-230	0.32		1047.4	1059.5
	1-Chlorononane	8	190-230	0.08		1146.3	1160.3
	1-Chlorodecane	7	190-230	0.10		1246.9	1260.9
<i>1-Bromoalkanes</i>							
	Bromoethane	11	50-170	0.49	509.6	523.0	2.24
	1-Bromopropane	19	50-190	2.46	614.2	629.4	644.6
	1-Bromobutane	22	50-210	0.81	716.8	732.7	748.6
	1-Bromopentane	19	90-210	2.46	817.7	835.0	852.3
	1-Bromohexane	14	130-210	1.00	918.3	936.4	954.5
	1-Bromoheptane	14	130-250	1.13		1036.2	1056.8
	1-Bromooctane	14	130-250	0.88		1136.3	1157.6
	1-Bromononane	8	190-250	0.65		1235.2	1258.0
	1-Bromodecane	5	210-250	1.05		1334.5	1358.0

(Continued on p. 78)

TABLE VII (continued)

Type of compounds	Compounds	m	Temperature V range (°C)	I			10 ($\partial I/\partial T$)	
				70 °C	130 °C	190 °C		
<i>1-Iodoalkanes</i>								
	Iodomethane	14	50-150	0.30	528.6	548.8	569.0	3.36
	Iodoethane	16	50-190	0.29	617.6	638.9	660.2	3.55
	1-Iodopropane	20	70-210	0.57	720.3	743.8	767.3	3.92
	1-Iodobutane	18	90-210	0.49	819.3	844.6	869.9	4.21
	1-Iodopentane	18	110-250	1.32	917.8	944.6	971.4	4.47
	1-Iodohexane	12	150-250	0.44		1045.1	1072.9	4.63
	1-Iodoheptane	10	170-250	0.52		1144.9	1173.6	4.79
	1-Iodooctane	6	190-250	0.41		1247.2	1275.2	4.67
<i>1-Cyanoalkanes</i>								
	1-Cyanopropane	16	50-190	8.14	587.4	593.6	599.8	1.03
	1-Cyanobutane	19	70-210	0.97	689.1	697.4	705.7	1.39
	1-Cyanopentane	18	90-210	0.56	789.5	799.1	808.7	1.60
	1-Cyanoheptane	16	110-230	0.62	888.2	899.7	911.2	1.91
	1-Cyanoheptane	7	130-230	1.08	990.3	1001.3	1012.3	1.84
	1-Cyano-octane	17	150-250	2.34		1102.9	1114.7	1.97
	1-Cyanononane	10	170-250	0.64		1202.9	1215.3	2.07
	1-Cyanodecane	7	190-250	0.15		1302.4	1315.6	2.20
<i>1-Nitroalkanes</i>								
	Nitroethane	12	50-170	2.15	563.7	578.6		2.48
	1-Nitropropane	20	50-190	1.33	654.7	665.1	675.5	1.73
	1-Nitrobutane	15	90-230	0.68	754.6	767.2	779.8	2.10
	1-Nitropentane	14	110-230	0.90	855.1	868.8	882.5	2.29
	1-Nitrohexane	10	130-230	0.91		969.9	984.8	2.48
<i>1-Acetoxyalkanes</i>								
	1-Acetoxyethane	11	50-170	2.35	548.6	544.0	539.4	-0.77
	1-Acetoxypropane	19	50-190	1.37	644.1	638.9	633.7	-0.87
	1-Acetoxybutane	17	90-230	2.01	743.7	740.9	738.1	-0.46
	1-Acetoxy-pentane	23	90-250	1.90	843.7	841.1	838.5	-0.44
	1-Acetoxyhexane	14	130-250	0.85	940.8	939.4	938.0	-0.24
	1-Acetoxyheptane	13	130-250	1.16		1039.9	1038.8	-0.19
	1-Acetoxyoctane	11	130-250	0.64		1138.2	1138.5	0.05
	1-Acetoxy-nonane	8	190-250	0.52		1237.7	1238.1	0.07
<i>1-Alkanols</i>								
	1-Butanol	21	50-190	4.29	602.2	600.9	599.6	-0.22
	1-Pentanol	26	70-190	1.67	700.3	701.9	703.5	0.27
	1-Hexanol	25	90-230	0.57	798.0	803.6	809.2	0.94
	1-Heptanol	19	130-250	1.45	898.3	905.6	912.9	1.22
	1-Octanol	16	130-250	1.90		1006.6	1014.3	1.29
	1-Nonanol	8	190-250	2.80		1110.9	1117.5	1.10
<i>2-Alkanols</i>								
	2-Propanol	7	70-110	2.21	446.0	442.0		-0.66
	2-Butanol	13	70-150	2.32	547.9	552.0		0.69
	2-Pentanol	18	70-230	1.74	643.6	648.2	652.8	0.77
	2-Hexanol	21	90-230	1.99	742.4	748.0	753.6	0.94
	2-Heptanol	22	110-230	0.87	841.8	848.0	854.2	1.04
	2-Octanol	16	130-230	0.95		948.3	955.1	1.13
<i>2-Methylalkan-2-ols</i>								
	2-Methylpropanol-2	8	50-110	1.12	478.1	473.3		-0.80
	2-Methylbutanol-2	14	50-190	1.12	596.6	600.9	605.2	0.71
	2-Methylpentanol-2	19	50-230	3.11	688.8	693.8	698.8	0.83
	2-Methylhexanol-2	17	90-230	0.90	782.4	788.3	794.2	0.99
	2-Methylheptanol-2	15	110-230	0.98	879.9	885.8	891.7	0.99
	2-Methyloctanol-2	12	150-230	1.46		986.5	988.3	0.97

