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USE OF 24,24-DIETHYL-19,29-DIOCTADECYLHEPTATETRACONTANE ($C_{87}H_{176}$) AS A NON-POLAR BASE STATIONARY PHASE IN ROHRSCHEIDER-McREYNOLDS TYPE SCHEMES

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SUMMARY

An examination of the hydrocarbon $C_{87}H_{176}$ (24,24-diethyl-19,29-dioctadecylheptatetracontane) developed by Kováts as a standard stationary phase is reported. The hydrocarbon is compared with squalane and dimethylpolysiloxane and a thermal stability equal to that of the siloxane is apparent at both 120° and 180° determined by repetitive measurement of McReynolds constants.

Some discussion is also included of a further recently described hydrocarbon produced by exhaustive hydrogenation of Apiezon M, which exhibits McReynolds constants substantially identical to those of squalane, is apparently thermal stable to 200° and may well be of lower cost.

INTRODUCTION

It has been proposed almost since the inception of gas chromatography¹ that paraffinic solvents exhibit retention characteristics with solutes owing almost exclusively to the interaction of dispersion forces. Increased retention is apparent on solvents of greater solubility, and low-polarity alkanes have established themselves as reference phases.

The effect of intermolecular interactions was considered by Rohrschneider², who, assuming dispersion or London forces to be non-polar and induction, orientation, charge transfer and hydrogen-bonding forces to be polar, found it possible substantially to eliminate non-polar forces by focusing attention on the difference in retention between a polar and a non-polar column. The non-polar basis of comparison was squalane, this having been proposed earlier by the same worker³ as a reference in an arbitrary polarity scale. The polar interactions were further assumed to be due to a summation of additive portions of several interactions, and it was suggested that, for each type of polar intermolecular attraction, an interaction energy proportional to a value characteristic of the solute and to a value characteristic of the solvent existed. This scheme and the conceptionally identical one of McReynolds⁴, which employs a better selection of solute probes, operate at 100° and 120°, respectively. These are near the maximum operating temperature of squalane although Rohr-

schneider-McReynolds constants for stationary phases so determined are used for selection of phases to achieve separations that are frequently conducted at much higher temperatures. Elimination of squalane as a reference in calculating retention index differences is possible 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 postulated⁵⁻⁷.

Dimethylpolysiloxane has been reported⁵ as an alternative low-polarity reference phase but has not found acceptance owing to both its increased polarity relative to squalane and the corresponding differences in the solvent constants with regard to the established values used by the principal suppliers^{8,9} of chromatographic specialties and also to objections on theoretical ground concerning stability and performance¹⁰.

The present work considers these objections and demonstrates the stability of dimethylpolysiloxane whose performance together with that of the C₈₇H₁₇₆ hydrocarbon (24,24-diethyl-19,29-dioctadecylheptatetracontane) recently introduced by Kováts and co-workers¹⁰ is compared with that of squalane; the necessity of using an inactive support to reproduce literature retention values is indicated.

EXPERIMENTAL

The analyses were carried out using 10% of the stationary phases on Chromosorb W AW DMCS. Columns of 1/8-in. 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 providing that the support is inactive. Determinations were carried out at 100°, 120° and 180°.

In order to increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph has been interfaced to a 16 K P.D.P. 11/40 digital computer. Interfacing was achieved by the use of an LPS 11 Laboratory Peripheral System consisting of a 12-bit A/D converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit D/A converters. All programming was done in CAPS 11 Basic with LPS options. The hardware in all cases being provided by Digital Equipment (Maynard, Mass., U.S.A.).

DISCUSSION AND RESULTS

Stationary phase classification and squalane as the non-polar reference

The Rohrschneider scheme proposes that the retention index differences ΔI for a compound A due to polar interactions may be determined by elimination of non-polar interactions by focusing attention on the retention differences observed on a polar and a squalane stationary phase according to eqn. 1:

$$\Delta I^A = I_P^A - I_{Sq}^A \quad (1)$$

where ΔI^A is the increased retention or index difference due to the polar interacting forces, and I_P^A and I_{Sq}^A are the retention indices of substance A on a polar and a squalane column, respectively.

The index difference ΔI defined in this way was expressed as the sum of a number of product terms, containing factors characteristic of both the solvent and the solute. The factors characteristic of the solvent or the stationary phase polarity factors are readily obtained and have found some acceptance as a means of comparing stationary phases⁹, the temperature dependence of the values being ignored.

The solute or substance polarity factors are more difficult to obtain and must be calculated from retention data of the solute and the stationary phase polarity constants at the arbitrarily specified temperatures^{2,4} by solution of eqn. 2, preferably by the method of least squares

$$\Delta I^A = ax + by + cz + du + es \quad (2)$$

A detailed study of both series of constants has not been reported although stationary phase polarity factors, *i.e.*, $x \dots s$, are well known as the Rohrschneider constants or more recently as the McReynolds constants² which are finding increasing acceptance, as previously mentioned, following the introductory work of Supelco⁹.

