GAS–LIQUID CHROMATOGRAPHY IN QUALITATIVE ANALYSIS

PART VII. THE RÔLE OF THE SUPPORT IN GAS CHROMATOGRAPHIC RETENTION MEASUREMENTS

M. B. EVANS

Department of Chemistry and Biology, Hatfield College of Technology, Hatfield, Hertfordshire (Great Britain)

AND

J. F. SMITH

The Natural Rubber Producers' Research Association, Tewin Road, Welwyn Garden City, Hertfordshire (Great Britain)

(Received April 24th, 1967)

INTRODUCTION

In a previous paper of this series[1] it was shown that the adsorption of solute molecules at the liquid–solid interface leads to perturbed values for retention with concomitant peak asymmetry. This work has now been extended and additional factors influencing the reproducibility of retention data recognised. On the basis of these results, a range of commercially available supports have been classified according to their effective adsorptivities.

EXPERIMENTAL

Apparatus

Chromatograms were obtained using an apparatus consisting of glass columns (5 ft. long and 4 mm I.D.) with a modified flame ionisation detector[2]. The carrier gas was a 3:1 (by vol.) mixture of hydrogen and nitrogen. The columns were packed with 10 % w/w mixtures of stationary phase: either dinonyl phthalate (B.D.H.), polyoxyethylene glycol-400 (Merck), or squalane (B.D.H.) and support (for details see Table I). The column temperature was regulated by a vapour jacket consisting of boiling water (100°). Samples for analysis (~ 10 μg) were introduced by means of stainless steel capillary pipettes[3]. All the solutes used were obtained commercially with the exception of the tertiary alcohols which were kindly prepared by Miss M. J. STOREY (N.R.P.R.A.).

Measurement of retention data

Relative retentions, in KOVÁTS' retention index units[4], were obtained from chromatograms of suitable mixtures containing *n*-alkanes as internal standards. Retention distances, measured between point of injection and peak maxima on the chromatographic record, were corrected for the column gas hold-up volume by means

TABLE I

DETAILS OF THE SUPPORT MATERIALS USED IN THE INVESTIGATION OF SUPPORT ADSORPTIVITY

Support	Mesh range	Origin
Anakrom	60–80	Analytical Engineering Laboratories (U.S.A.)
Celite	60–70	J.J.s Chromatography (U.K.)
Chromosorb G non acid-washed	60–80	Johns-Manville (U.S.A.)
Chromosorb G silanized by dimethyldichlorosilane (by manufacturer)	60–80	Johns-Manville (U.S.A.)
Chromosorb P	60–80	Johns-Manville (U.S.A.)
Chromosorb W	60–80	Johns-Manville (U.S.A.)
C-22 Firebrick	60–70	J.J.s Chromatography (U.K.)
Gas Chrom Q	60–80	Applied Science Laboratories (U.S.A.)
Microsorb W [Chromosorb W coated with poly-(tetrafluoroethylene)]	60–80	Toshin Chemicals (Japan)

of the retention of methane[5]. The adjusted retentions were then used to calculate values for retention index by means of the expressions:

$$I = 100N + 100n \left(\frac{\log_{10}R_x - \log_{10}R_N}{\log_{10}R_{N+n} - \log_{10}R_N} \right)$$

where R_x, R_N and R_{N+n} are the adjusted retentions of the solute, and n-alkane standards containing N and $N+n$ carbon atoms, respectively.

DISCUSSION AND RESULTS

Previous work[1] has revealed that the oxidation of apolar liquid phases, such as squalane, is accompanied by large changes of retention, which may be negative or positive depending upon the extent of oxidation, the chemical nature of the solutes, and the adsorptivity of the support. Furthermore, in respect of the latter, the results, suggested that the differences between the observed retentions and those corresponding to partitioning into the pure solvent alone, might be used to compare the adsorptivities of support materials, in so far as it affects the elution of the solute molecules.

In order to test this hypothesis, values for retention index of solutes, of a wide range of chemical types, have been determined for columns prepared using purified squalane as stationary phase and a selection of commercially available support materials. As it is well known that the retentions of solutes which are adsorbed on the support surface are highly dependent upon sample size, unless the isotherm is linear, every care was taken to ensure the injection of constant sample sizes throughout the investigation. Thereby it proved possible to obtain reasonably reproducible retention data for asymmetric peaks (tailing), both for the same column on separate occasions, and also for different columns prepared using the same batches of liquid phase and support.

