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RETENTION OF POLYCYCLIC AROMATIC HYDROCARBONS ON AN IMPROVED TETRACHLOROPHTHALIMIDOPROPYL SILICA

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SUMMARY

An improved synthesis of a chemically bonded electron acceptor, namely tetrachlorophthalimidopropyl silica, is described. Factors governing the silane preparation and its bonding to silica have been studied, namely reaction temperature and duration, pretreatment of silica, specific area, pore diameter, washing of the bonded silica, influence of solvent drying. A ligand density of 2.7 μmol/m² is obtained with reduced plate heights in the range 5–20 which demonstrate the absence of polymerization. The retention of six polycyclic aromatic hydrocarbons has been studied. The minimum capacity factors allow high recovery rates in non-polar media.

INTRODUCTION

The determination of polycyclic aromatic hydrocarbons (PAHs) is complicated by their carcinogenic properties[1]. In many cases their content is very low and a concentration step is necessary[2–4]. When PAHs are dissolved in a polar medium, *e.g.*, water, good recoveries are obtained using classical *n*-alkyl bonded silica due to their hydrophobic properties. The problem is much more complicated when the PAHs are contained in complex non-polar mixtures such as crude oil or petrochemical fractions and products, *e.g.*, lubricants or temper oils. In such instances an highly specific interaction with a stationary phase may solve the problem. PAHs are electron donors and an electron donor–acceptor complex may be formed with a suitable chemically bonded electron-acceptor stationary phase.
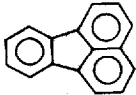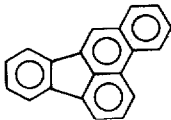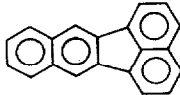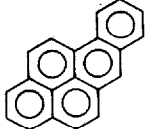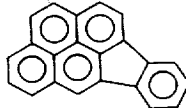
Liquid chromatography on chemically bonded electron-donor and -acceptor silica has recently been reviewed by Nondek[5]. On the basis of published results, we decided to study the retention of PAHs on tetrachlorophthalimidopropyl bonded silica the synthesis of which was described by Holstein[6]. An improved synthesis taking into account the properties of silica and the experimental conditions will be discussed.

EXPERIMENTAL

Apparatus
A Varian 5000 liquid chromatograph was used in conjunction with a LDC Spectromonitor III absorptiometric detector.

TABLE I

IDENTIFICATION AND STRUCTURES OF PAHs USED

PAH	Number of rings	Structure	Mol. weight
Fluoranthene	4		202
Benzo[b]fluoranthene	5		252
Benzo[k]fluoranthene	5		252
Benzo[a]pyrene	5		252
Indeno[1,2,3-cd]pyrene	6		276
Benzo[ghi]perylene	6		276

The columns were polished stainless-steel tubes (10 cm × 4.6 mm I.D.), fitted with a 2-μm porous stainless-steel frit. They were packed by using the classical slurry packing technique. The bonded silica was suspended in carbon tetrachloride–methyliodide (67:33) and the slurry was forced with methanol into the chromatographic column for 30 min under a pressure of 500 bar.

