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Review

Application of crown ether compounds as gas chromatographic stationary phases

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Abstract

Crown ether compounds have a unique structure owing to the cavity structure and the strong electronegative effect of heteroatoms. In recent years, some groups have succeeded in applying these ligands in gas chromatography. Typically, crown ethers have been coated on supports, polymerized and covalently bonded to a polysiloxane backbone. The last technique resulted in a series of significant GC stationary phases which show excellent thermostability and provide unique separations of polar compounds and aromatic hydrocarbons, especially positional isomers. Work about the application of crown ethers as GC stationary phases is reviewed.

Contents

1. Introduction	203
2. Methods of application	204
2.1. Low-molecular-mass crown ethers	204
2.2. Polymeric crown ether stationary phases	205
2.3. Crown ether cross-linking with silicone <i>in situ</i> inside a capillary column	207
2.4. Crown ether-anchored polysiloxanes	208
3. Characteristics of crown ether stationary phases in GC	210
3.1. Selectivity of crown ether stationary phases	210
3.2. Average polarity and thermostability of crown ether stationary phases	212
4. Conclusions	217
5. Acknowledgement	217
6. References	217

1. Introduction

Crown ether compounds have been studied for over two decades since the first synthesis by

Perderson [41] and Lehn [42]. All crown ethers are characterized by a cyclic carbon structure, containing heteroatoms such as oxygen, nitrogen and sulphur, which provide an electron-rich environment for solutes, some of which may fit into the central cavity of the molecule forming

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stable complexes. Owing to these advantages, crown ethers have been found wide applications in chemistry. In particular their application in analytical chemistry, such as in extraction, electrochemical analyses and chromatographic separations, has been extensively developed. Numerous publications have appeared concerning the applications of crown ether compounds for separating both cations and anions and organic solutes by high-performance liquid chromatographic and other methods, and two important review papers on the use of crown ethers in liquid chromatographic separations have been published by Kimura and Shono [1] and Lamb and Smith [2].

Poly(ethylene glycol) ether phase (Carbowax 20M) is a widely used stationary phase in capillary gas chromatography (GC) because of its high coating efficiency and unique selectivity for polar compounds. However, its usefulness as a stationary phase is limited owing to its relatively low thermal stability (220–240°C), high minimum operating temperature (160°C) and poor chemical stability (susceptibility to oxidation, resulting in short column life times). Clearly, there is a great need for more stable polar and medium polarity phases offering new and different selectivities for the separation of high-boiling polar compounds in high-temperature capillary GC.

It is well known that good diffusion of solutes in the stationary phase is a necessary condition for optimum performance in chromatography, and polysiloxane phases possess the best diffusion properties of the known polymeric materials [3]. Moreover, polysiloxane phases have also historically provided the highest thermal stability. Therefore, almost all new phases developed for capillary chromatography are based on a polysiloxane backbone, which range from polar cyanophenyl-substituted to non-polar alkyl-substituted polysiloxanes.

In recent years, some workers have tried to use crown ether compounds as GC stationary phases. These include low-molecular-mass crown ethers, polymeric crown ethers and crown ether polysiloxanes. In some instances, excellent separations among polar compounds and polar posi-

tional isomers have been achieved on these phases. Attempts to substitute polysiloxanes with crown ethers have proved successful in extending the applicable temperature range and creating an "inert" surface on fused-silica capillary materials.

This review deals with the application of crown ethers in GC, chiefly the application of crown ether polysiloxanes as GC stationary phases. The purpose is to stimulate work on the application of crown ethers in this field, because there are still few examples concerning their practical use in GC, particularly the application of crown ether polysiloxanes as stationary phase.

2. Methods of application

Four types of crown ethers incorporated in GC stationary phases have been achieved: low-molecular-mass crown ethers; polymeric crown ethers; crown ethers cross-linked with silicone *in situ* in a capillary column; and crown ether-substituted polysiloxanes.

2.1. Low-molecular-mass crown ethers

The first example of the use of crown ethers as stationary phases was the use of 18-crown-6 reported by Vigalok and Bubachinkowa [4]. Early work on the application of crown ethers often involved coating them on different supports such as Gas Chrom Q, firebrick or white 101 support for packed column chromatography [5–10]. Carbochromes have been modified with dibenzo-18-crown-6 and dinitrobenzo-18-crown-6 and used as stationary phases for the separation of aromatic and chlorinated compounds [11]. This modification leads to decreases in the number of non-specific interaction sites and in the energy of interaction and thus to a shortening of the retention times with preservation of the original elution order. Decreased retention makes it possible to perform chromatographic analyses at lower temperatures and within shorter periods of time, which is important for the determination of thermally unstable solutes, such as chlorine-containing pesticides (Fig. 1).

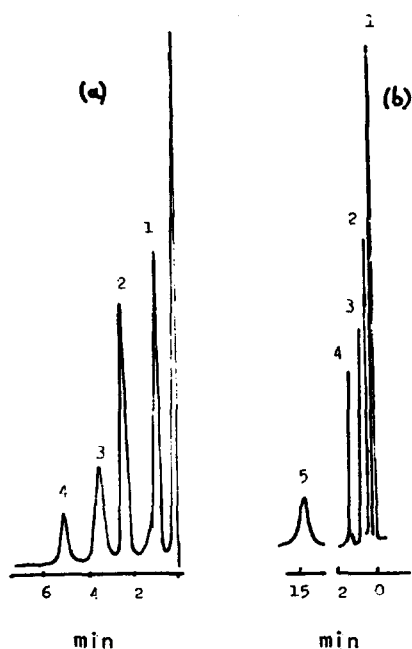


Fig. 1. Separations of chlorine-containing compounds (1 = α -HCL; 2 = γ -HCH; 3 = aldrin; 4 = heptachlor; 5 = DDE) (a) on Carbochrome at 260°C and (b) on Carbochrome modified with dibenzo-18-crown-6 at 200°C. Column, 100 cm \times 1.2 mm I.D.; carrier gas (helium) flow-rate, 14 ml/min. From ref. 11.

