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EVALUATION OF A THERMALLY STABLE HYDROCARBON AS A NON-POLAR BASE STATIONARY PHASE FOR USE IN ROHRSCHEIDER-McREYNOLDS-TYPE SCHEMES

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SUMMARY

While efforts to develop an alternative low-polarity stationary phase to squalane with high thermal stability to allow Rohrschneider-McReynolds-type schemes to be applied over a more realistic temperature range have been enhanced by the recent introduction of the hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracontane ($C_{87}H_{176}$), its high price will seriously restrict its acceptance.

Exhaustively hydrogenated Apiezon M (Apiecon MH) possesses column constants and thermal stability essentially identical with those of $C_{87}H_{176}$. An examination of a series of samples of Apiezon MH is reported to illustrate that a reproducible stationary phase is possible with this refined inexpensive material and offers an attractive alternative to the expensive synthetic hydrocarbon.

INTRODUCTION

Although the important area of stationary phase classification has been considered by many workers, it is apparent that any general acceptance has been restricted to the scheme of Rohrschneider¹ and the conceptionally identical one of McReynolds². These schemes, which consider the differences in retention of selected substances on a particular stationary phase and on the non-polar phase squalane, have been restricted by the low operating temperature, *i.e.*, 120-130°, possible with the non-polar reference phase. This limitation requires that stationary phases are selected on the basis of low-temperature behaviour to achieve separations at much higher operating temperatures and conversely materials potentially suitable for use at high temperature cannot be characterized at lower temperatures owing to their physical conditions, *i.e.*, melting or glass transition points, at these lower temperatures.

Elimination of squalane as a reference in calculating retention differences has

been reported³⁻⁶ as it has been shown that Rohrschneider-type schemes are based on differences in intermolecular interactions between a substance and each of two stationary phases rather than on polar interactions alone as originally postulated. Such a scheme has found little acceptance as realistically interest has concentrated on a modified procedure which would allow use of the considerable amount of available Rohrschneider- and McReynolds-type data.

Dimethyl polysiloxane, available with a wide range of molecular weights and suitable for use over an extended temperature range, has been reported⁷ as an alternative low-polarity reference phase but has not found acceptance. With increased polarity relative to squalane the differences in the solvent constants are not readily related to the established values used by the principal suppliers^{8,9} of chromatographic specialties. Other objections on theoretical grounds concerning stability and performance¹⁰ would appear to be largely unjustified.

The requirements of a hydrocarbon for use at high temperature have been considered by Huber and Kováts¹¹, who deduced that a molecular weight in excess of 1100 would allow an upper temperature limit of 300°. Within this specification Rieđo *et al.*¹⁰ synthesized the hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracotane of empirical formula $C_{87}H_{176}$, which was suggested to be suitable for use at 280°. The material was subsequently evaluated by Haken and Ho¹². Prolonged use at 180° was possible without any significant increase in the phase constants or deterioration of the peak shape as occurs with squalane due both to its loss by bleeding and its increased polarity by oxidation. The material has been recently offered commercially as Apolane-87 by Applied Science Labs. (State College, Pa., U.S.A.)¹³. Its high price of \$ 70 per gram is undoubtedly due to the twelve-step synthetic procedure involved and makes it one of the most expensive stationary phases offered. Utilization of the material, which would appear to have been restricted to one report¹⁴ concerning wool wax methyl esters, will not be enhanced by the high cost and gives further impetus to the study of alternative non-polar stationary phases.

Vernon and co-workers have considered various hydrocarbon phases^{15,16} and have recently reported¹⁶ the use of exhaustively hydrogenated Apiezon materials as a non-polar stationary phase with column constants slightly higher than that of squalane, which has since been shown to be essentially identical¹² with those of Apolane-87. By considering the molecular weight requirements suggested by Huber and Kováts¹¹, Apiezon M with a reported average molecular weight of 2340 was recommended rather than Apiezon L with an average molecular weight of 3970¹⁶.