Chemicals and reagents

The porous silicas used to synthesize the bonded electron-acceptor phase were 5-μm LiChrosorb Si 100, 5-μm LiChrosorb Si 60 and silica gel 100 (Merck, Darmstadt, F.R.G.). The 2,4,5,7-tetranitrofluoreniminopropyl silica (TENF silica) was obtained from E. S. Industries (Marlton, NJ, U.S.A.). 3,4,5,6-Tetrachlorophthalic anhydride (TCPA), allylamine, trichlorosilane, hexachloroplatinic(IV) acid (hexahydrate), benzene, dichloromethane, o-xylene, 1,2,4-trimethylbenzene and quinoline
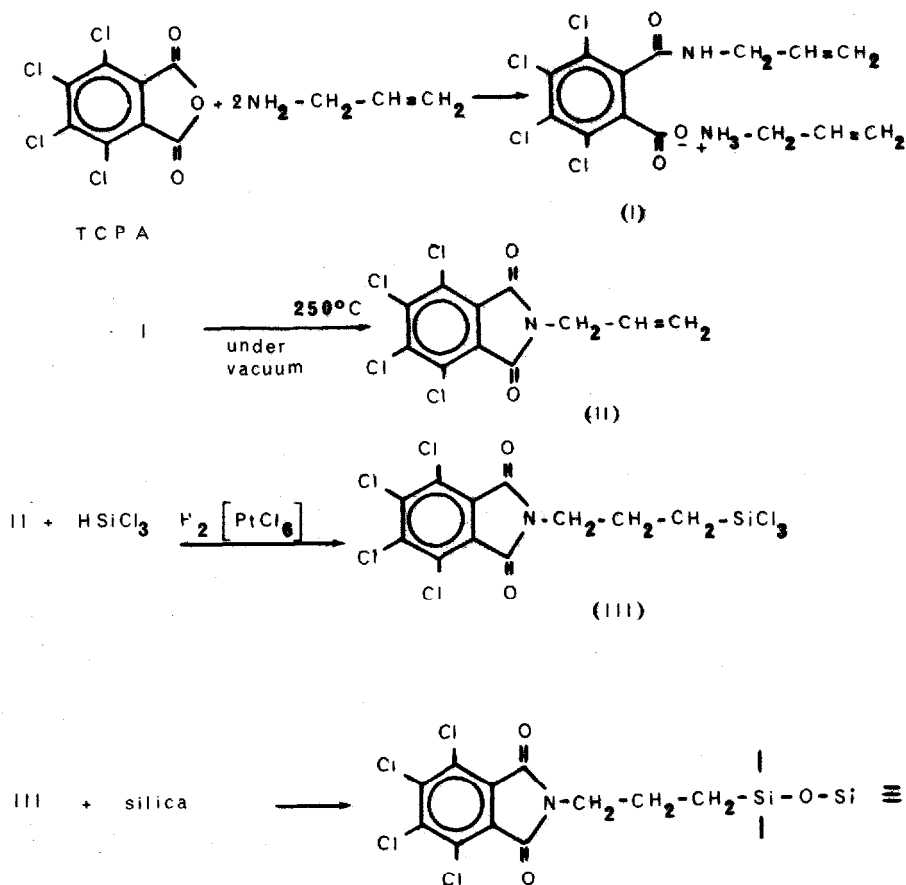
were from Merck, methanol and acetone from Prolabo (Paris, France). Solvents were dried and kept on 4-Å molecular sieves (Merck).

The PAHs used were provided by B.C.R. (Brussels, Belgium) (Table I).

RESULTS AND DISCUSSION

Silane and stationary phase synthesis

The synthesis scheme, as reported by Holstein[6], is as follows:

TCPA + $2 NH_2-CH_2-CH=CH_2$ ⟶ (I)

I $\xrightarrow[\text{vacuum}]{\text{under } 250°C}$ (II)

II + $HSiCl_3$ $\xrightarrow{H_2[PtCl_6]}$ (III)

III + silica ⟶

Procedure

Synthesis of the silane. A 20-g amount of TCPA and 32 g of allylamine were mixed, with cooling as the reaction is exothermic. Then the mixture was boiled until the TCPA was completely dissolved. Evaporation of the excess of allylamine yielded 25 g of white crystals (I), m.p. 166°C. IR (KBr): 3210, 3040, 1660–1450, 1405, 1380, 1355, 1320, 1280, 1245, 970, 905 cm⁻¹. Microanalysis: (calculated) 42.0% C, 7.0% N, 30.5% Cl; (experimental) 42.9% C, 6.9% N, 30.1% Cl.

A 20-g amount of compound I was then heated under vacuum to 250°C for 10 min. The brownish product obtained was recrystallized from benzene, giving 14 g of yellow crystals (II), m.p. 185°C. IR (KBr): 1778, 1710, 1430, 1395, 1373, 1360,

1300, 1200, 1122, 932, 758, 738 cm^{-1}. Microanalysis: (calculated) 40.6% C, 4.3% N, 43.6% Cl; (experimental) 41.5% C, 4.7% N, 42.7% Cl.

A 10-g amount of compound II, 13 g of freshly distilled trichlorosilane and 3 ml of 0.1 M hexachloroplatinic(IV) acid in isopropanol were mixed in 100 ml of dichloromethane, then refluxed with mechanical stirring under an atmosphere of argon (U quality, containing less than 5 ppm water) for 24 h. Trichlorosilane and dichloromethane were removed by distillation under vacuum; the remaining 14 g of yellow crystals (III) were immediately dissolved in 100 ml of anhydrous 1,2,4-trimethylbenzene. IR (KBr): 2940, 1778, 1715, 1440, 1400, 1370, 1355, 1298, 1250–970, 752, 740 cm^{-1}.