Several types of crown ethers have been applied in coated column chromatography. Dibenzo-18-crown-6 or dicyclohexo-24-crown-8 (DCH-24C8) coated on Chromosorb W AW DMCS is useful for the direct determination of nitrophenol and nitroaniline isomers without any derivatization [8]. Tribenzopyridine-21-crown-7 [9] and biazocrown ether [6,7] can separate amines (Fig. 2). The properties of (DCH-24C8) [8] and benzo-15-crown (B15C5) [10] were found to be similar to those of tricyresyl phosphate and di(2-methoxyethyl)adipate, respectively. All of these experiments using crown ethers as stationary phases achieved good separations of small numbers of homologous series of *n*-alkanes, alcohols and aromatic compounds.

Specifically, Jin *et al.* [12] coated two saturated urushiol crown ethers inside a glass or fused-silica capillary column. They gave excellent separations of alcohols without any tailing owing to the deactivation of the residual silanol groups on

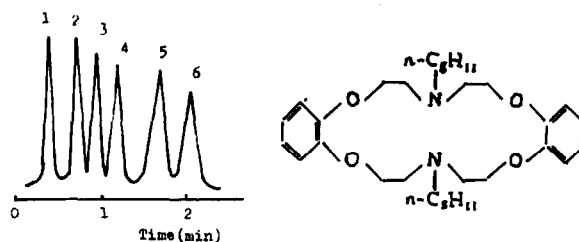


Fig. 2. Separation of nitrogen-containing compounds on a diaza-crown ether-packed column at 220°C. Carrier gas (hydrogen) flow-rate, 30 ml/min. Peaks: 1 = aniline; 2 = nitrobenzene; 3 = *o*-diaminobenzene; 4 = *m*-dinitrobenzene; 5 = *N*-hydroxyethenyl-*N,N*-ethylamine; 6 = *o*-aminophenol. From ref. 7.

the surface of the column wall by crown ether rings. Andrews *et al.* [13] attempted to separate C_2 -naphthalene isomers by the use of 24-crown-8 on a 60 m \times 0.2 mm I.D. column (Supelco), but it was found to be unable to separate all of these isomers, presumably because the size of the crown ether cavity did not fit the isomers.

The poor film forming ability, poor column efficiency and column bleeding at high temperatures are problems with the use of low-molecular-mass crown ethers as coated column stationary phases.

2.2. Polymeric crown ether stationary phases

The only work dealing with crown ether polymers as stationary phases was reported by Fine *et al.* [14] in 1985. They used poly(vinylbenzo-15-crown-5) (PVB-15C5) statically coated on the inside of a roughened, deactivated glass capillary, but no useful chromatographic characteristics were achieved. PVB-15C5 had a polarity similar to that of Carbowax 20M, but the maximum operating temperature was only 220°C. The poor efficiency of PVB-15C5 is probably due to the poor diffusion ability of polyethylene linkages. No other examples of the use of polymeric crown ethers as stationary phases have been reported since Fine *et al.*'s work, although the preparation of polymeric crown ethers is chemically easy.

