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Note

Poly(crown ether) stationary phase for open-tubular capillary column chromatography

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Applications of crown ethers and cryptands in analytical chemistry have been extensively developed [1], one of the most important being in high-performance liquid chromatography (HPLC) for the separation of ionic species [2]. Some low-molecular-weight crown ethers, *e.g.*, dibenzo-24-crown-8, were used as packed column stationary phases by Li [3,4] for the separation of alcohols, phenols, amines, aromatic compounds and halides. Fine *et al.* [5] prepared and characterized open-tubular columns coated with three types of poly(crown ether), poly(vinylbenzo-15-crown-5), vinylmethylsila-17-crown-6 and vinylmethylsila-14-crown-5. Zagorevskaya and Kovaleva [6] used dibenzo-18-crown-6 and dinitrodibenzo-18-crown-6 as gas chromatographic stationary phases coated on a carbon sieve for the separation of paraffinic and aromatic hydrocarbons. More recently, Rouse *et al.* [7] synthesized an oligo (ethylene oxide)-substituted polysiloxane and 18-crown-6-substituted polysiloxane as open-tubular column stationary phases and compared them with Carbowax 20M. In our previous work [8], two kinds of crown ethers were used as capillary column stationary phases.

In this work, 3-allylbenzo-15-crown-5-substituted polysiloxane was synthesized and coated on fused-silica capillary columns. The retention behaviour was studied and compared those of three columns coated with low-molecular-weight crown ethers. The crown ethers investigated are shown in Fig. 1.

EXPERIMENTAL

Model SP-2305 and SP-3700 gas chromatographs (Beijing Analytical Instrument Factory, Beijing, China) equipped with flame ionization detectors were used for evaluation of retention behaviour. Glass capillary columns statically coated with dibenzo-24-crown-8 were prepared as described previously [8]. Fused-silica capillary

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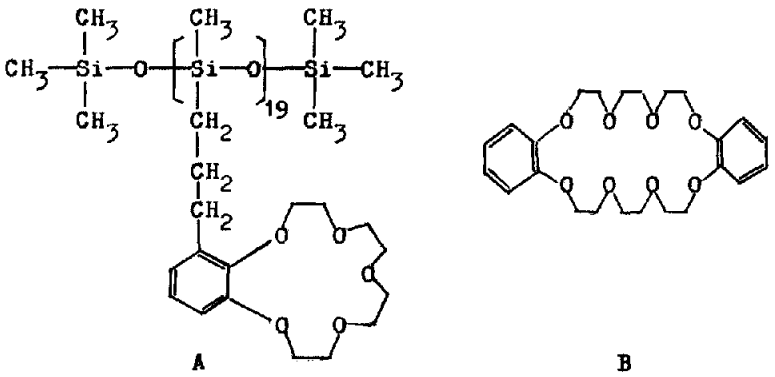


Fig. 1. Structure of crown ether stationary phases studied. A = PAB15C5S; B = DB24C8.

columns (0.25 mm I.D.) (Yongnian Optical Fibre Factory, Hebei, China) were purged with dry nitrogen at 250°C for 2 h before coating, then filled with a solution of poly(crown ether) stationary phase in dichloromethane and sealed at one end, evaporating the solvent under vacuum at 35°C from the other end. After solvent evaporation, the column was dried with dry nitrogen at room temperature for 1 h, then connected to the gas chromatograph and conditioned at 180°C. Allylbenzo-15-crown-5 and dibenzo-24-crown-8 were obtained from the Department of Environmental Science, Wuhan University (Wuhan, China). Poly(methylhydrosiloxane) (PHMS) was obtained from the Second Beijing Chemicals Factory (Beijing, China). All other chemicals used for synthesis or characterization purpose were of analytical-reagent grade. Benzo-15-crown-5-substituted (crown) polysiloxane was synthesized from allylbenzo-15-crown-5 and PHMS by a procedure similar to that in the literature [7].