Synthesis of bonded silica. A 3-g amount of pretreated 5-μm LiChrosorb Si 100 and, optionally, 5 ml of quinoline (to neutralize the hydrochloric acid formed) was added to 3 g of the silane III in 100 ml of 1,2,4-trimethylbenzene. The mixture was refluxed with mechanical stirring under an atmosphere of argon (U quality) for 8 h. Finally, the bonded silica was washed in four steps. As the washing is very important it is described in detail. The bonded silica was filtered off and washed with 100 ml 1,2,4-trimethylbenzene. Then a slurry of the silica with 100 ml o-xylene was stirred for 30 min and filtered (twice); after a washing with 100 ml o-xylene, this operation was repeated with 100 ml methanol instead of xylene and then with acetone. Finally the silica was dried at 80°C for 12 h.

Optimum synthesis conditions

The synthesis of bonded silica is governed mainly by two kinds of parameters: those related to the bare silica used, namely the pretreatment, specific area and pore diameter, and those related to the experimental conditions, *i.e.*, the water content of the solvents, temperature, reaction duration, stirring. These were studied through measurement of the ligand density obtained by microanalysis; a good correlation between % C, % N and % Cl with ligand density has been observed.

Parameters related to silica

Pretreatment. The ligand density depends on the number of reactive silanol groups. Treatment of silica with concentrated sulphuric and nitric acids (50:50) (100 ml for 10 g of silica) has been advocated[7] to obtain the maximum number of reactive silanol groups. Then the silica is thoroughly washed with distilled water and dried at 180°C under vacuum or at 400°C 12 h to remove physisorbed water before silanization (these two methods were shown to be equivalent).

Effect of the specific area and pore diameter. The number of bonded ligands per gram increases with the number of silanol groups and, thus, an high specific surface area is desirable. However, it is well known that the pore diameter of silica decreases with increasing specific surface area; so a compromise must be found between an high specific surface area and a minimum pore diameter. In general, the pore diameter must be greater than twice the ligand length. Since in the present case the length of silane III is 16 Å, the minimum pore diameter must be greater than 32 Å.

Table II shows that for silicas having pore diameter of 100 Å the ligand density is constant within experimental error whatever the specific surface area, and is independent of the nature of the silica.

Two values of the pore diameter have been studied: 60 and 100 Å. Table III

TABLE II

EFFECT OF THE SPECIFIC AREA ON THE LIGAND DENSITY

Mean values calculated from % C, % N and % Cl; pore diameter 100 Å.

Silica	Specific area (m²/g)	Ligand density (μmol/m²)
LiChrosorb SI 100	305	2.4
Silica gel 100	340	2.6

demonstrates the interest of an high pore diameter: the ligand density (in $\mu mol/m^2$) of the 100-Å silica is higher than that of the 60-Å silica. However, the number of ligands bonded per gram of silica is slightly greater than for LiChrosorb Si 60. Taking into account the difficulty in obtaining reproducible batches of silica gel, LiChrosorb Si 100 (Merck) with particle diameters of 5, 10 and 20 μm was chosen. The measured pore diameter is 110 Å (nominal value: 100 Å) and the specific surface area 305 m²/g (nominal value: 300–400 m²/g).

We should point out that a pore diameter greater than 110 Å is probably without interest as the specific surface area becomes very low (less than 200 m²/g) in that case.

Parameters related to experimental conditions

Water content. The main problem associated with the silanization reaction is the water content of the solvents and of the atmosphere in the reaction vessel since water induces polymerization of silanes (trichlorosilane and tetrachlorophthalimidopropylsilane) on the surface of silica or inside the pores[8].

Polymerization of the ligand results in an higher ligand density and, consequently, increased capacity factors and selectivities. As demonstrated by Wise and Sander[9] in the case of octadecyl chains, the efficiency of such controlled polymerized phases can remain high. On the other hand, silane polymerization in the pores of the silica will often result in a decrease in column efficiency. Therefore, the use of very anhydrous solvents and a strict washing procedure in order to completely remove the excess of silane contained in the pore volume of silica are essential.