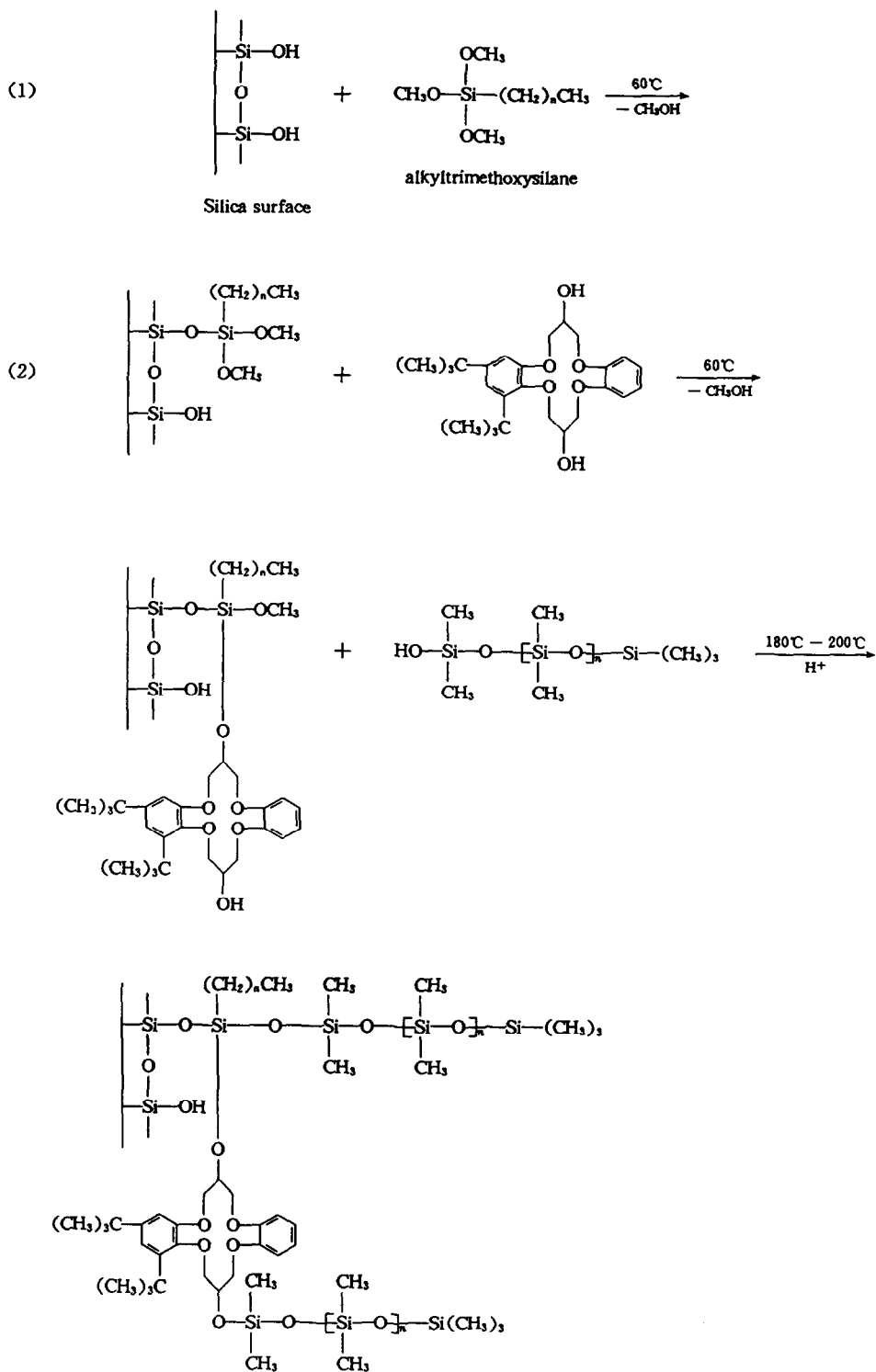


Fig. 3. Possible mechanism of the condensation reaction inside the glass capillary column. From ref. 17.

2.3. Crown ether cross-linking with silicone *in situ* inside a capillary column

In order to overcome the bleeding of low-molecular-mass crown ethers and the poor efficiency of polymeric crown ethers, some workers tried to incorporate crown ethers into polysiloxanes, and useful applications have been developed.

Fine *et al.* [14] pioneered the technique of preparing crown ether polysiloxanes by *in situ* cross-linking directly inside the column. Columns containing vinylmethylsila-17-crown-6 (VMSi17C6) and vinylmethylsila-14-crown-5 (VMSi14C5) were prepared by polymerization of the crown ether inside the capillary. Before this *in situ* polymerization, the capillary was treated with γ -methacryloxypropyltrimethoxysilane (MAPTMS), which can provide methacryloxy groups that copolymerize with the vinylsilacrown ether, and hydrolysis of the methoxy groups provides silanols bonded to the glass surface. Although the separation of alcohols was achieved, the column efficiency was poor and the operating temperatures were only 70–100°C for VMSi17C6 and 58–154°C for VMSi14C4. A possible reason for the lower maximum allowable operating temperatures is incomplete polymerization of the vinyl groups in the sila-crown ether.

Wu *et al.* [15] cross-linked used ω -undecylenoxymethyl-15-crown-5 or -18-crown-6 with an SE-54 matrix by treatment with dicumyl peroxide (DCUP), which formed a crown ether polysiloxane film on the inner surface of a fused-silica capillary. No increase in polarity or activity was observed on cross-linking with DCUP. These two columns are convenient for separating apolar and polar compounds.

Zeng and co-workers [16–18] prepared some crown ether-containing polysiloxane columns by condensing dihydroxy-substituted saturated urushiol crown ethers or dicarboxyl-crown ether with OH-terminal silicone oil (Gy202) in different proportions on a glass capillary surface, using γ -chloropropyltriethoxysiloxane or alkyltrimethoxysilane as coupling agent. The hydroxyl or carboxyl groups in the crown ether are conveni-

ent for condensation reactions. A possible mechanism of the condensation reaction is given in Fig. 3. These columns can provide high thermal stability and good inertness.

The above methods of preparing crown ether-containing polysiloxane columns are straightforward and free from the difficulties involved in the hydrosilylation technique discussed below. In this technique one or two active substituted groups in the crown ether such as terminal vinyl, hydroxyl or carboxyl groups are necessary for cross-linking or condensation.

Lack of reproducibility, a vague mechanism of reaction and an unknown composition of the final polysiloxane are still problems with this method.

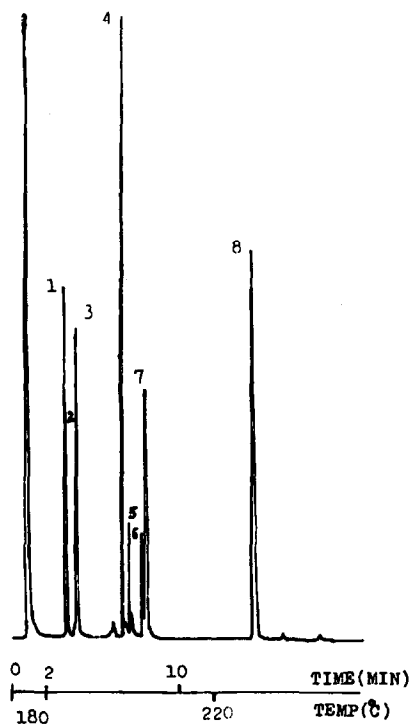


Fig. 4. Chromatogram of a series of secondary and tertiary nitrogen-containing polycyclic aromatic compounds on a crown ether stationary phase with cyanopropyl deactivation, coated on a 20 m \times 200 μ m I.D. fused-silica column with a film thickness of 0.25 μ m. Peaks: 1 = indole; 2 = 3-methylindole; 3 = 2-methylindole; 4 = acridine; 5 = benzo[*h*]-quinoline; 6 = phenanthridine; 7 = benzo[*f*]quinoline; 8 = carbazole. From ref. 19.