Values of the substance polarity factors, *i.e.*, $a \dots e$, however, have been reported in the original work of Rohrschneider², and with only thirty compounds selected to cover a wide range of functional classes it is not apparent whether the values have any real meaning when a series of close homologues are considered. There has in practice been some difficulty in evaluating the constants for a series of compounds owing to the severe temperature limitations imposed by the use of squalane as a basis of reference. Recent work¹¹ has shown that Rohrschneider-type schemes are based on the difference in intermolecular interactions between a substance and each of two stationary phases according to eqn. 3 and squalane with its low temperature limitations may be eliminated and thus studies may be conducted at more realistic temperatures.

$$\Delta I_{1,2}^A = I_1^A - I_2^A = a(I_1^x - I_2^x) + b(I_1^y - I_2^y) + c(I_1^z - I_2^z) + d(I_1^u - I_2^u) + e(I_1^s - I_2^s) \quad (3)$$

where I_1^A and I_2^A are the retention indices for compound A determined on the two stationary phases 1 and 2, and I_1^x, \dots, I_1^s and I_2^x, \dots, I_2^s are the retention indices of the five standard substances on columns 1 and 2, respectively. This relationship has been studied with a large series of aliphatic esters¹² using dimethylpolysiloxane as the base stationary phase, and, while the substance polarity factors obtained showed significant trends, the values have not found wider acceptance and interest has been directed to other materials.

Alternative base stationary phases

The use of dimethylpolysiloxane has been included in lists of preferred phases but has been criticized by Kováts and co-workers¹⁰ for several reasons. Molecular weight variations between batches has been suggested to influence the retention, and, although in fact this may be true, the effect is very minor while it is apparent that molecular weight distributions may be fairly accurately controlled and are readily characterized. The molecular weight distributions of dimethylpolysiloxanes and trifluoropropylmethylpolysiloxanes have been reported by Trash¹³ and by Hanneman

TABLE I

VARIATIONS OF McREYNOLDS CONSTANTS OF SE-30 WITH EXTENDED USE AT 120–200°

	<i>I</i>				
	<i>Benzene</i>	<i>1-Butanol</i>	<i>2-Pentanone</i>	<i>Nitropropane</i>	<i>Pyridine</i>
Initial value	668	643	671	716	740
3 months	669	645	671	718	742
12 months	672	647	673	719	744

and Klimisch¹⁴, respectively, using gel permeation chromatography. While the sp^3 -hybridized silicon atoms of the polysiloxanes are Lewis acids capable of forming weak complexes by π (p , d) bonds with bases such as ethers and alcohols, there is little supporting evidence as dimethylpolysiloxane shows outstanding stability. Tests have shown that an SE-30 column operated almost continuously for almost a year generally at 150° experienced only minor increases in McReynolds constants (Table I). Methyl-substituted siloxanes have been reported¹⁰ to alter during column conditioning owing to the higher temperatures experienced where the methyl silicone chains substitute the hydroxyl groups of the support. There is, however, little evidence of this reaction occurring with the temperatures experienced. Tests have shown that diatomaceous earth supports which have not been inactivated or which have been partially silanized when coated with dimethylpolysiloxane show increased McReynolds values with the more polar probes and this effect is little altered or reduced by conditioning or use. The use of support that has not been sufficiently inactivated is even more apparent with squalane where higher values of the phase constants as shown in Table II are obtained using Celatom acid-washed and silanized in the laboratory with dimethyldichlorosilane.

Huber and Kováts¹⁵ have reported that the molecular weight of a hydrocarbon to be used as a stationary phase should be in excess of 1100, to provide a material with an upper operating temperature near 300°. Lower-molecular-weight products have been evaluated by McReynolds⁴ but are unsuitable for use at the temperatures

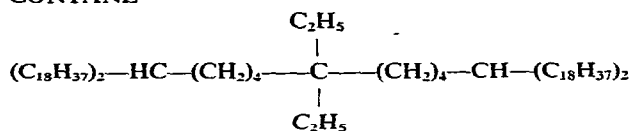
TABLE II

ROHRSCHEIDER AND McREYNOLDS CONSTANTS OF $C_{87}H_{176}$ HYDROCARBON AND OF SQUALANE

	<i>I of Rohrschneider solutes (100°)</i>					
	<i>Benzene</i>	<i>Ethanol</i>	<i>2-Butanone</i>	<i>Nitromethane</i>	<i>Pyridine</i>	
$C_{87}H_{176}$	670	498	542	463	715	
	<i>I of McReynolds solutes (120°)</i>					
	<i>Benzene</i>	<i>1-Butanol</i>	<i>2-Pentanone</i>	<i>Nitropropane</i>	<i>Pyridine</i>	$\Sigma 5$
$C_{87}H_{176}$	674	600	630	664	724	3292
Squalane	653	590	627	652	699	3236
Squalane (inactive support)	657	604	636	664	714	

