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Preparation and gas chromatographic characterization of some immobilized crown ether–polysiloxane stationary phases

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(First received August 2nd, 1989; revised manuscript received November 23rd, 1989)

SUMMARY

The cross-linked fused-silica capillary columns, SE-54–30% 18-crown-6, SE-54–50% 18-crown-6 and SE-54–50% 15-crown-5, were prepared and characterized by gas chromatography, including the determination of column bleeding, phase transition temperature, polarity and selectivity. The polarity and selectivity of these phases are comparable to those of SE-54 and OV-1701. The hydrogen bonding contribution of crown ether phases in separating solutes is discussed.

INTRODUCTION

Crown ethers have a polar ring formed by the oxygen atoms and the ring structure confers the ability to form stable complexes with metal cations and electrically neutral organic solutes[1,2] They have received considerable attention especially in analytical chemistry[3–8], and a few gas chromatographic (GC) studies have been reported[9–13]. Crown ethers have great potential in GC because of their unique selectivity. However, small-molecule crown ether stationary phases have low maximum operating temperatures and the column efficiency and thermal stability are poor[13].

Polysiloxane polymers provide the best performance as stationary phases in GC. They have good solute diffusivity, thermal stability and film-forming ability. Most of the phases developed recently for capillary chromatography are based on the polysiloxane backbone, substituted with different organic groups. These polar side-groups on the polysiloxane backbone give specific selectivities for particular components.

In this work, a new method for preparing crown ether–polysiloxane stationary phases by direct cross-linking crown ether with SE-54 stationary phase in different proportions was developed. These polymeric phases were tested for efficiency, polarity, selectivity, phase transition temperature and thermal stability.

EXPERIMENTAL

Reagents

ω-Undecyleneoxymethyl-18-C-6 and ω-undecyleneoxymethyl-15-C-5 (C = crown), shown in Fig. 1, were obtained from the Department of Chemistry, Wuhan University. All other chemicals used were of analytical-reagent grade.
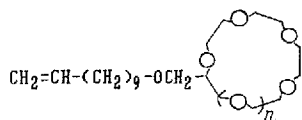

CH$_2$=CH-(CH$_2$)$_9$-OCH$_2$-

Fig. 1. Structure of alkylene crown ethers. $n = 1$, Monomer I; $n = 2$, monomer II.

Preparation of crown ether polysiloxane columns

Fused-silica capillary tubing (Academy of Post and Telecommunication, Wuhan, China) was rinsed with water and methanol and purged with nitrogen at 280°C for 2 h. Columns were then statically coated at room temperature with 0.5% (w/v) mixed stationary phase (SE-54 with monomer I or II in different proportions) and 5% (w/v) dicumyl peroxide (DCUP) in methylene chloride, which was previously filtered through a 0.2-μm Millipore filter. Both ends of the colomn were sealed and the latter was placed in an oven at 150°C for 1 h, then heated to 190°C at 8°C min^{-1} and held at 190°C for 1 h. The non-cross-linked molecules of the stationary phase were removed during the first washing with ten column volumes of methylene chloride and the column capacity was decreased by 10–14%, as indicated by the decrease in the capacity factors of the test substances. Prolonged washing of the column with five column volumes of this solvent did not lead to additional removal of the stationary phase, with an unchanged capacity. Finally, the column was conditioned at 280–300°C for 12 h.

Column evaluation

Column evaluation was performed with a Shimadzu Model GC-7A gas chromatograph equipped with a capillary split injection system and flame ionization detector, using nitrogen as the carrier gas. Grob's test mixture, an isomer mixture and two samples were used to demonstrate the selectivity of the phases. The columns were tested for polarity and efficiency by measuring the retention indices and number of plates per metre for naphthalene at 120°C. The thermal stabilities of the crown ether polysiloxane stationary phases were tested by measuring the column bleeding.