2.4. Crown ether-anchored polysiloxanes

In 1988, Rouse *et al.* [19] first synthesized an 18-crown-6-modified poly(hydromethylsiloxane) by hydrosilylation with a propyloxymethyl spacer group, and used it as a capillary GC stationary phase. The crown-silica linkage was Si-CH₂- in this phase, which showed good thermostability and film forming ability. This phase exhibits excellent separations of polynitro-containing aromatic hydrocarbons (Fig. 4) [19,20]. Wu *et al.* [21] developed an 18-crown-6-substituted polysiloxane phase with an undecenylloxymethyl group as a spacer. The longer spacer of the polymeric phase facilitates immobilization on a fused-silica capillary with a coupling agent consisting of aza-*tert.*-butane (ATB) and DCUP [22,23]. The typical reaction scheme of this technique is illustrated in Fig. 5.

Several other types of crown ether compounds have also been used to prepare crown ether-anchored polysiloxane phases by Wu's group [24–26] and Fu's group [27,28], such as 2,3-benzo-9-[(propenyloxy)methyl]-15-crown-5, 2,3-benzo-9-[(propenyloxy)methyl]-18-crown-6 [24], di(*tert.*-butylbenzo)propenyl-15-crown-5, dibenzopropenyl-15-crown-5 [25], allylbenzo-

-15-crown-5 [27], dibenzo-14-crown-4 [28] and N-undecenylaza-15-crown-5 [26]. The use of substituted phenyl groups on the crown ring provides a π -electron and adds polarizability to the phases. All of these stationary phases had a selectivity similar to that of Carbowax 20M, but a much broader working temperature range and a unique selectivity for polar isomers.

As a special example, non-cyclic polyethers (*e.g.*, oligoethylene glycol) sometimes act as if they were crown ether derivative analogues [39,40]. Noncyclic polyethers are easily synthesized and have a high percentage yield compared with crown ethers. The attachment of end-capped polyethers to a well defined polymethylhydrosiloxane polymer has been reported. Rouse *et al.* [19] synthesized a polysiloxane phase containing a 3-[4-(2-methoxyethoxy)ethoxyphenyl]propyl substituent, which was found to be useful in the temperature range of 20–280°C and had a selectivity similar to that of Carbowax 20M. A series of similar phases have also been synthesized and studied by Tarbet *et al.* [29]. Among these materials, phases that have a phenyl unit in the side-chain were found to have higher thermal stability (260–270°C) than those without such a unit. The latter phases showed

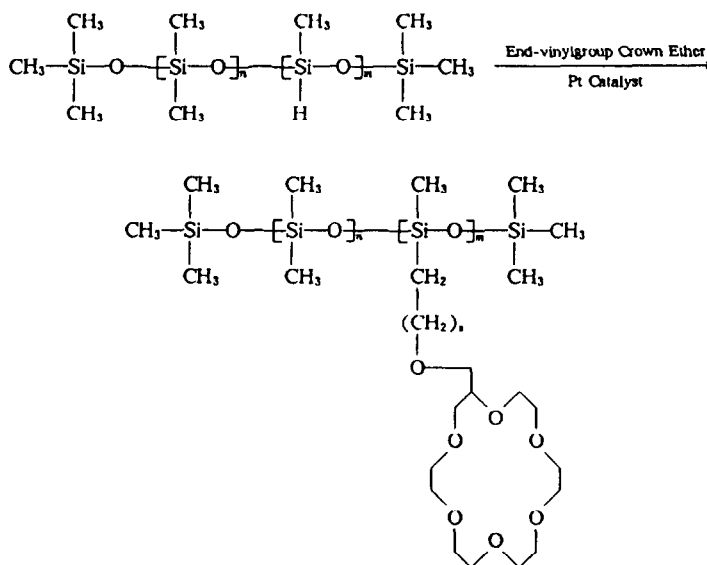


Fig. 5. Typical reaction scheme of hydrosilylation ($s = 2$, ref. 13; $s = 10$, ref. 21).

serious degradation above 240°C. The higher stability of the former phases is possibly due to the phenyl group affording some steric protection to the polysiloxane backbone. Bradshaw *et al.* [30] prepared another series of polysiloxane phases containing polar or polarizable 4-cyanophenyl, 4-nitrophenyl, 2,4-dinitrophenyl or 8-quinolinyl units at the ends of diethylene oxide side-groups. These phases were found to possess both polar and polarizable characteristics, which facilitate the analysis of samples having components covering a broad polarity range, as shown in Fig. 6. Particularly, the 8-quinoline-substituted stationary phase satisfies the need for an efficient basic stationary phase for open-tubular columns. Recently, two α,ω -dialkenyl-substituted oligoethylene glycols were also attached to a polysiloxane backbone in our laboratory [31]. The maximum operating temperature of this phase is up to 300°C. The high thermal stability is due to various factors, but it is possible that it forms a net-like structure.