A considerable reluctance to the use of processed Apiezon, which is of somewhat indefinite composition¹⁷ with possible residual olefinic and aromatic unsaturation, can be expected as experiences with the use of industrial products as stationary phases have often been unsatisfactory¹⁸. While most industrial products are completely suitable for their prime purpose, their performance and specifications do not require close tolerances on chemical composition. With gas chromatography where the column processes are directly dependent on chemical composition, widely variant retention behaviour may be experienced.

These objections are considered in the present work, in which a series of Apiezon M samples have been exhaustively hydrogenated. The residual unsaturation has been determined and the McReynolds constants of the samples reported at 120° and 180°. The availability of hydrogenated Apiezon M is analogous to the situation existing

with polysiloxanes where industrial materials have been superseded by a wide range of specially prepared materials which have found universal acceptance.

EXPERIMENTAL

Hydrogenation of Apiezon grease

A 10-g amount of Apiezon M and 5 g of freshly prepared Raney nickel catalyst in 200 ml of cyclohexane are hydrogenated at 260° for 24 h with stirring and using a hydrogen pressure of 100 atm. After removal of catalyst by filtration, the solvent is removed by rotary evaporation.

Degree of residual unsaturation

The UV spectrum of Apiezon M shows clearly defined maxima at 238 and 260 nm, being the absorbance maxima of olefinic and aromatic unsaturation, respectively. Measurement of absorbances at these two wavelengths, (a) of a suitably diluted sample of the Apiezon M in cyclohexane, and (b) of the hydrogenation solution after removal of catalyst and re-adjustment of solution volume to 200 ml, will give the percentages of residual unsaturation of each type directly. Table I shows results of UV absorbance measurements.

TABLE I

ULTRAVIOLET ABSORBANCE MEASUREMENTS AT 238 AND 260 nm ($E_{1\%}^{1\text{cm}}$)

Stationary phase	Commercial product		Hydrogenated product	
	238 nm	260 nm	238 nm	260 nm
Apiezon M (16)	64.0	38.0	1.02	0.46
Apiezon M (S746)	66.5	33.0	2.54	0.76
Apiezon M (S877)	29.0	14.4	2.15	0.60

Gas chromatography

The analyses were carried out using 10% of the stationary phases on Chromosorb W AW DMCS. Columns of 1/8 and 1/4-in. O.D. of aluminium and stainless steel were employed, there being no variation of the retention indices of test compounds on squalane with either column material provided that the support is inactive. Determinations were carried out at 120° and 180°.

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph has been interfaced to a 16K PDP 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors with injection by a Hewlett-Packard 7670A automatic sampler. Calculation of dead time and of retention indices was conducted mathematically within the system.

Gel permeation chromatography

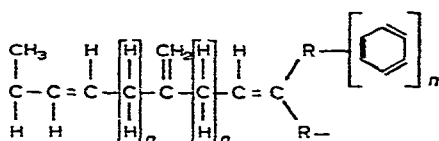
The samples of Apiezon L and the hydrocarbon $C_{87}H_{176}$ as a control of known molecular weight were examined using a Waters Assoc. ALC gel permeation chromatograph with an M600 pump and a UK-6 injector. The columns were μ Styragel of 10^5 , 10^4 , 10^3 , 500 and 100 Å. The solvent used was tetrahydrofuran at a flow-rate of 2 ml/min at 21°.

RESULTS AND DISCUSSION

Apiezon products

Apiezon oils, greases and waxes were discovered early this century during Burch's original experiments on the molecular distillation of petroleum oils^{19,20}. The residual compounds were found to possess extremely low vapour pressures and although they possessed the low vapour pressure of a solid they acted as efficient lubricants and heat-exchange media and for many years have been offered commercially for these purposes.

The compositions of the Apiezon products have not been extensively disclosed but on the basis of some not completely convincing IR studies¹⁷ a molecular structure has been reported with various olefinic and aromatic unsaturation as shown below:



The use of the materials as stationary phases is well established and while the first report is unknown the materials were reported in one of the early works of James and Martin²¹ in 1956 where Apiezon M was used for the separation of C₅-C₁₈ fatty acid methyl esters at 197-205°. At that time the effect of the increased polarity on retention as compared to a saturated hydrocarbon was reported.