The results obtained (see Table II) clearly reveal that supports may be classified

according to values for retention index, and that in terms of the changes of retention caused by the adsorption of solute molecules at the liquid–solid interface, silanized Chromosorb G is the least adsorptive of the supports examined. It is also interesting to note that with this support the retention indices for benzonitrile and nitrobenzene are close to those believed to be due to partitioning into the pure stationary phase alone[1], namely 891 and 1002, respectively. Owing to their extreme adsorptivity meaningful retention indices could be obtained for neither C-22 firebrick nor Chromosorb P. The large shifts of retention experienced by the alcohols, compared with those exhibited by the other solutes, indicate that the principle forces of interaction between these solutes and the support surface are hydrogen bonding in character. This viewpoint is supported by the retention indices of the alcohols shown in Table III which indicate that the changes of retention with support are determined by the steric hindrance of the hydroxyl groups by adjacent alkyl groups.

TABLE II

THE EFFECT OF THE SUPPORT UPON THE RETENTION CHARACTERISTICS OF SQUALANE COLUMNS
Column: 5 ft. × 4 mm, 10 % w/w squalane (B.D.H.) at 100°.

Support	Hexan-2-one	Pentan-1-ol	Chloro-benzene	2-Methyl-heptan-2-ol	Benzoni-trile	Nitro-benzene
Chromosorb W	774.0	800.0	825.7	939.5	918.6	1016.9
Microsorb W	755.3	781.9	827.1	908.5	910.4	1011.6
Celite	747.2	763.5	826.0	902.3	904.2	1009.7
Anakrom	733.3	714.9	826.8	885.2	896.5	1005.2
Chromosorb G	732.6	714.4	826.9	885.3	896.6	1005.4
Gas Chrom Q	730.9	703.9	826.8	883.2	893.1	1004.3
Silanized Chromosorb G	728.7	694.9	826.5	883.8	893.9	1005.1

The foregoing experiments reveal that hydroxylic solutes are strongly adsorbed on to the surface of diatomaceous supports. Therefore, it is reasonable to expect that the hydroxyl groups of hydroxylic stationary phases, such as the polyoxyethylene glycols, will behave similarly. Thereby reducing the concentration of hydroxyl groups available in the bulk liquid phase for partitioning purposes, and in turn values for retention index; previous work having established an approximately linear relationship between values for retention index and the hydroxyl content of a series of polyoxyethylene glycol fractions[6]. Consequently the highest values for retention index for a particular sample of polyoxyethylene glycol would be expected for the least adsorptive support. The results obtained for a series of support materials, using a particular batch of polyoxyethylene glycol-400 as stationary phase, are in accord with this hypothesis (see Table IV), in as far as the lowest values for retention index were obtained with what are regarded to be the most adsorptive supports. A particularly disturbing feature, from a qualitative analytical standpoint, of the type of adsorption encountered with polyoxyethylene glycol, and presumably other hydroxylic liquid phases, is that it does not give rise to the abnormally shaped peaks generally associated with adsorption phenomena.

Since the above experiments yield materially the same order of effective adsorptivities, for the supports examined, it may be concluded that the hypotheses upon

TABLE III

THE INFLUENCE OF THE ENVIRONMENT OF THE HYDROXYL GROUPS OF ALKANOLS UPON THEIR AD-
SORPTION UPON THE SURFACE OF DIATOMACEOUS SUPPORTS
Column: 5 ft. × 4 mm, 20% w/w squalane at 100°.

Substance	I_W*	I_G**	δI	Mean value
Pentan-1-ol	800.0	694.9	105.1	} 105
Hexan-1-ol	900.0	795.5	104.5	
Hexan-2-ol	815.2	742.2	73.0	} 73
Heptan-2-ol	915.8	842.2	73.6	
2-Methylhexan-2-ol	839.3	785.9	53.4	} 54
2-Methylheptan-2-ol	939.5	883.8	55.7	
2-Methyloctan-2-ol	1035.7	984.2	51.5	

* I_W = retention index with Chromosorb W as support.
** I_G = retention index with silane-treated Chromosorb G as support.