All of these crown ether polysiloxane phases

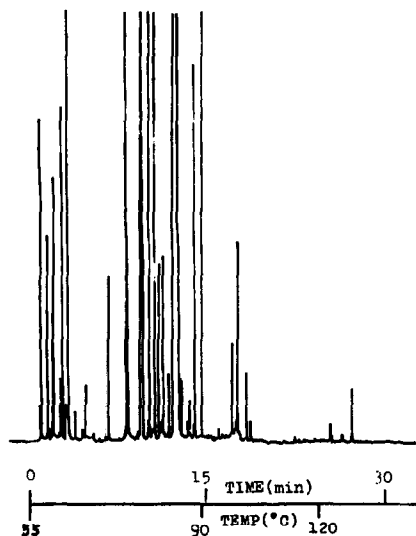


Fig. 6. Capillary gas chromatogram of peppermint essential oil. Column, 15 m \times 20 μ m I.D. fused silica, coated with a 0.15- μ m film of 4-nitrophenyl-substituted poly(eugenol)-methylsiloxane as stationary phase; temperature, programmed from 55°C (2 min) to 150°C at 3°C min. From ref. 30.

were expected to be gums, which is required for efficient coating of capillary columns.

The technique of attaching crown ethers or non-cyclic polyethers to polysiloxanes has been used for the preparation of polysiloxanes with complicated side-chains such as those containing liquid crystalline [32,33] and chiral carboxamide [34] units.

In these methods, a spacer of at least three carbons between the backbone of the polysiloxane and the crown ether ring or oligoethylene glycol is necessary to preserve the helical structure of the silicone backbone and high solute diffusivity. Moreover, for the objective to have a cross-linked phase, a measured amount of 1-octene in the hydrosilylation reaction along with a three-carbon-spacer crown ether or oligoethylene oxide-containing alkene was essential, and it was shown that 2–5% octyl substitution can greatly enhance the cross-linkability of the phase [19,29,30].

It has been reported that phenyl substitution in the stationary phase hinders chemically induced cross-linking [35,36]. We failed to cross-link PSOB-3-15C5 phase (with a propyl-oxyethyl group as spacer) without octyl substitution in the phase using DCUP as a coupling agent. However, the experiments showed that cross-linking was effective with a much longer spacer group, such as undecyloxymethyl.

The method of preparing crown ether polysiloxanes by hydrosilylation provides some advantages. The yields in these hydrosilylation reactions are usually greater than 90%, and the molecular mass of the final polysiloxane phase and the percentage substitution can be fixed by using a starting polymethylhydrosiloxane of the appropriate molecular mass and SiH group content. Moreover, this procedure allows for the preparation of polysiloxane phases of known composition in a reproducible manner, which is helpful for elucidating the mechanism of selectivity.

On the other hand, we found that the beneficial effect of a crown ether substituent is optimum at a level of *ca.* 50% of the substituent for preserving good solute diffusivity. The residual catalyst in the polymer which used in the re-

action may result in some acidity, and the residual catalyst should be carefully removed with methanol and water. Despite these constraints, the hydrosilylation technique is feasible, and much of the recent research into the application of crown ethers as GC stationary phase has been focused on the attachment of crown ethers to a polysiloxane backbone.

3. Characteristics of crown ether stationary phases in GC

The selectivity, polarity and thermostability of crown ether stationary phases have been reported by many workers. Each of these features is treated in detail below.

3.1. Selectivity of crown ether stationary phases

In GC, selectivity results from interactions between the solute and the stationary phase. These interactions are thought to be a complex combination of the following forces: charge transfer, hydrogen bonding, acid–base, dipole–dipole, dipole–induced dipole and dispersion. It is difficult to identify which forces are participating in any given separation as most stationary phase–solute interactions involve several of the forces listed above.

A crown ether stationary phase has a polar ring formed by the oxygen atoms or heteroatoms which are inside the crown. The polarity and electron cloud density of the crown ring vary with the type, number and placement of heteroatoms, the conformational flexibility and the shape(diameter) of the crown cavity and substituent group on the basic skeleton. Therefore, the selectivity of a crown ether stationary phase is assumed to be dominated mainly by hydrogen bonding, dipole–dipole and dispersion forces, and also the inclusion of the crown ring and the substituent functional group on the skeleton of the crown.

Hydrogen bonding plays an important role in the retention behaviour of alcohols and amines. For example, secondary amines that can form

weaker hydrogen bonds with crown ether oxygen atoms than primary amines are eluted more rapidly; triethylamine, incapable of forming hydrogen bonds, is eluted most rapidly with a dibenzo-18-crown-6 or tribenzopyridine-21-crown-7 stationary phase [9]. Although the polarities of all crown ether phases are lower than that of Carbowax 20M, they show a higher selectivity for hydroxyl compounds than Carbowax 20M, especially for low-boiling alcohols, owing to the greater hydrogen bonding forces. A comparison of the resolution of alcohols on PEG and crown ether-substituted polysiloxane columns is shown in Fig. 7.

