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Note

Comparative gas chromatographic studies of bonded and physically coated PEG 20M and its derivative phases with reference to some high-boiling isomeric solutes

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Aue and co-workers[1,2] first reported the abnormal behaviour of polyethylene glycol (PEG) stationary phases which remain chemically bonded with siliceous supports. Rapid mass transfer in the chemically bonded phases occurs as the film thickness is small[3]. They are sufficiently thermally stable and efficient[4]. Six to ten-fold reductions in retention times with enhancement of resolution have been observed on bonded phases compared with the corresponding coated phaes. Their advantages over physically coated stationary phases have also been reported[4]. Even though the characteristics of PEG have been studied in detail[1], its possible utility over a wide temperature range needs further investigation. This paper describes the utility of chemically bonded PEG 20M and its derivatives as stationary phases for gas chromatography (GC). The retention behaviour of some high-boiling isomeric solutes, such as naphthols, naphthylamines and dihydroxybenzenes, has been studied.

EXPERIMENTAL

Materials

The following stationary phases based on PEG 20M (Varian Aerograph, Cat. No. 82-11:5) were used: PEG 20M diterephthalate (CTPA), PEG 20M disalicylate (CS) and PEG 20M dioleate (CoA), synthesized by methods described in the literature[5–7].

Chemically bonded stationary phases based on PEG-20M were prepared by Aue *et al.*'s procedure[1]. Packed columns for bonded and conventional coated phases were prepared using stainless-steel tubes (2 m × 3 mm I.D.).

The solid support used was Celite (80–120 mesh) (BDH, Poole, UK). The column parameters are given in Table I.

Solutes

Anisidines, toluidines, nitrotoluenes, naphthylamines, naphthols, catechol, hydroquinone and resorcinol were used. Their purities were tested by measuring their melting points and were greater than 95%.

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TABLE I

COL'JMN PARAMETERS

No.	*Stationary phase*	*Coating (%)*	*Total filling (g)*	*No.*	*Stationary phase*	*Amount bonded (%)*	*Total filling (%)*
I	PEG 20M	1	10	I′	PEG 20M	0.1	10
II	CTPA	3	10	II′	CTPA	0.27	10
III	Cs	3	10	III′	Cs	0.28	10
IV	CoA	3	10	IV′	CoA	0.28	10

Apparatus

For GC studies, an AMIL-NCL dual-column gas chromatograph equipped with a thermal conductivity detector and a data processing system was used.

Procedure

The following operating parameters were used: column temperature, 130, 170 and 200°C; injector temperature, 170, 220 and 240°C, respectively; detector temperature, temperature, 180, 230 and 250°C, respectively; flow-rate of carrier gas (hydrogen), 100 ml/min; bridge current, 125 nA; and recorder operating speed, 600 mm/h.

RESULTS AND DISCUSSION

GC analysis on bonded stationary phases at 200°C showed a considerable reduction in retention time and efficient resolution compared with the results given by the corresponding coated stationary phases (Table II). Efficient resolution of *m*- and *p*-anisidines, -toluidines and -nitrotoluenes was achieved at 130°C. Usually nonpolar stationary phases are recommended for analysis of high-boiling compounds such as naphthylamines, naphthols and dihydroxybenzenes. However, they are conveniently eluted and separated on all bonded phases. They cannot be eluted on the corresponding coated phases (1%) even at 200°C.

The order of bonding of PEG 20M and its derivative phases with the silanol (SiOH) groups of the support[8] was expected to be PEG 20M > CS > CTPA > CoA. However, alsmost identical amounts of each derivative remained unextractable and assumed to be chemically bonded. Probably these molecules lie within the Van der Waals radius where Van der Waals forces[9] interact to form partial chemical bonds such as hydrogen bonds, preventing their solvent extraction. The enhanced resolving power may be the result of sieving through gaps among the bristles in addition to donor–acceptor end groups.

CONCLUSION

The advantages of the bonded stationary phases are a substantial reduction in retention time and a lower operating temperature of about 70°C, a higher resolving power and sharp peaks as the absorption is negligible.

TABLE II

RESULTS OF ANALYSES ON COATED AND BONDED STATIONARY PHASES

The relative retention times (for *m*- and *p*-isomers relative to the corresponding *o*-isomers = 1) are given. Values in parentheses are absolute retention times (s). Column temperature, 200°C.

Sample	*Coated phase*				*Bonded phase*			
	I	*II*	*III*	*IV*	*I'*	*II'*	*III'*	*IV'*
o-Anisidine	1 (28.5)	1 (114.7)	1 (156.5)	1 (101.1)	1 (6.5)	1 8.0)	1 (9.6)	1 (13.0)
m-Anisidine	2.40	2.33	2.31	2.32	2.15	2.00	2.24	2.15
p-Anisidine	1.97	1.83	1.79	1.82	2.02	1.79	2.00	2.00
o-Toluidine	1 (17.5)	1 (68.1)	1 (94.0)	1 (61.0)	1 (4.4)	1 (5.0)	1 (5.6)	1 (7.5)
m-Toluidine	1.14	1.14	1.10	1.12	1.32	1.04	1.23	1.23
p-Toluidine	1.09	1.03	1.03	1.04	1.14	1.22	1.09	1.21
o-Nitrotoluene	1 (17.2)	1 (68.6)	1 (92.5)	1 (61.0)	1 (5.0)	1 (5.5)	1 (5.5)	1 (8.1)
m-Nitrotoluene	1.23	1.28	1.26	1.23	1.1	1.16	1.29	1.28
p-Nitrotoluene	1.41	1.43	1.42	1.41	1.4	1.44	1.73	1.49
α-Naphthylamine	–	–	–	–	1 (49.0)	1 (65.0)	1 (86.7)	1 (122.5)
β-Naphthylamine	–	–	–	–	2.18	2.05	2.16	2.15
α-Naphthol	–	–	–	–	1 (94.0)	1 (119.0)	1 (153.6)	1 (231.0)
β-Naphthol	–	–	–	–	1.04	1.13	1.24	1.08
Catechol	–	–	–	–	1 (54.0)	1 (62.0)	1 (84.5)	1 (129.5)
Hydroquinone	–	–	–	–	1.44	1.72	2.74	2.57
Resorcinol	–	–	–	–	1.81	3.45	3.63	3.03

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