Polymerization can be detected by measurements of the ligand density and

TABLE III

EFFECT OF THE PORE DIAMETER AND SPECIFIC SURFACE AREA ON THE LIGAND DENSITY

Mean values calculated from %C, % N and % Cl.

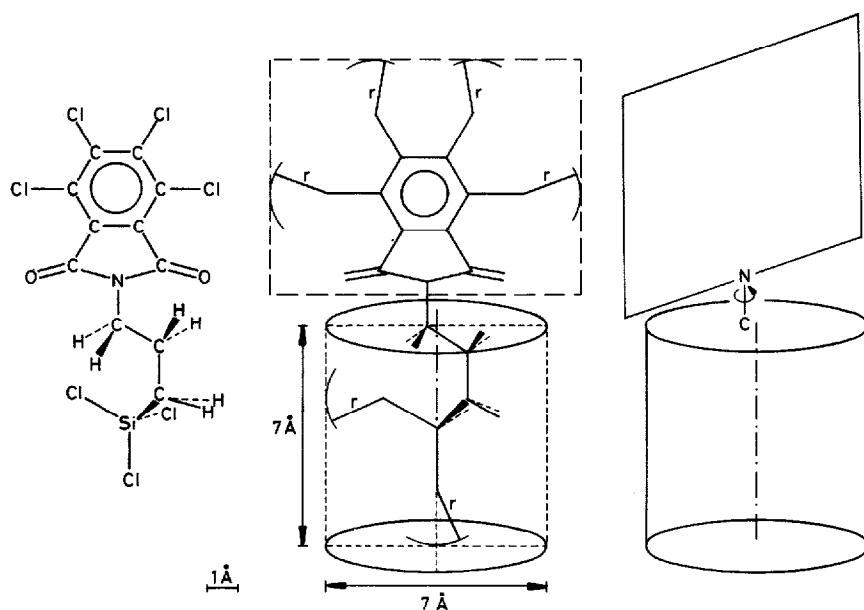| Silica	Pore diameter (Å)	Specific area (m²/g)	Ligand density	
			μmol/m²	mmol/g
LiChrosorb Si 100	100	305	2.4	0.73
LiChrosorb Si 60	60	425	1.9	0.81

Fig. 1. Structure and steric hindrance of the tetrachlorophthalimidopropyl silane III (r = Van der Waals radius of Cl).

reduced plate height, h. The mean concentration of silanol groups is 8 $\mu mol/m^2$ (ref. 10), the mean silanol group area is 0.21 nm^2 and the mean distance between two neighbouring silanol groups is 0.5–0.6 nm^8. As shown in Fig. 1, the steric hindrance of silane III does not depend on the tetrachlorophthalimidic structure: because of the free rotation of the N–C bond of the alkyl chain, the steric hindrance of one such planar group with respect to another may be negligible when they are parallel. Thus, the ligand density depends on the hindrance of the $-(CH_2)_3SiCl_3$ group, *i.e.*, of a cylinder 7 Å long and 7 Å in diameter. The cross-sectional area of this cylinder is 0.38 nm^2, so that polymerization is expected to occur when the ligand density exceeds

TABLE IV

LIGAND DENSITY, REDUCED PLATE HEIGHT AND CAPACITY FACTOR OBTAINED WITH FLUORANTHENE FOR SEVERAL TETRACHLOROPHTHALIMIDOPROPYL BONDED PHASES

Mobile phase for capacity-factor measurement: isooctane–dichloromethane (50:50).

Reduced plate height, h	Reduced velocity, v	Ligand density ($\mu mol/m^2$)	Fluoranthene capacity factor
5	8.9	1.6	1.2
12	6.2	2.1	1.8
20	6.0	2.8	3.5
80	5.7	5.2	6
140	3.2	6.8	5

TABLE V

EFFECT OF THE REACTION TEMPERATURE AND OF THE REACTION TIME ON THE LIG-
AND DENSITY

Mean values calculated from % C, % N and % Cl.