The heteroatoms or substituent group on the basic skeleton of the crown ether also affect the selectivity for some kinds of compounds. The slightly basic aza-crown ether-substituted polysiloxane phases have the ability to separate anilines and other basic compounds without derivatization (Fig. 8) [26]. Polarizable phenyl or

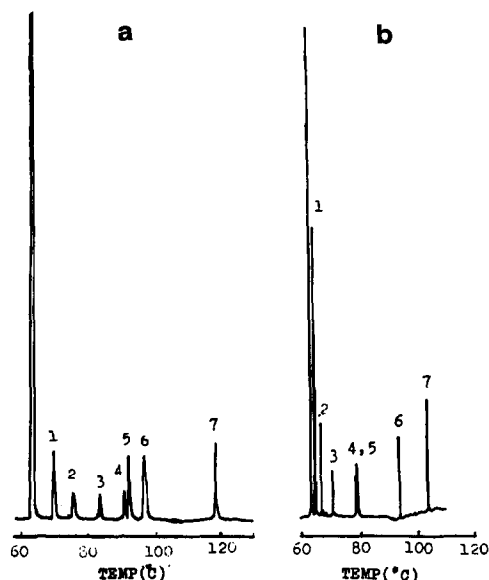


Fig. 7. Comparison of the resolution of *n*-alkanols on (a) a PSOB-3-15C5 column (15 m × 0.25 mm I.D.) and (b) a Carbowax 20M column (30 m × 0.24 mm I.D.). The column temperature was programmed from 60°C (1 min) to 130°C at 4°C min. Peaks: 1 = butanol; 2 = pentanol; 3 = hexanol; 4 = heptanol; 5 = octanol; 6 = nonanol; 7 = decanol. From ref. 24.

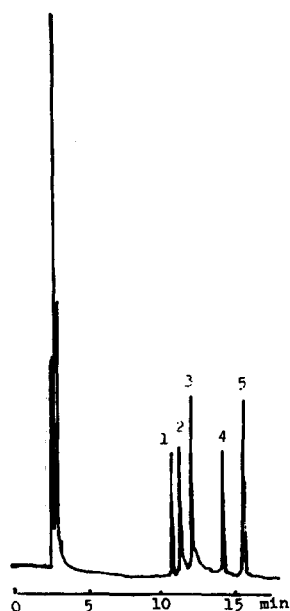


Fig. 8. Chromatogram of aniline compounds on a PUAC-18C6 column (15 m \times 0.25 mm I.D.). Temperature, 120°C (isothermal). Peaks: 1 = *o*-methylaniline; 2 = *p*-methylaniline; 3 = *m*-methylaniline; 4 = N,N-diethyl-N-methylaniline; 5 = N-ethylmethylaniline. From ref. 26.

nitrophenyl substituents on the crown ether have been found to increase the selective separation of isomeric polar polyaromatic compounds and cresols. The resonating π -electrons in the phenyl ring add polarizability to the phases and introduce “soft” dipole–induced dipole interactions between the stationary phase and sample solute, which give excellent resolution of isomeric pairs without excessive retention of these isomers; such results are not usually possible using highly polar stationary phases. An excellent separation of phenolic compounds is shown in Fig. 9.

The cavity structure of the crown ether is another important factor with regard to the selectivity. Initially, the influence of the cavity was described as “the fitting ability with the crown ring” of solute molecules by some workers.

There have been many investigations of the contribution of the crown ether cavity to the retention behaviour of solutes. For example, the *para* isomers of nitrophenol and nitroaniline fit well in the cavities of dibenzo-24-crown-8 and

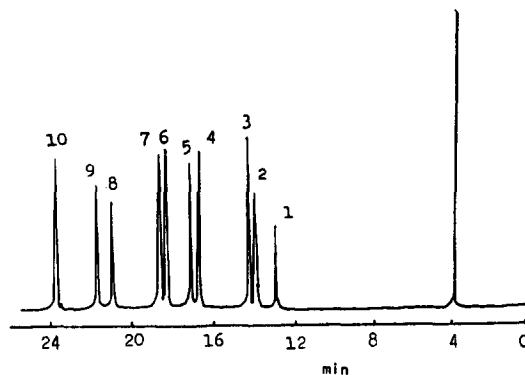


Fig. 9. Separation of a mixture of phenolic compounds on a 30 m \times 0.28 mm I.D. PSOB-DB-14C4 column. Column temperature, programmed from 120 to 180°C at 2°C/min. Peaks: 1 = phenol; 2 = 2,6-dimethylphenol; 3 = *o*-cresol; 4 = *p*-cresol; 5 = *m*-cresol; 6 = 2,4-dimethylphenol; 7 = 2,5-dimethylphenol; 8 = 2,3-dimethylphenol; 9 = 3,5-dimethylphenol; 10 = 3,4-dimethylphenol. From ref. 28.

dicyclohexanol-24-crown-8, respectively, in contrast to the *ortho* and *meta* isomers, as is indicated by their long retention times [8]. In the separation of alcohols using DB-18C6 [8], the retention of methanol exhibits a significant increase because of the inclusion of the whole molecule in the crown cavity, and the retention decreases with increasing length of the *n*-alkanol chain, in agreement with decreasing stability of the complexes between DB-18C6 and *n*-alkanols [9].

According to the study of the thermodynamic properties at infinite dilution of several solutes in 18-crown-6 reported by Arancibia *et al.* [37], the more negative values of ΔH_E^∞ (partial molar enthalpies of solutions) of methanol, chloroform and dichloromethane confirm that a complex is formed in the separation procedure.

Wu *et al.* [38] studied the dissolution entropies, $\Delta(\Delta S)$, of some isomers on five kinds of crown ether stationary phases (CSPS) and PEG-20M and OV-1701 stationary phases. The $\Delta(\Delta S)$ values, which reflect the effect of the configuration of the solute molecules on the stationary phase, are larger on CSPS than that on PEG-20M or OV-1701. This finding confirms the assumption that the cavity of the crown ether has an effect on the retention behaviour of solutes on CSPS. However, it cannot form inclusion

complexes with solutes as do the cyclodextrins, because the shape of many organic solutes is larger than the normal crown ether cavity; the unique selectivity of crown ether polymers for larger solutes is probably due to the fact that they are capable of forming sandwich-type 2:1 (crown ether ring:solute molecule) complexes.