The average molecular weights of Apiezon M and L have been reported by Vernon and Ogundipe¹⁶ as 2340 and 3970, respectively, on the basis of measurements using a vapour-phase osmometer. Gel permeation chromatography, however, would suggest much lower values. The C₈₇H₁₇₆ hydrocarbon with a molecular weight of 1222 has an elution volume of 44.6 ml while Apiezon L has very similar value of 44.6 ml and Apiezon M 45.7 ml. Thus the molecular weight of Apiezon L is marginally lower than 1222 and Apiezon M is slightly lower. An estimate of the individual values could be made if other standards were available, but the behaviour of the C₈₇H₁₇₆ is such that the relative values of the two greases is clearly shown and both have values close to that recommended by Huber and Kovats¹¹. These values are in reasonable agreement with the manufacturer's literature²², which lists values of 1300 and 950 for Apiezon L and M, respectively.

The chromatograms of the three materials are shown in Fig. 1, where it is apparent that both of the Apiezon materials possess narrow molecular weight distributions.

Retention indices

The retention indices of the McReynolds test solutes are shown in Table II for the hydrogenated Apiezon M reported previously¹⁶, for two additional samples of Apiezon M, the C₈₇H₁₇₆ hydrocarbon, squalane and the commercial Apiezon compounds. The results show that the hydrogenation reduces the polarity of the phases and the retention index of each of the solutes and produces a material which

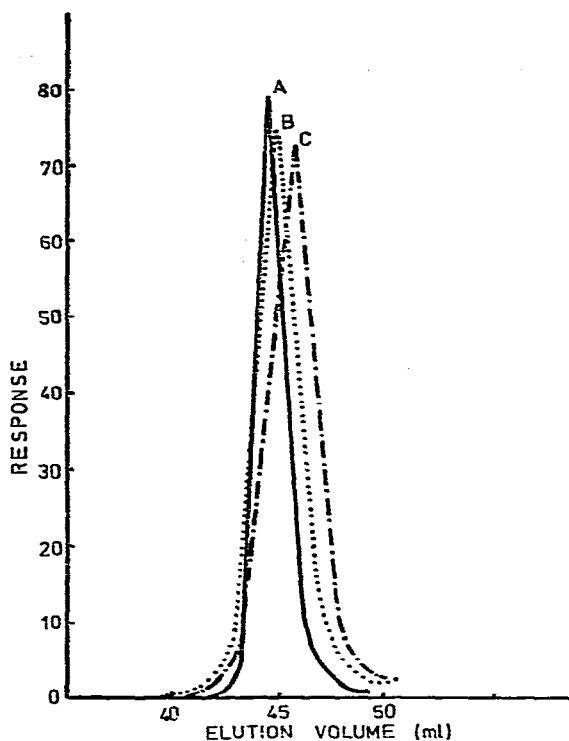


Fig. 1. Gel permeation chromatogram showing molecular weight distributions of (A) $C_{87}H_{176}$ hydrocarbon (mol.wt. 1222), (B) Apiezon L and (C) Apiezon M.

possesses values essentially identical with that of the $C_{87}H_{176}$ hydrocarbon. In both instances the values are slightly higher than those obtained with squalane.

The low upper temperature limit possible with squalane is well known and the lack of stability even at 120° as required for the McReynolds evaluation has been demonstrated¹² together with the considerable stability of dimethyl polysiloxane and the $C_{87}H_{176}$ hydrocarbon. Table III shows that the stabilities of the hydrogenated Apiezon M and $C_{87}H_{176}$ at 120° are essentially identical, a conclusion which is not unexpected as both materials are hydrocarbons of similar molecular weight, each with some chain branching and both with low unsaturation.