RESULTS AND DISCUSSION

Table I gives the characteristics of three fused-silica capillary columns coated

TABLE I

CHARACTERISTICS OF THE CAPILLARY COLUMNS STUDIED

Column No.	Column dimension (length × I.D.)	Stationary phase[a]	Column efficiency (plate/m)	Column temperature (°C)	Test compound
1	8.5 m × 0.25 mm	PAB15C5S	2675	140	n-C_{13}
2	15 m × 0.25 mm	PAB15C5S	3578	140	n-C_8-OH
3	10 m × 0.25 mm	PAB15C5S	4705	150	n-C_1
4	20 m × 0.29 mm[b]	DB24C8	350	120	n-C_{15}
5	20 m × 0.22 mm	DSU30C10	2680	165	n-C_{13}
6	20 m × 0.22 mm	SU15C5	2770	170	n-C_{13}

[a] PAB15C5S and DB24C8, see Fig. 1; DSU30C10 = 4,4-dipentadecyl- or 4,3′-dipentadecyl-30-crown-10; SU15C5 = 3-pentadecylbenzo-15-crown-5.

[b] Glass capilary column.

TABLE II

SELECTIVITIES AND POLARITIES OF THE CROWN ETHERS STUDIED

X' = Benzene; Y' = butanol; Z' = 2-pentanone; U' = nitropropane; S' = pyridine.

Stationary phase	McReynolds constants (ΔI)						b
	X'	Y'	Z'	U'	S'	Mean	
DB24C8	301	448	355	526	479	422	0.2340
SU15C5	121	218	165	242	195	189	0.2730
DSU30C10	82	116	128	213	166	141	0.2720
PAB15C5S	198	390	196	371	434	318	0.2563
SE-30[a]	15	44	53	64	41	43	0.2495
PEG-20M[a]	322	536	368	572	510	461	0.2235

[a] From ref. 9.

with PAB15C5S and a glass capillary column coated with dibenzo-24-crown-8, and two columns coated with SU15C5 and DSU30C10 for comparison. The results indicate that the efficiency of the glass capillary column coated with DB24C8 is the lowest, and those of the fused-silica capillary columns with PAB15C5S are the highest.

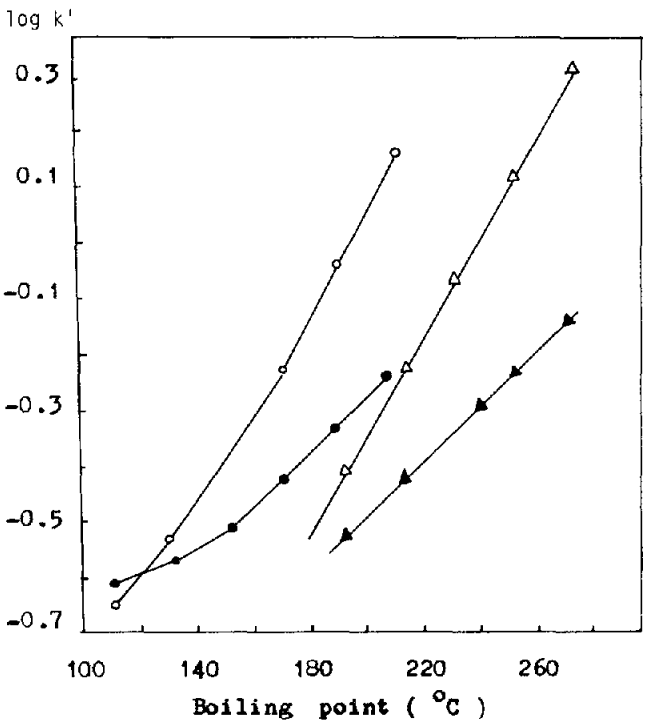


Fig. 2. Plot of log k' against boiling point for (○) alcohols at 140°C, (●) alcohols at 180°C, (△) alkanes at 140°C and (▲) alkanes at 180°C on column 3.

This occurs mainly because DB24C8 cannot form an even film on the wall of a glass capillary column, whereas PAB15C5S is a polysiloxane polymer, which can easily form a thin film on the wall of a fused-silica capillary column. Therefore, the use of a poly(crown ether) as a stationary phase in an open-tubular column gives a higher column efficiency than a low-molecular-weight crown ether.