TABLE III

PHYSICAL CONSTANTS OF 24,24-DIETHYL-19, 29-DIOCTADECYLHEPTATETRA-CONTANE



Empirical formula	C ₈₇ H ₁₇₆
Molecular weight	1222.37
Volatile matter	1.2% (250°)
Melting point	28.0–34° (10)
Density (130°)	0.776
Specific volume (130°)	1.289 (cm ³ /g)
Recommended temperature range (10)	30–300°

required. The C₈₇H₁₇₆ hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracontane, developed by Kováts and co-workers¹⁰ and produced by Fluka (Buchs, Switzerland), has been suggested as to be suitable for use at 280°. The physical constants of the material used here are slightly different from those of the earlier report¹⁰ and are shown in Table III, while the retention indices of the Rohrschneider and McReynolds compounds are shown in Table II. The values are determined on Chromosorb W AW DMCS which, when used with squalane, produced values in agreement with the literature values⁴. Less inactive supports produced significantly higher values of the 1-butanol and 1-nitropropane solutes. These values at 120° as required were not reported in the earlier work¹⁰ but are very similar to the values that were reported at 130°, the values with all solutes being slightly higher than for squalane.

Use of squalane repetitively over 8 h leads to increased phase constants while use for short periods on successive days also soon causes increases to occur. Table IV shows data obtained at 120° on squalane, dimethylpolysiloxane (SE-30) and the C₈₇H₁₇₆ hydrocarbon obtained on successive days on which the columns were operated for 1-h periods. With the squalane column serious deterioration of the various constants commenced after 4 to 5 days, the increases being most apparent with the more polar solutes. The C₈₇H₁₇₆ hydrocarbon and the SE-30 are essentially unaltered after ten successive daily periods of use and then a continuous period of 24 h. Further testing of the hydrocarbon column was not carried out both to conserve the column and because its superiority compared with squalane was obvious, particularly as our experience has been to prepare new squalane columns each time a stationary phase is characterized. The evaluations shown in Table V were repeated using new columns of C₈₇H₁₇₆ and SE-30 at 180°. The results are shown in Table V where it is apparent that the performance is little different from that observed at 120° and accordingly an acceptable thermal and operating stability is evident at 180°. Additional testing at higher temperatures will be undertaken when further supplies of the stationary phase become available.

Since the commencement of this work a report by Vernon and Ogundipe¹⁶ has appeared where a further hydrocarbon phase has been proposed as a non-polar standard phase. The product Apiezon M, a well known hydrocarbon grease with aromatic

TABLE IV

STABILITY AT 120° OF SQUALANE, C₈₇H₁₇₆ HYDROCARBON AND DIMETHYLPOLY-SILOXANE

	<i>I</i>				
	<i>Benzene</i>	<i>1-Butanol</i>	<i>2-Pentanone</i>	<i>Nitropropane</i>	<i>Pyridine</i>
SE-30	668	643	671	716	740
1 day	668	643	672	716	740
2	668	643	672	716	740
3	668	643	672	716	740
4	668	644	672	716	740
5	668	643	672	717	740
6	668	644	672	716	741
7	668	644	672	717	741
8	669	644	672	717	741
9	669	644	672	717	741
Squalane	653	590	627	652	699
1 day	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
C ₈₇ H ₁₇₆	674	600	630	664	724
1 day	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	631	664	723
7	674	601	632	664	724
8	674	601	631	664	724
9	674	601	631	664	724

TABLE V

RETENTION INDICES OF THE McREYNOLDS SOLUTES AT 180°

	<i>I</i>				
	<i>Benzene</i>	<i>1-Butanol</i>	<i>2-Pentanone</i>	<i>Nitropropane</i>	<i>Pyridine</i>
C ₈₇ H ₁₇₆	694	600	634	673	748
10 days	696	601	637	674	749
SE-30	672	679	753	714	770
10 days	672	680	752	716	770

and olefinic unsaturation, has been hydrogenated and rehydrogenated to provide a product with very similar McReynolds constants (Table VI). The authors report the molecular weight as 2340, which is well within the specification prescribed by Huber and Kováts⁴⁵, while testing has shown acceptable performance at 200°. The material

described as Apiezon MH may well prove to be more acceptable than the C₈₇H₁₇₆ hydrocarbon as a standard stationary phase. The cost and availability of the C₈₇ material are not yet known although it has been reported that twelve¹⁷ steps are involved in the synthesis, and this may well mean that the cost would be substantially greater than that of an available product which has been exhaustively hydrogenated.

TABLE VI
RETENTION INDICES OF APIEZON GREASES AT 120°

Stationary phase	I					
	Benzene	1-Butanol	2-Pentanone	Nitropropane	Pyridine	Σ5
Apiezon L	687	627	651	700	770	3435
Apiezon M	686	627	651	698	767	3430
Apiezon M (hydrogenated)	671	599	632	667	736	3305
Squalane	653	590	627	652	714	3236

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