TABLE II
RETENTION INDICES OF McREYNOLDS SOLUTES AT 120°

Stationary phase	X	Y	Z	U	S
Apiezon M hydrogenated (16)	671	599	632	667	736
Apiezon M hydrogenated (S746)	674	600	634	670	729
Apiezon M hydrogenated (S877)	671	600	630	667	727
$C_{87}H_{176}$	674	600	630	664	724
Squalane	653	590	627	652	699
Apiezon M (8)	684	611	642	682	739
Apiezon M (S746)	680	611	643	680	744
Apiezon M (S877)	682	611	642	682	739

TABLE III
STABILITY OF HYDROGENATED APIEZON M, $C_{87}H_{176}$ HYDROCARBON AND SQUALANE AT 120°

Stationary phase	Time (days)	<i>I</i>				
		Benzene	1-Butanol	2-Pentanone	2-Nitropropane	Pyridine
Apiezon M hydrogenated (S746)		674	600	634	670	729
	1	674	600	634	670	729
	2	674	600	634	670	729
	3	674	600	634	670	729
	4	674	600	634	670	730
	5	674	601	635	670	730
	6	674	600	634	670	730
	7	674	601	635	670	730
	8	674	601	634	670	730
	9	674	601	634	670	730
$C_{87}H_{176}$		674	600	630	664	724
	1	674	600	630	664	724
	2	674	600	630	664	724
	3	674	600	630	664	724
	4	674	601	631	664	724
	5	674	601	631	664	724
	6	674	601	632	664	723
	7	674	601	631	664	724
	8	674	601	631	664	724
	9	674	601	631	664	724
Squalane		653	590	627	652	699
	1	654	613	636	662	708
	2	654	623	642	673	716
	3	654	640	648	684	731
	4	654	646	655	691	742
	5	659	686	678	722	749
	6	674	690	681	726	780
	7	677	692	683	730	781
	8	678	695	684	731	783
	9	679	696	687	734	782

TABLE IV
RETENTION INDICES OF THE McREYNOLDS SOLUTES AT VARIOUS TEMPERATURES

Stationary phase	Temperature (°C)	<i>I</i>				
		Benzene	1-Butanol	2-Pentanone	2-Nitropropane	Pyridine
Apiezon MH	120	674	600	634	670	729
	140	678	594	633	671	732
	160	684	593	634	677	740
	180	691	593	634	683	748
	200	705	593	638	691	757
$C_{87}H_{176}$	120	674	600	630	664	724
	140	679	596	630	665	728
	160	684	594	631	671	735
	180	691	596	633	678	744
	200	705	596	635	684	753

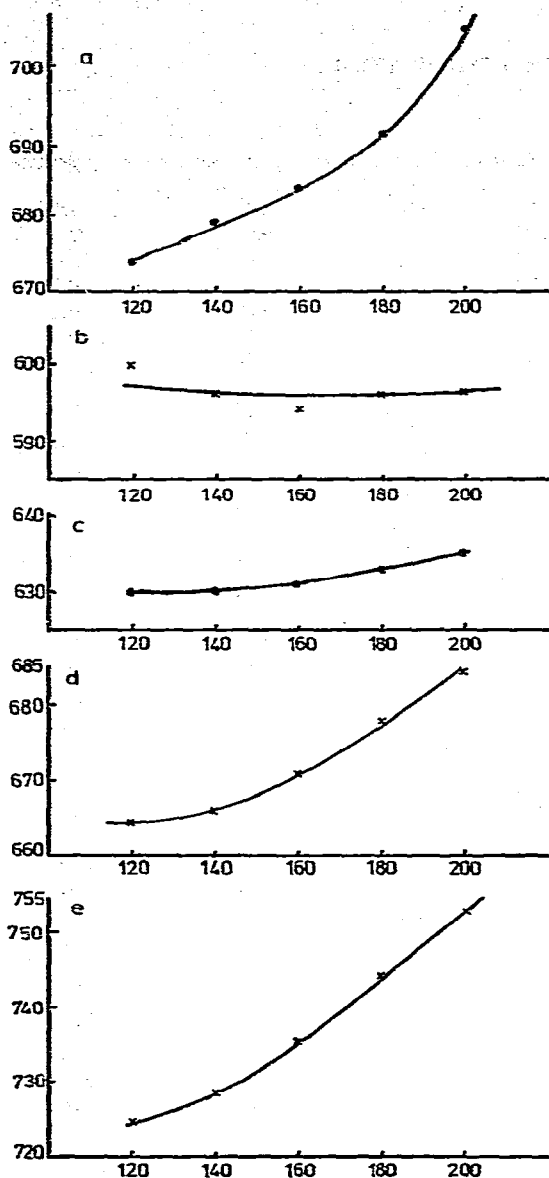


Fig. 2. Plots of retention indices (I) versus temperature for the McReynolds solutes. (a) Benzene; (b) 1-butanol; (c) 2-pentanone; (d) nitropropane; (e) pyridine, for the high-temperature hydrocarbon phases.