TABLE IV

THE EFFECT OF THE SUPPORT UPON THE RETENTION CHARACTERISTICS OF POLYOXYETHYLENE
GLYCOL COLUMNS
Column: 5 ft. × 4 mm, 10% w/w polyoxyethylene glycol-400 (Merck) at 100°.

Support	Hexan-2-one	Chloro-benzene	Pentan-1-ol	2-Methyl-heptan-2-ol	Benzo-nitrile	Nitro-benzene
Chromosorb P	1118.4	1213.3	1306.0	1343.8	1588.2	1684.2
C-22 Firebrick	1121.7	1215.5	1310.6	1345.2	1593.2	1691.6
Chromosorb W	1147.1	1252.9	1347.2	1377.0	1644.4	1745.0
Celite	1170.0	1275.0	1369.4	1397.9	1675.8	1779.4
Chromosorb G	1179.0	1284.2	1381.3	1409.2	1693.3	1798.2
Anakrom	1177.9	1283.5	1384.2	1408.8	1696.8	1801.2
Gas Chrom Q	1181.8	1287.6	1386.6	1414.9	1702.3	1810.5
Silanized Chromosorb G	1186.4	1293.0	1390.7	1419.1	1709.0	1817.0

which these comparisons are based are essentially correct. Furthermore, as the surface
areas of the supports examined are markedly different, the results of these experiments
suggest that adsorption at the gas–liquid interface does not contribute significantly to
overall retentions on the polyoxyethylene glycol columns, at the liquid phase loading
employed.

At first sight the results obtained for columns prepared using polytetrafluoro-
ethylene as support are inconsistent with those of previous workers[7-10],which suggest
that this material is particularly inert and non-adsorptive (see Table V). Whereas the
retention indices obtained with dinonyl phthalate and squalane are lower than those
given by the corresponding Chromosorb G columns, consistent with teflon having the
lower adsorptivity, the results obtained with polyoxyethylene glycol imply that
teflon is considerably more adsorptive. In fact, even more so than firebrick. However,
in contrast with the other teflon columns, the polyoxyethylene glycol column gave

TABLE V

COMPARISON OF THE RETENTION CHARACTERISTICS OF DINONYL PHTHALATE, POLYOXYETHYLENE GLYCOL, AND SQUALANE COLUMNS PREPARED USING SILANIZED CHROMOSORB G AND CHROMOSORB T (TEFLON) AS SUPPORT MATERIALS

Column: 5 ft. × 4 mm., 10 % w/w stationary phase at 100°.

Substance	Dinonyl phthalate		Polyoxyethylene glycol-400		Squalane	
	Chromo-sorb G	Chromo-sorb T	Chromo-sorb G	Chromo-sorb T	Chromo-sorb G	Chromo-sorb T
Benzonitrile	1144.8	1130.2	1709.0	1514.5	893.2	888.3
Chlorobenzene	940.9	930.3	1293.0	1168.4	827.4	823.7
Hexan-1-ol	990.3	979.8	1498.2	1328.0	795.5	792.3
Hexan-2-ol	910.6	900.7	1350.6	1219.8	842.2	842.0
Hexan-2-one	877.5	870.2	1186.4	1074.4	729.2	728.4
2-Methylhexan-2-ol	933.2	926.6	1319.2	1186.0	785.9	787.3
Nitrobenzene	1250.2	1235.6	1817.0	1602.0	1005.4	1001.2
Slope of n-alkane "log plot" (b)	0.312	0.312	0.230	0.275	0.330	0.328

rise to asymmetric (tailing) peaks for the n-alkanes. As tailing peaks are generally associated with an adsorption phenomenon, and that these usually give rise to positive shifts of absolute retention, it is tempting to suggest that the anomalous retentions obtained with the polyoxyethylene glycol/teflon column are a consequence of a displacement of the n-alkane retentions relative to those of the other solutes, rather than a change in the concentration of available hydroxyl groups in the bulk liquid phase, arising from the adsorption of these groups on to the support surface. Thus far we have been unable to elucidate the mechanism of this selective retardation of the n-alkanes on these columns. As physical adsorption in the accepted sense can be discounted the only other plausible explanations of the phenomena are occlusion or capillary condensation of the n-alkane molecules in the micro pores which are known to exist on the surface of teflon[9]. Either of these processes might be expected to give rise to the observed peak broadening and concomitant selective retardation. Similar behaviour was exhibited by a column prepared from a sample of Camlag Kieselguhr.