The steric hindrance of solute molecules to the crown ether also adds some selectivity for CSPS. In the separation of nitrotoluene isomers on PSOB-15C-5, although the dipole-induced dipole force of 2,6-DNT is larger than that of 2,5-DNT and 2,4-DNT, it eluted first because of the steric hindrance effect. That is, the *ortho* substituent decreased the fitting ability of the solute molecule to the crown ether cavity (Fig. 10) [24].

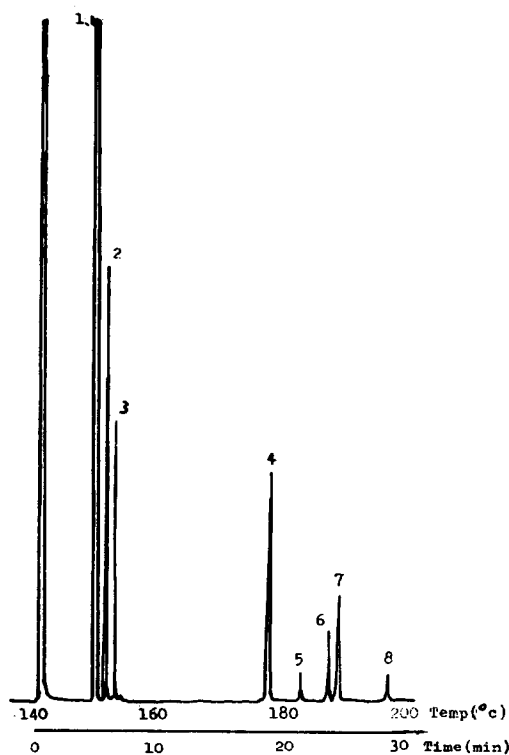


Fig. 10. Separation of mono-(MNT) and dinitrotoluene (DNT) isomers on a 15 m × 0.25 mm I.D. PSOB-3-15C5 column. Column temperature, programmed from 140 to 200°C at 2°C/min. Peaks: 1 = *o*-MNT; 2 = *m*-MNT; 3 = *p*-MNT; 4 = 2,6-DNT; 5 = 2,5-DNT; 6 = 2,4-DNT; 7 = 3,5-DNT; 8 = 3,4-DNT. From ref. 24.

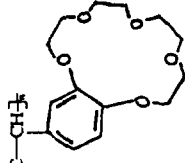
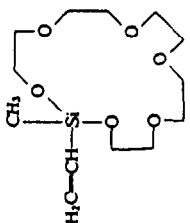
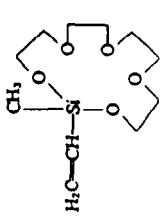
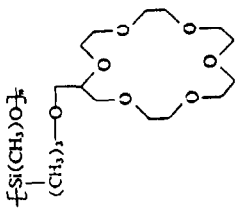
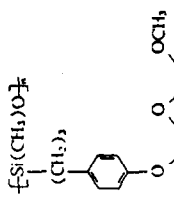
3.2. Average polarity and thermostability of crown ether stationary phases

The polarity of low-molecular-mass crown ethers is mainly dominated by the crown ether structure. When the crown ether has a hydrophobic substituent such as a long apolar alkyl or cyclohexylene group, its polarity is low, whereas a polar or polarizable substituent such as phenyl or nitrophenyl may increase the polarity. All of the crown ether polysiloxane phases are of medium polarity, which is between 200 and 400 as represented by McReynolds constants. However, the polarity of crown ether-substituted polysiloxanes prepared by immobilization *in situ* inside the column is lower than that of the phases prepared by hydrosilylation, probably owing to the degree of polymerization of the crown ether in the former method being lower than that in the latter. Table 1 summarizes the chromatographic characteristics of some crown ether stationary phases.

The maximum allowable operating temperature (MAOT) of low-molecular-mass crown ether columns is relatively high, if the molecular masses are taken into account, because the crown ether compounds have intrinsically good chemical stability. The minimum allowable operating temperatures for these columns are dominated by the melting points of the crown ethers, because the column efficiency is low below the melting point owing to the increase in the mass-transfer resistance.

The MAOT of a polymeric crown ether which has a polyethylene backbone is higher than that of low-molecular-mass crown ether columns, but it is much lower than that of crown ether polysiloxanes. Crown ether polysiloxanes have been found to be stable up to 300°C, which is higher than for bondable PEG-20M (260°C). A phenyl ring included in a medium-polarity oligoethylene oxide or a crown ether can particularly increase the thermostability of a polysiloxane stationary phase. The minimum allowable temperature of a crown ether polysiloxane is determined by the glass transition temperature. However, because the changes in the thermodynamic and kinetic properties of many

Table 1
Characteristics of crown ether polymers used as GC stationary phases

Stationary phase ^a	Structure	Average polarity	Phase transition temperature (°C)	Min./max. operating temperature (°C)	Ref.
PVB-15C5		526	73, 155	55/220	14
VMS17C6 ^b		448	70	70/100	14
VMS14C5 ^b		327	155	58/154	14
		144		120/300	19
				20/280	19

(Continued on p. 214)

Table 1 (continued)