The similarity of performance of the materials is further shown in Table IV by the behaviour of the McReynolds probes at a series of temperatures from 120° to 180°. The data are plotted in Fig. 2, where it is evident that an increase in retention indices is experienced with temperature with three of the series while two are little influenced by temperature. Earlier work²³ has shown that linear relationships exist between temperature and polarity over a restricted temperature range, *i.e.*, 90–150°,

TABLE V
 VARIATION OF RETENTION INDICES WITH TEMPERATURE²³

Stationary phase	Column temperature (°C)	I				
		Benzene	1-Butanol	2-Pentanone	2-Nitropropane	Pyridine
Squalane	90	648	603	634	663	699
	100	648	595	632	663	699
	110	649	594	631	662	701
	120	651	594	630	663	702
	130	650	590	628	662	703
	140	650	587	623	660	703
	150	652	582	624	660	703
OV-1	90	657	654	671	721	736
	100	658	654	669	722	741
	110	658	650	668	719	741
	120	659	646	668	719	742
	130	659	643	670	721	743
	140	659	642	672	720	742
	150	660	641	672	722	746
OV-17	90	762	766	798	901	901
	100	762	760	795	900	903
	110	767	761	794	899	904
	120	765	756	791	901	907
	130	770	754	790	900	911
	140	773	752	789	897	912
	150	777	750	786	896	917
OV-210	90	777	826	972	1099	985
	100	779	825	974	1105	992
	110	781	824	976	1110	994
	120	784	822	981	1112	1003
	130	785	825	984	1119	1003
	140	789	826	984	1123	1010
	150	794	831	987	1132	1014
XF-1150	90	926	1100	1068	1274	1186
	100	930	1101	1075	1291	1200
	120	941	1105	1088	1317	1222
	130	945	1107	1094	1338	1237
	140	952	1107	1100	1351	1245
	150	958	1109	1107	1365	1259

and indeed with the present work the relationships are near by linear over part of the higher temperature range considered. Continued use of the two phases was undertaken at 180° and after a period of 10 days of constant use the relative retention indices of the material each showed increases of 1-2 index units with the various solutes but the two materials tended to increase together such that no marked deterioration of either material was experienced. The general polarity ($\Sigma 5$ McReynolds solutes) of squalane at 120° is 3230-3240 and of the two higher molecular hydrocarbons about 3300. While this increase might be of concern as a replacement phase for the characterization of low-polarity phases, its importance with highly polar phases is much smaller. The influence of temperature increases with increasing polarity of

several stationary phases at lower temperatures as shown in Table V²³ and under these circumstances the increased polarity of the base phase is of even less significance.

Retention index dispersions of a McReynolds probe and of dispersions of the higher temperature solute produced nearly linear relationships with the slopes indicating the degree of solute-solvent interaction. From these studies it would seem that data might be interchangeable for various phases and related to performance on squalane.

The behaviour of the test solutes of Vernon and Gopal²⁴ on both Apolane 87 and Apiezon MH have been examined and it is apparent that the behaviour on both of the stationary phases is very similar at high temperature.

From the examination it would appear that the Apiezon MH product is essentially identical with the C₈₇H₁₇₆ hydrocarbon with regard to column constants and thermal stability. It is of narrow molecular weight distribution with molecular weights comparable to those suggested by Huber and Kovats¹¹ and may be produced as a reproducible stationary phase.

Evans and Newton^{25,26} have recently demonstrated a considerable stabilization of squalene at 100° by the use of antioxidants of the type commonly employed in polymer processing and have deduced that a prolonged life of squalane can be achieved by this technique. While the phases considered in this work show considerable stability at 200° it is probable that some reliable operation at higher temperatures might be achieved by the use of antioxidants.

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