The present investigations reveal that the rôle of the support phase in retention measurements is far more complicated than thought previously; it having been widely regarded as the inert phase. In the first place, it has been shown that adsorptive sites upon the surface of diatomaceous supports can cause large changes in retention by either the adsorption of solute molecules at the liquid-solid interface or by the adsorption of the polar functional groups of hydroxylic stationary phases. Furthermore, it has been deduced that n-alkanes, and presumably other appropriately shaped molecules, can be trapped within the porous regions of certain supports when chromatographed on columns coated with liquid phases in which they are only sparingly soluble. On the basis of these observations it is possible to formulate a list of properties which support materials should possess if they are to be used for qualitative

TABLE VI

THE RETENTION CHARACTERISTICS OF DINONYL PHTHALATE, POLYOXYETHYLENE GLYCOL-400, AND SQUALANE COLUMNS PREPARED FROM THREE DIFFERENT BATCHES OF SILANIZED CHROMOSORB G*

Column: 5 ft. × 4 mm, 10% w/w stationary phase, silanized Chromosorb G at 100°.

Substance	Dinonyl phthalate			Polyoxyethylene glycol-400			Squalane			Recovered**
	A	B	C	A	B	C	A	B	C	
Benzonitrile	1144.0	1144.5	1144.8	1707.6	1711.9	1709.0	894.4	893.9	893.2	893.9
Chlorobenzene	940.2	940.6	940.9	1292.9	1294.4	1293.0	827.1	826.5	827.4	827.3
Hexan-1-ol	991.1	990.1	990.3	1497.2	1499.8	1498.2	795.7	796.1	795.5	796.0
Hexan-2-ol	909.4	909.8	910.6	1350.3	1352.2	1350.6	742.3	742.5	742.2	743.6
Hexan-2-one	877.3	877.9	877.5	1186.2	1187.5	1186.4	729.0	728.7	729.2	729.6
2-Methylhexan-2-ol	933.0	933.2	933.2	1317.8	1319.4	1319.2	785.7	786.7	785.9	786.7
Nitrobenzene	1249.2	1249.1	1250.2	1815.6	1818.4	1817.0	1005.7	1005.1	1005.4	1005.6
Slope of n-alkane "log plot" (b)	0.313	0.313	0.312	0.231	0.231	0.230	0.329	0.328	0.330	0.329

* Three different samples (A, B and C) of Chromosorb kindly supplied by Dr. D. M. Ottenstein.
** Column prepared using support recovered from the dinonyl phthalate and polyoxyethylene glycol columns (batch A) by solvent extraction.

analysis, in which values for retention are to be used for peak identification purposes. These are as follows:

(i) they should possess the minimum adsorptivity consistent with the maintenance of coherent films of liquid phase,

(ii) the surface should be free of fine pores, *i.e.* those with diameters less than 50 Å,

(iii) they should have the minimum surface area consistent with the preparation of columns with good efficiency and resolution characteristics. In addition they should be homogeneous, have good handling properties, and should be batch invariant.

Of the supports thus far examined silanized Chromosorb G appears to fulfil the above requirements better than the remainder. The batch invariance of this material is illustrated by the retention data shown in Table VI. The data shown in the column on the extreme right of this table are of special interest as they suggest that silanized Chromosorb G can be recovered from used columns by solvent extraction without loss of performance, thus offsetting the high initial cost of this material.

SUMMARY

The support phase has been shown to influence values for relative retention by either the adsorption of solute molecules or the adsorption of the hydroxyl groups of certain polar liquid phases. Also, it has been deduced that appropriately shaped molecules, which have a low affinity for the solvent, can be selectively retained by trapping in the micro pores in the surface of certain supports, in particular teflon. On the basis of these observations it has been found that silanized Chromosorb G is the least adsorptive of a wide range of commercially available support materials.

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