TABLE VII (continued)

Type of compounds	Compounds	m	Temperature range (°C)	V			I	10 (∂I/∂T)
				70 °C	130 °C	190 °C		
	<i>2-Alkanones</i>							
	2-Butanone	18	50-150	8.25	540.2	543.5		0.55
	2-Pentanone	21	50-190	1.71	629.6	632.2	634.8	0.43
	2-Hexanone	24	70-230	0.82	729.4	733.7	738.0	0.72
	2-Heptanone	17	90-250	0.63	828.8	833.4	838.0	0.76
	2-Octanone	12	150-250	0.68	927.9	933.2	938.5	0.88
	2-Nonanone	12	150-250	0.35	1033.4	1039.5	1039.5	1.02
	2-Decanone	10	170-250	0.76	1134.4	1139.7	1139.7	0.89
	2-Undecanone	8	190-250	0.45	1234.6	1240.4	1240.4	0.96
	<i>Ethers</i>							
	Diethyl ether	11	70-130	0.98	482.6	470.7		-1.99
	Dipropyl ether	24	50-190	1.29	659.0	655.2	651.4	-0.64
	Dibutyl ether	20	110-210	1.20	858.0	855.1	852.2	-0.49
	Dipentyl ether	8	170-250	0.49		1053.0	1051.0	-0.34
	<i>Halogenomethanes</i>							
	Dichloromethane	13	50-170	0.94	497.9	509.1		1.86
	Trichloromethane	18	50-210	1.66	595.2	610.3	625.4	2.51
	Tetrachloromethane	22	70-210	1.22	663.1	681.8	700.5	3.12
	Dibromomethane	20	90-210	3.67	681.7	706.2	730.7	4.08
	Tribromomethane	14	130-210	1.10	873.1	912.9	952.7	6.44
Halogenobenzenes	Fluorobenzene	24	50-230	1.70	651.3	665.9	680.5	2.44
	Chlorobenzene	27	90-250	1.20	838.4	866.1	893.8	4.61
	Bromobenzene	26	110-250	0.94	925.8	961.1	996.4	5.89
	Iodobenzene	20	150-250	0.95		1081.1	1125.7	7.43
Alkylpyridines	Pyridine	18	90-230	3.42	705.9	728.3	750.7	3.73
	2-Picoline	20	90-230	3.41	786.6	805.4	824.8	3.23
	3-Picoline	11	110-190	2.24	826.8	848.0	869.2	3.54
	4-Picoline	16	90-230	2.51	823.2	846.7	870.2	3.91
	2-Ethylpyridine	10	110-210	0.66	871.8	890.2	908.6	3.06
	3-Ethylpyridine	17	130-230	2.30	918.0	941.7	965.4	3.95
	4-Ethylpyridine	10	150-210	2.72	921.4	945.9	970.4	4.08
	2,4-Lutidine	12	130-230	2.68	903.4	922.7	942.0	3.22
	2,5-Lutidine	15	130-230	1.71	903.2	922.3	941.4	3.18
	2,6-Lutidine	20	110-210	3.58	863.8	876.1	888.4	2.05
	3,4-Lutidine	9	150-210	5.78		992.3	1018.6	4.38
	3,5-Lutidine	13	130-230	2.67		967.7	991.6	3.99
	2-Propylpyridine	16	130-230	1.20		976.6	998.3	3.62
	4-Propylpyridine	16	130-230	3.71		1034.7	1061.1	4.40
	4-tert.-Butylpyridine	6	150-210	0.97		1073.3	1101.9	4.76
Miscellaneous	Tetrahydrofuran	16	50-170	1.92	602.6	612.9	623.2	1.71
	Dioxan	17	50-170	1.58	660.3	675.0	689.7	2.45
	Thiophen	17	50-190	3.23	664.6	685.3	706.0	3.45
	Tetramethylsilane*		30-230		429.4	427.1	424.8	-0.38

* See Table VI.

phase has a certain polarity if compared with squalane with Rohrschneider's empirical constants. However, it has been shown that the effect of increasing molecular weight of the stationary phase is to displace retention data in the same sense but not by the same amount as increasing polarity^{7,15}.