Stationary phase ^a	Structure	Average polarity	Phase transition temperature (°C)	Min./max. operating temperature (°C)	Ref.
PSO-11-18C6 (a) PSO-11-15C5 (b)		229 206	136 150	70/300 70/300	21 22
PSOB-3-15C5 (a) PSOB-3-18C6 (b)		231 239	119 121	70/300 70/300	26
PSO-DTB-3-15C5		211	100	<310	25
PSO-DB-3-15C5		352	104	<310	25

$\begin{array}{c} \text{---Si(CH}_3\text{)}_2\text{O---} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{---[CH}_2\text{OCH}_2\text{]}_n\text{---} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{CH}_2 \end{array}$	<p>(a) $n = 3$; (b) $n = 5$</p>	<p>296 309</p>	<p>150 970</p>	<p><300 <300</p>	<p>31</p>
$\begin{array}{c} \text{---Si(CH}_3\text{)}_2\text{O---} \\ \\ \text{(CH}_2\text{)}_m\text{---N---} \\ \\ \text{---[O(CH}_2\text{)}_m\text{]}_n\text{---} \end{array}$	<p>(a) $m = 4$ (b) $m = 3$</p>	<p>394 265</p>	<p>137 140</p>	<p>75/305 75/305</p>	<p>24</p>
$\begin{array}{c} \text{---Si(CH}_3\text{)}_2\text{O---} \\ \\ \text{(CH}_2\text{)}_3\text{---} \\ \\ \text{---[C}_6\text{H}_4\text{---(C}_6\text{H}_4\text{)}_2\text{---}]_n\text{---} \end{array}$		<p>318</p>	<p>124</p>	<p>300</p>	<p>27</p>
$\begin{array}{c} \text{---Si(CH}_3\text{)}_2\text{O---} \\ \\ \text{(CH}_2\text{)}_3\text{---} \\ \\ \text{---[C}_6\text{H}_4\text{---(C}_6\text{H}_4\text{)}_2\text{---}]_n\text{---} \end{array}$		<p>286</p>	<p>58, 156</p>	<p>280</p>	<p>28</p>

(Continued on p. 216)

Table 1 (continued)

Stationary phase ^a	Structure	Average polarity	Phase transition temperature (°C)	Min./max. operating temperature (°C)	Ref.
	$\begin{array}{c} \text{---}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{---} \\ \\ \text{R} \\ \\ \text{C}_6\text{H}_{11} \end{array}$				29
	$\text{R} = (\text{CH}_2)_3\text{---} \langle \text{C}_6\text{H}_4 \rangle \text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{CH}_3$			260–270	
	$\text{R} = (\text{CH}_2)_3\text{---} \langle \text{C}_6\text{H}_3(\text{OCH}_3) \rangle \text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{CH}_3$				
	$\text{R} = (\text{CH}_2)_3\text{---} \langle \text{C}_6\text{H}_3(\text{OCH}_3) \rangle \text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{CH}_3$				
	$\text{R} = (\text{CH}_2)_3\text{---} \langle \text{C}_6\text{H}_3(\text{OCH}_3)_2 \rangle \text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{CH}_3$				
	$\text{R} = (\text{CH}_2)_3\text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{CH}_2\text{CH}_3$			240	29
	$\text{R} = (\text{CH}_2)_3\text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{OCH}_3$			240	
	$\text{R} = (\text{CH}_2)_3\text{---} \text{O} \text{---} (\text{CH}_2)_2 \text{---} \text{O} \text{---} \text{OCH}_3$			240	

^a PVB-15C5 = poly(vinylbenzo-15-crown-5); VMSi17C6 = vinylmethylsila-17-crown 6; VMSi14C5 = vinylmethylsila-14-crown-4; PSO-11-18C6 = *n*-undecyloxymethyl-18-crown-6 polysiloxane; PSO-11-15C5 = *n*-undecyloxymethyl-15-crown-5 polysiloxane; PUAC-11-18C6 = ω -undecyleneaza-18-crown-6 polysiloxane; PUAC-11-15C5 = ω -undecyleneaza-15-crown-5 polysiloxane; PSOB-3-18C6 = 2,3-benzo-11-[(propenyloxy)methyl]-18-crown-6 polysiloxane; PSOB-3-15C5 = 2,3-benzo-9-[(propenyloxy)methyl]-15-crown-5 polysiloxane; PSO-DTB-3-15C5 = Di(*tert*-butylbenzo)propyl-15-crown-5 polysiloxane; PSO-DB-15C5 = dibenzopropyl-15-crown-5 polysiloxane; PSO-DB-14C4 = dibenzopropyl-14-crown-4 polysiloxane; PAB-15C5 = 3-allylbenzo-15-crown-5 polysiloxane; PPATEG = α -propyl- ω -allyltrimethylene glycol polysiloxane; PPADEG = α -propyl- ω -allyldiethylene glycol polysiloxane.

^b Cross-linked with silicone *in situ* inside column.

crown ether polysiloxanes are very close for the two states at the glass transition temperature, the minimum allowable temperature will be much lower below the transition temperature. Hence the crown ether polysiloxane phases have a wide operating temperature range.

4. Conclusions

Crown ether (or non-cyclic polyether) polysiloxane stationary phases exhibit medium polarity and a selectivity similar to that of Carbowax 20M, but a much wider working temperature range. They also provide unique selectivity for polar compounds such as alcohols, aromatic amines and polar isomers. Especially samples having components covering a broad polarity range can be analysed using these phases. Moreover, the benzo-crown ether polysiloxanes show intrinsic thermostability and excellent resolution for polar isomers, and aza-crown ether polysiloxane phases can satisfy the need for an efficient basic stationary phase for open-tubular columns.

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6. References

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