Solvent	Boiling point (°C)	Reaction time (h)	Ligand density ($\mu mol/m^2$)
Dichloromethane	40	48	3.0
o-Xylene	138	8	3.6
1,2,4-Trimethylbenzene	190	4	2.5
1,2,4-Trimethylbenzene	190	8	3.6
1,2,4-Trimethylbenzene	190	16	3.5

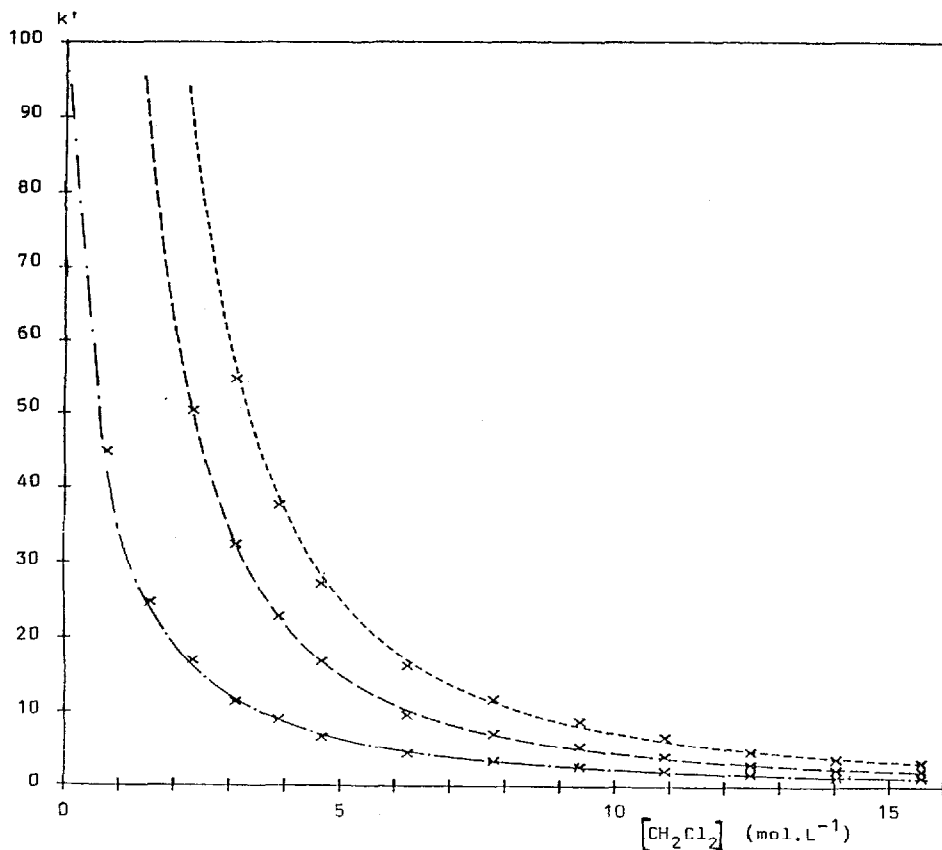Fig. 2. Capacity factors, k', of PAHs on tetrachlorophthalimidopropyl silica as a function of the dichloro-
methane content in the mobile phase (isooctane–dichloromethane). Chromatographic conditions: column,
10 cm × 4.6 mm I.D., tetrachlorophthalimidopropyl silica, 5 μm; flow-rate 1 ml/min, detection, UV
absorptiometry at 254 nm. Solutes: — · —, fluoranthene; – – –; benzo[k]fluoranthene; --------, benzo[a]-
pyrene.

4 μmol/m^2 (Table IV). When the ligand density is lower than 4 μmol/m^2, h takes classical values, when the ligand density exceeds 4 μmol/m^2, h increases tremendously.

Reaction temperature and duration. It is well known for octyl and octadecyl bonded silica that an higher temperature increases the yield of silanization and a short reaction time is sufficient to obtain the maximum coverage.

Three solvents were studied at three temperatures: 1,2,4-trimethylbenzene (b.p. 190°C), *o*-xylene (b.p. 138°C) and dichloromethane (b.p. 40°C). Table V shows the influence of the experimental conditions. When the reaction temperature is constant, the ligand density increases with the reaction time up to a maximum. The optimum reaction time is 7–8 h for 1,2,4-trimethylbenzene. The ligand density also depends on the temperature in dichloromethane and *o*-xylene or trimethylbenzene. However, the last two solvents are equivalent: the maximum ligand density is reached with both solvents.