The selectivity and polarity of PAB15C5S and DB24C8 are represented by McReynolds constants and b (the slope of the curve obtained when the logarithm of the adjusted retention times of n-alkanes are plotted as a function of the number of carbon atoms). These parameters and average polarities are listed in Table II. These parameters are also listed for SU15C5, DSU30C10, SE-30 and PEG-20M for comparison. The average polarity of PAB15C5S is higher than that of SU15C5 and DSU30C10, but is lower than that of DB24C8 and PEG-20M. It is surprising that the average polarity of PVB15C5, which was used as stationary phase for capillary columns by Fine *et al.* [5], is much higher than that of PAB15C5S (526 for PVB15C5 and 318 for PAB15C5S), and even higher than that of PEG-20M.

Of the six stationary phases in Table II, SU15C5 and DSU30C10 have the highest b values, owing to the long alkane chains, and therefore they are suitable for the separation of apolar compounds. On the other hand, PAB15C5S has a medium b value, similar to that of SE-30, so PAB15C5S is suitable for the separation not only of apolar compounds but also of hydroxyl compounds owing to the high selectivity for alcohols.

Fig. 2 shows the plots of log k' (capacity factor) *vs.* boiling points of homologous alkanes and alcohols, wich demonstrates the above-mentioned explanation about the selectivity of PAB15C5S. The slopes of the plots (Fig. 2) at the same temperature are

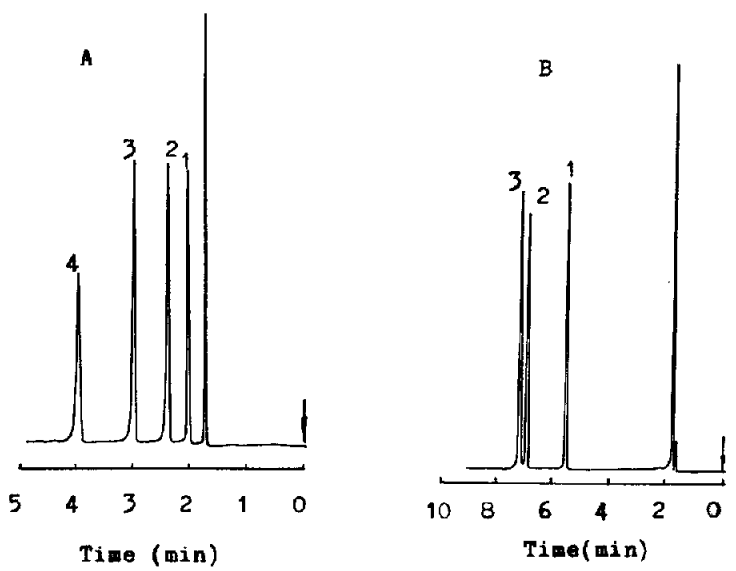
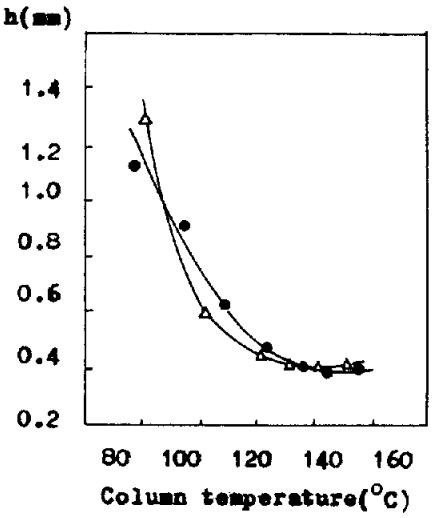


Fig. 3. Chromatograms of (A) alcohols (n-C_4–n-C_7) and (B) cresols on column 1 (PAB15C5S). (A) Column temperature = 146°C; 1 = n-butanol; 2 = n-heptanol; 3 = n-hexanol; 4 = n-heptanol. (B) Column temperature = 136.6°C; 1 = o-cresol; 2 = m-cresol; 3 = p-cresol.