TABLE VIII

RETENTION INDICES OF NEOPENTANE AND TETRAMETHYLSILANE CALCULATED WITH SPECIFIC RETENTION VOLUMES RELATED TO THE REGRESSION COEFFICIENTS LISTED IN TABLE IV

Differences, δ , for 20 °C steps are given in italics.

Compound	Temperature (°C)										
	30	50	70	90	110	130	150	170	190	210	230
Neopentane	403.6	405.1	406.3	407.6	408.8	409.8	410.6	411.3	411.8	412.1	412.3
δ		1.5	1.2	1.3	1.2	1.0	0.8	0.7	0.5	0.3	0.2
Tetramethylsilane	430.0	429.8	429.4	429.0	428.4	427.6	426.8	425.9	424.8	423.6	422.4
δ		-0.2	-0.4	-0.4	-0.6	-0.8	-0.8	-0.9	-1.1	-1.2	-1.2

In Fig. 9, we have marked on the abscissa the retention index differences

$$\Delta^*I_{130} = I_{130}(\text{HC-}\infty) - I_{130}(\text{HC-30}) \quad (11)$$

for compounds used by McReynolds to compare stationary phases⁴. In eqn. 11, $I_{130}(\text{HC-}\infty)$ is the retention index of the compound on a hypothetical branched alkane of infinite molecular weight at 130°C and $I_{130}(\text{HC-30})$ is that on a C₃₀ hydrocarbon with the structure I, from ref. 15. By plotting ΔI values of the same substances, obtained as differences between indices on any two hydrocarbon phases, against the Δ^*I_{130} values as defined in eqn. 11, a linear relationship must be obtained.

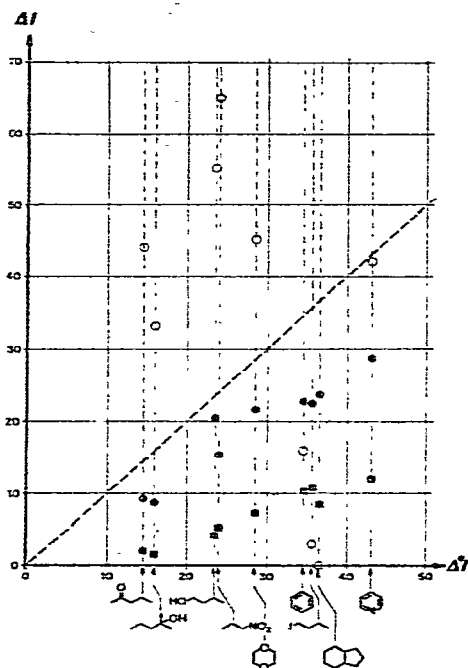


Fig. 9. ΔI values of selected substances on hydrocarbon stationary phases as a function of Δ^*I value of the same substances measured on a hypothetical hydrocarbon of infinite molecular weight referred to a hydrocarbon of carbon number C₃₀ of structure I. For details, see text. ■, Average ΔI values on nujol, mineral oil and liquid paraffin referred to squalane from ref. 4; ●, ΔI values on hydrocarbon II referred to a C₃₀ hydrocarbon of structure I; ○, average ΔI values on methylsilicones from ref. 4. ΔI values on a hypothetical alkane of structure I of infinite molecular weight referred to a C₃₀ hydrocarbon should fall on the broken line.

Inspection of data on hexatriacontane, nujol, mineral oil and liquid paraffin listed in McReynolds' compilation show that ΔI values on these hydrocarbons (relative to squalane at 120°C) are very similar⁴. We therefore plotted their average value. The points are indeed aligned. Also, the ΔI values on hydrocarbon II relative to the C₃₀ hydrocarbon of structure I (130°C from ref. 15) show a linear relationship. ΔI values of methylsilicones, on the contrary, show no correlation, which demonstrates clearly that this class of stationary phases has a different separating character.

As an example, it is interesting to calculate the retention indices of two sub-

stances by using the coefficients of the regression equations in terms of chemical potentials. In Table VIII, the retention indices of neopentane and tetramethylsilane are shown as a function of the temperature. It can be seen that, in fact, the temperature dependence of the retention index is hyperbolic but the error introduced by the linear approximation amounts only to ± 0.5 in a temperature range of 200°C. Probably, retention indices with higher temperature dependence will show a more pronounced curvature.

Finally, it should be noted that the results of an investigation of column packings prepared with hydrocarbon II in combination with different supports suggest that a good column performance can easily be obtained with this substance as stationary phase³⁰.

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