RESULTS AND DISCUSSION

The presence of terminal vinyl groups in the synthetic crown ether monomers I and II facilitates its cross-linking with the SE-54 matrix by treatment with DCUP, forming a crown ether polysiloxane in the inner surface of the capillary column which is non-extractable by solvents. Table I summarizes the chromatographic characteristics of those crown ether columns. The results indicate that the theoretical plate
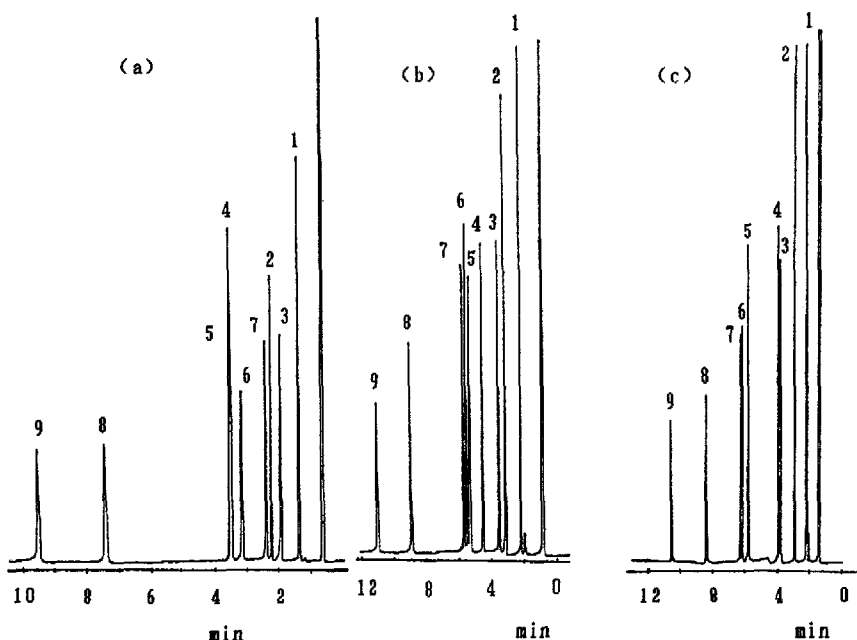
Fig. 2. Chromatogram of the Grob test mixture. (a) On SE-54. Column temperature programmed from 100 to 160°C at 6°C min⁻¹. (b) On SE-54–50% monomer II. Column temperature programmed from 100 to 170°C at 6°C min⁻¹. (c) On SE-54 – 50% monomer I. Columnn temperature programmed from 100 to 150°C at 4°C min⁻¹. Peaks 1 = n-decane; 2 = n-undecane; 3 = 1-octanol; 4 = n-dodecane; 5 = naphthalene; 6 = 2,6-dimethylphenol; 7 = 2,4-dimethylaniline; 8 = methyl undecanoate; 9 = methyl dodecanoate.

number is over 3800 per metre for all of the columns and the column efficiency decreases slightly with increasing crown ether content. The peak–area ratio of acidic P (2,6-dimethylphenol) and basic A (2,4-dimethylaniline) test substances and the peak asymmetry factor of octanol on fused-silica columns coated with SE-54–crown ether and cross-linked with DCUP showed no increase in polarity and activity.

Fig. 2 shows chromatograms of the Grob test mixture obtained on the different columns. For the SE-54–50% 18-C-6 and SE-54–50% 15-C-5 columns, the polar components of the Grob test mixture, 1-octanol, 2,4-dimethylaniline and 2,6-dimethylphenol, elute after undecane and naphthalene, in contrast to the reference SE-54 column. It can be concluded that crown ether–polysiloxane columns have different polarities and selectivities to the SE-54 column. The results also indicate that crown ether monomers were cross-linked to the SE-54 polysiloxane backbone and contributed to the separation mechanism.

The selectivity and average polarity of those crown ether––polysiloxane stationary phases, represented by the McReynolds constants (I), are shown in Table II. It can be seen that the crown ether phases have an average polarity between those of SE-54 and OV-1701 and SE-54 – 50% 18-C-6 has a slightly lower polarity than SE-54–50% 15-C-5, owing to the similar D_{3d} comformation of 18-C-6.

As illustrated in Table III, the relative retention values of all the test samples

TABLE I

CHARACTERISTICS OF CROWN ETHER–POLYSILOXANE CAPILLARY COLUMNS

Column No.	Column dimensions [length (m) × I.D. (mm)]	Stationary phase	Naphthalene capacity factor (k')	Efficiency (n/m)	P/A	Peak asymmetry[14]
1	12 × 0.24	SE-54 – 30% monomer II	2.80	4633	1.03	1.00
2	14 × 0.26	SE-54 – 50% monomer II	2.76	3806	1.05	1.00
3	14 × 0.26	SE-54 – 50% monomer I	3.41	4176	1.01	1.00

TABLE II

SELECTIVITY (McREYNOLDS CONSTANTS, *I*) AND POLARITY OF THE CROWN ETHER-POLYSILOXANES

Stationary phase	Benzene	Butanol	2-Pentanone	Nitropropane	Pyridine	Average polarity
SE-54	33	72	66	99	67	60
SE-54 – 30% monomer II	61	129	75	132	128	105
SE-54 – 50% monomer II	63	152	84	151	126	115
SE-54 – 50% monomer I	64	149	86	163	133	119
OV-1701	67	170	153	228	171	158

with the SE-54–crown ether columns are greater than those with the SE-54 column. With the exception of trimethylbenzene, this indicates that the former have much better selectivity than SE-54. In comparison with OV-1701, which has a higher polarity, they have roughly the same selectivity with respect to nitro-substituted benzene positional isomers, but with respect to cresol, chlorophenol and nitrophenol compounds, SE-54 – crown ether columns provide a higher selectivity. This suggests that the crown ether–polysiloxanes are convenient for separating apolar and polar compounds, especially compounds that have the ability to form hydrogen bonds with the oxygen atom in the crown ether ring.