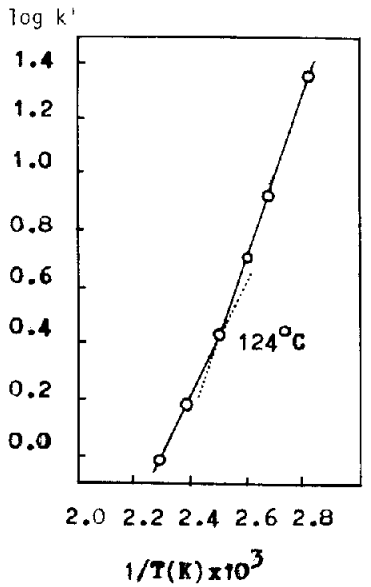


Fig. 4. Plots of column efficiency *vs.* column temperature. (●) Column 2; (△) column 3.

Fig. 5. Plot of log *k'* *vs.* reciprocal of column temperature for octanol on column 2.

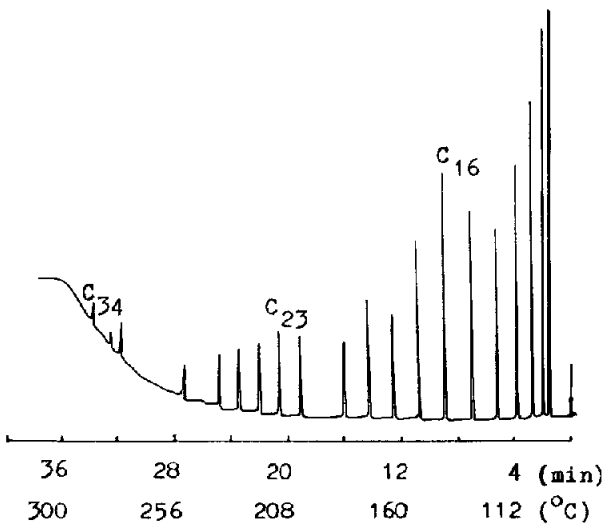


Fig. 6. Gas chromatogram of *n*-alkane mixture on column 3. Column temperature: 100 C for 2 min then programmed to 300°C at 6°C/min. Injection temperature: 350°C.

similar, which means that PAB15C5S stationary phase has a similar resolving power. On the other hand, at the same boiling point, the k' values of alcohols are higher than those of the corresponding alkanes. This demonstrates that crown ether stationary phases undergo a special interaction with alcohols. A fused-silica capillary column coated with PAB15C5S is suitable especially for the separation of phenols; *e.g.*, the cresol isomers can be separated completely. Fig. 3 shows chromatograms for the separation of phenols and alcohols.

To test the effect of temperature on the column efficiency, the height equivalent to a theoretical plate (HETP) was determined at different temperatures and a constant flow-rate of the carrier gas. Fig. 4 illustrates a plot of HETP (k) *vs.* column temperature (t) for *n*-octanol on the three poly(crown ether) capillary columns. It is clear that the column efficiency increases with increasing temperature and has a maximum value at about 150°C, which is higher than the transition temperature (discussed below). This behaviour is different from that of SU15C5 and DSU30C10 columns, on which the plot of HETP *vs.* t has a maximum [8]. As with other crown ether columns, PAB15C5S columns also have a liquid–liquid transition temperature point (Fig. 5) at about 124°C.

To investigate the thermal stability of the PAB15C5S capillary columns, an *n*-alkane mixture was separated on column 3, which was cross-linked with V4 [tetra(methylvinyl)cyclotetrasiloxane] and DCUP (dicumyl perioside), and the chromatogram is shown in Fig. 6. The baseline drift was $1.1 \cdot 10^{-12}$ A when the column temperature was programmed from 100 to 300°C at 6°C/min. Therefore, it can be concluded that the fused-silica capillary column coated with PAB15C5S possesses high thermal stability, and it is better than that of low-molecular-weight crown ether stationary phases and PEG-20M.

Fused-silica capillary columns coated with PAB15C5S were used to separate polar and apolar compounds, such as isomers of cresol, mono- and dinitrotoluene, nitrohalogenated benzenes and dimethoxybenzene, and excellent results were obtained.

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