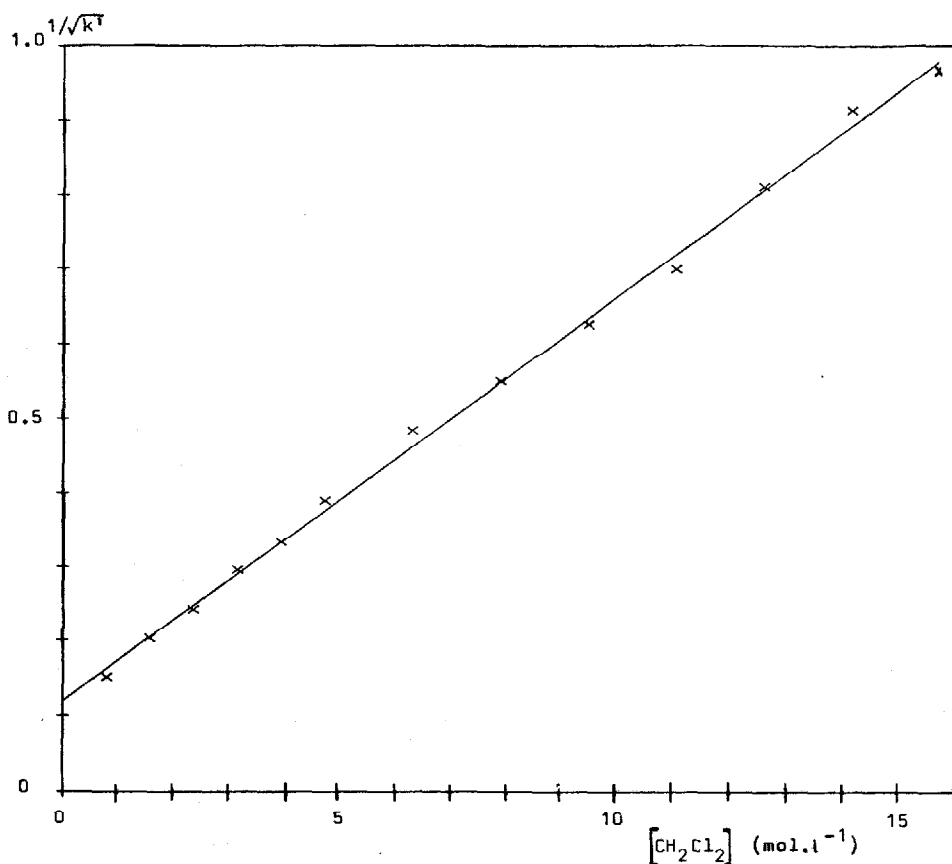*Stirring.* During the silanization reaction, the mixture is stirred mechanically

Fig. 3. Dependence of the reciprocal of the square root of the fluoranthene capacity factor on tetrachlorophthalimidopropyl silica on the dichloromethane content in the mobile phase (isooctane–dichloromethane). Chromatographic conditions as in Fig. 2.

TABLE VI

CAPACITY FACTORS OF PAHs

Column: 10 cm × 4.6 mm I.D., tetrachlorophthalimidopropyl silica, 5 μm, ligand density 2.7 μmol/m^2. Flow-rate: 2 ml/min. Detection: UV absorptiometry at 254 nm. Nph = naphthalene.

Mobile phase, isooctane– dichloromethane	Capacity factor						
	Nph	Ft	B(b)F	B(k)F	B(a)P	I(1,2,3-cd)P	B(ghi)Per
10:90	0.22	1.2	2.6	2.2	3.6	6.1	9.4
20:80	0.28	1.5	3.2	2.8	4.6	7.6	11.6
30:70	0.33	2.0	4.5	3.9	6.6	9.7	15.1
40:60	0.38	2.5	6.1	5.2	8.7	13.3	20.4
50:50	0.44	3.3	8.3	7.0	11.7	18.2	28.0
60:40	0.56	4.3	11.5	9.7	16.2	25.9	40.2
70:30	0.70	6.6	19.0	16.8	27.1	46.5	68*
75:25	0.83	8.9	27.1	22.6	37.6	61*	90*
80:20	1.02	11.3	38.4	32.2	54.7	88*	130*
85:15	1.35	16.9	63*	49.8	88*	140*	200*
90:10	1.69	24.6	115*	90*	160*	240*	350*
95: 5	2.52	44.8	280*	200*	370*	540*	750*
100: 0	6.54	75*	1300*	780*	1600*	2100*	2600*

* Extrapolated value.

in order to obtain an homogeneous suspension and, consequently, a uniform reaction rate controlled by the diffusion in the pores and not in the solution.