TABLE III

RELATIVE RETENTION VALUES OF TEST COMPOUNDS IN THE VARIOUS COLUMNS

| Compound	Isomer	SE-54	SE-54 – 50% 18-C-6	SE-54 – 50% 15-C-5	OV-1701
Ethylnitrobenzene	o-	1.00	1.00	1.00	1.00
	m-	1.32	1.40	1.37	1.36
	p-	1.46	1.61	1.63	1.60
Dinitrobenzene	o-	1.00	1.00	1.00	1.00
	m-	1.10	1.10	1.14	1.14
	p-	1.23	1.44	1.43	1.41
Cresol	o-	1.00	1.00	1.00	1.00
	p-	1.04	1.26	1.23	1.03
Chlorophenol	o-	1.00	1.00	1.00	1.00
	p-	2.23	6.30	5.39	4.49
Nitrophenol	o-	1.00	1.00	1.00	1.00
	m-	3.95	39.5	45.00	14.90
	p-	5.17	70.60	78.70	23.70
Trimethylbenzene	1,3,5-	1.00	1.00	1.00	1.00
	1,2,4-	1.15	1.17	1.14	1.19
	1,2,3-	1.36	1.33	1.36	1.47
Naphthalene		1.00	1.00	1.00	1.00
2-Methylnaphthalene		1.62	1.75	1.76	1.74
Biphenyl		1.97	2.27	2.44	2.22
Acenaphthylene		3.16	3.93	4.17	3.81
Dibenzyl		3.43	3.86	4.19	4.01
Fluorene		4.70	4.91	7.00	5.92
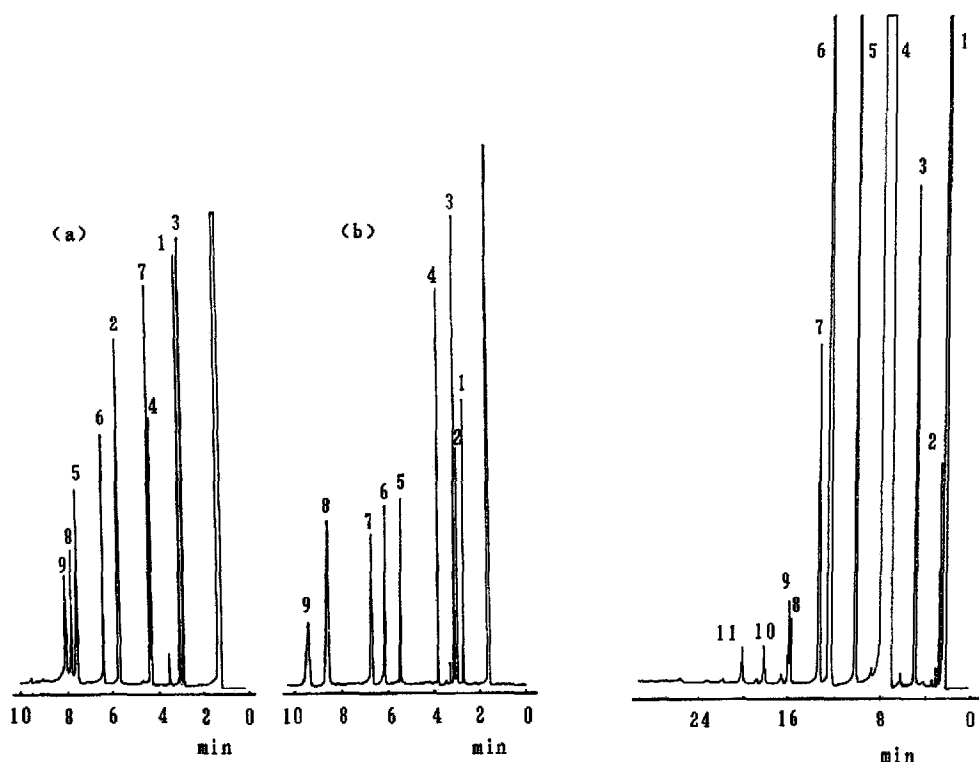
Fig. 3. Chromatogram of phenol compounds. (b) On SE-54−30% monomer I. Column 10 m × 0.25 mm I.D., temperature programmed from 105 to 230°C at 12°C min⁻¹. (a) On SE-54. Column, 16 m × 0.25 mm I.D., temperature programmed from 75° to 200°C at 12°C min⁻¹. Peaks: 1 = *o*-chlorophenol; 2 = *o*-nitrophenol; 3 = phenol; 4 = 2,4-dimethylphenol; 5 = 2,4,6-trichlorophenol; 6 = *p*-bromophenol; 7 = 2,4-dinitrophenol; 8 = *m*-nitrophenol; 9 = p-nitrophenol.

Fig. 4. Chromatogram of ethyl-substituted nitrobenzene compounds on SE-54–50% 15-C-5 (column). Column temperature programmed from 100 to 200°C at 4°C min⁻¹. Peaks: 1–3 = solvents; 4 = nitrobenzene; 5 = *o*-ethylnitrobenzene; 6 = *m*-ethylnitrobenzene; 7 = *p*-ethylnitrobenzene; 8 = 2,3-diethylnitrobenzene; 9 = 2,5-diethylnitrobenzene; 10 = 3,5-diethylnitrobenzene; 11 = 3,4-diethylnitrobenzene.

The ring structure of the crown compounds provides selectivity for organic compounds with hydroxyl groups, which is based on accessibility and availability of hydrogen bonding between the hydroxylic hydrogens and the ether oxygen atom. The separation of nitrophenol isomers is a good example, the relative retention of the *para*- and *ortho*-substituted pair on the crown ether–polysiloxane phases being higher than that on other phases. Because the *para* substituted compound is a rod-like molecule fitting into the cavity of the crown ether ring it shows a stronger hydrogen bonding interaction of the ether oxygen than the *ortho*-substituted compound, which forms intramolecular hydrogen bonds between the nitro oxygen atom and the phenolic hydrogen atoms, thus leading to a more pronounced difference in the relative retention times.
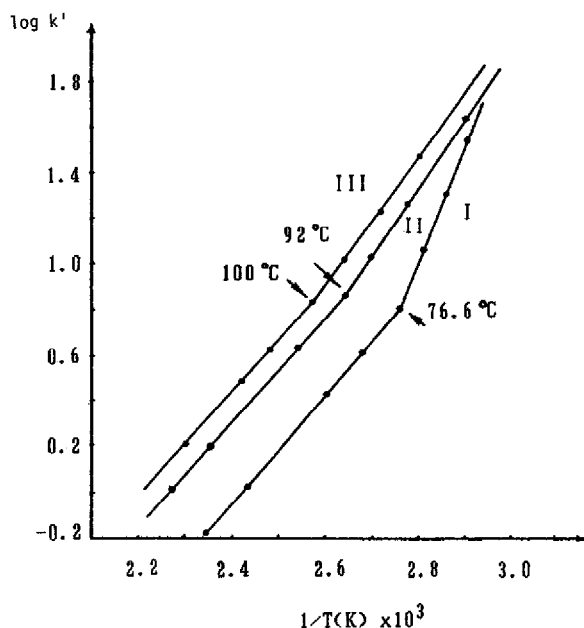
Fig. 5. Plots of log k' (capacity factor) against inverse of absolute temperature for 1-octanol. I, SE-54 – 30% monomer II; II, SE-54 – 50% monomer II; III, SE-54 – 50% monomer I.

The three crown ether–polysiloxane phases also gave excellent separations of various environmental substituted phenol mixtures (Fig. 3) and ethyl-substituted nitrobenzene products (Fig. 4). In comparison with an SE-54 column, SE-54–50% 18-C-6 results in a superior separation without tailing for phenol compounds.

To determine the operating temperature range of the SE-54 – crown ether columns, the phase transition temperature and maximum allowable operating temperature of each column were measured. Fig. 5 shows changes in the retention behavior of 1-octanol on columns 1, 2 and 3 at 76.6, 92 and 100°C respectively; these transitions occur at temperatures which may correspond to the glass transition temperature and a liquid–liquid transition. The maximum allowable operating temperature was determined by identifying the temperature (300°C) at which a shift in the baseline of $7.5 \cdot 10^{-13}$ A was observed. The baseline was not increased when the column temperature was below 245°C.

CONCLUSION

The three SE-54 – crown ether columns discussed exhibit a high column efficiency, a wide operating temperature range and possess unique selectivity for polar positional isomers and compounds with the ability to form hydrogen bonds with the crown ether ring. Their preparation is simple.

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