Chromatographic properties

Our main interest in this stationary phase concerns the concentration of PAHs from oils (lubricants, temper oils) which are highly apolar.

Capacity factors. A mixture of isooctane and dichloromethane was used as the mobile phase. Isooctane can be considered as equivalent to an apolar matrix, and the dichloromethane is used to obtain capacity factors, k', lower than 50.

Fig. 2 shows that the retention of PAHs decreases with increasing dichloromethane content in the isooctane–dichloromethane mixture. As shown in Fig. 3, a

TABLE VII

MINIMUM VALUES OF CAPACITY FACTORS FOR PAHs IN PURE ISOOCTANE WITH A 95% CONFIDENCE INTERVAL (EXTRAPOLATED VALUES)

PAH	Minimum capacity factor
Fluoranthene	70
Benzo[b]fluoranthene	500
Benzo[k]fluoranthene	450
Benzo[a]pyrene	600
Indeno[1,2,3-cd]pyrene	900
Benzo[ghi]perylene	1300

TABLE VIII

COMPARISON OF VARIOUS STATIONARY PHASES FOR PAH RETENTION

Mobile phase	PAH	Bare silica*	Nucleosil NO_2*	3,5-Dinitrobenzamide silica*	Picryl ether silica**	Caffeine silica***	TENF silica	TCPP silica synthesized by Holstein	TCPP silica synthesized by us	TNF silica§§
Hexane–dichloromethane (95:5)	Benzene	0.00	0.00	0.00	0.00	0.00	0.12		0.26	
	Biphenyl	0.15	0.25	0.52	0.69	0.46	–		0.97	
	Naphthalene	0.11	0.25	0.60	0.82	0.61	0.54		2.6	
	Anthracene	0.25	0.70	3.24	3.53	3.02	1.41		20.2	
	Phenanthrene	0.25	0.77	3.56	3.61	3.24	1.41		20.0	
	Pyrene	0.33	1.24	9.91	6.89	7.02	2.53		55§	
	Chrysene	0.49	2.00	11.87	12.50	12.00	6.11		100§	
Hexane–dichloromethane (80:20)	Benzene							0.1	0.2	
	Biphenyl							0.2	0.4	
	Naphthalene							0.6	1.1	
	Phenanthrene							2.9	5.1	
	Anthracene							3.1	5.3	
Hexane	Naphthalene									4.9
	1-Methylnaphthalene									5.6
	2-Methylnaphthalene									8.4

* Data from ref. 11.
** Data from ref. 12.
*** Data from ref. 13.
§ Extrapolated value.
§§ Data from ref. 14; ligand density of our TCPP silica 3.0 μmol/m^2.

linear relationship exists between $1/\sqrt{k'}$ and the dichloromethane content. This mathematical result does not seem to have any theoretical support, but allows one to extrapolate the capacity factors of the PAHs to pure isooctane. The measured and extrapolated capacity factors on tetrachlorophthalimidopropyl silica having a ligand density of 2.7 μmol/m^2 are given in Table VI.

We have synthesized several tetrachlorophthalimidopropyl silicas and Table VII shows the minimum k' values obtained for various PAHs. It is interesting to compare the tetrachlorophthalimidopropyl silica (TCPP silica) with other electron-acceptor bonded silicas, Table VIII[6,11-14]. The TCPP silica used for these studies was an unpolymerized sample with a ligand density of 3.0 μmol/m^2 and an h value of 30 (at reduced velocity, $v = 7$ and $k' = 4$). Our TCPP silicas have superior properties for PAH retention compared with the Holstein phase and other electron-acceptor phases (the TENF silica and o-propyl-2,4,5,7-tetranitrofluorenone oxime bonded silica, TNF silica).

CONCLUSIONS

The utilization of electron donor–acceptor complexation in liquid chromatography offers high retention for PAHs in a non-polar medium. A systematic study of the synthesis parameters has led to an improved tetrachlorophthalimidopropyl silica with high ligand density and column efficiency. For six representative PAHs, the capacity factors range from 70 to higher than 1000. So, real-life concentration problems of PAHs in oils and other apolar media can be solved with this stationary phase.

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