

Crown ethers as stationary phases in gas chromatography

Comparison between dibenzo-18-crown-6, dibenzo-24-crown-8 and dicyclohexano-24-crown-8 with respect to polarity, selectivity and stability^a

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ABSTRACT

Chromatographic characteristics, including thermal stability, polarity and selectivity, of dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8) and dicyclohexano-24-crown-8 (DCH24C8) were compared. Phase transition studies were carried out by plotting graphs of log(specific retention volume) against the inverse of absolute temperature. Nitrochlorobenzene, nitrophenol, nitroaniline, chloroaniline, cresol, chlorophenol and dimethylphenol isomers were injected onto these crown ether stationary phases at 3%, 10% and 20% loadings. Dimethylphenol and nitrochlorobenzene isomers were separated well on 10% DB24C8 and 10% DCH24C8 columns. DB18C6 is useful for the direct analysis of nitrophenol and nitroaniline isomers without any derivatization.

INTRODUCTION

Crown ether compounds have widely been used in analytical chemistry [1–3]. The use of crown ethers in chromatography was first reported by Blasius *et al.* [4] and Sousa *et al.* [5]. The effect of the hydrophobicity and cavity size of the crown ether in crown ether-containing mobile phases on the retention of amino compounds in reversed-phase high-performance liquid chromatography (RP-HPLC) has been studied [6]. RP-HPLC of substituted anilines utilizing the molecular recognition ability of crown ethers has been compared with ion-pair chromatography [7].

The use of crown ethers in gas chromatography (GC) has been rare. Vigalok and Bubachinkova [8] first reported the chromatographic characteristics of 18-crown-6. Ono [9] separated dichlorophenol isomers on 20% dibenzo-18-crown-6 coated on acid-washed firebrick C₂₂ (2.25 m × 3 mm I.D. stainless-steel column). Li [10,11] tried to separate hydrocarbons, alcohols and amines on various crown ether stationary phases. Fine *et al.* [12] reported preparation and GC characterization of

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some silacrown ether stationary phases. Lee *et al.* [13] compared oligo(ethylene oxide)-substituted polysiloxanes with polyethylene glycol as stationary phase for capillary GC and found that crown ether-polysiloxanes have unique selectivity because of the size and shape of the crown ether cavity. Separations of aromatic hydrocarbons, chlorine-containing compounds, etc. on Carbochrome modified with dibenzo-18-crown-6 have been reported [14]. The chromatographic characteristics of some dipentadecylcrown ethers and *n*-undecyloxymethyl-18-crown-6-polysiloxane have been studied recently [15,16]. The inclusion properties of some crown ethers have been studied by GC [17].

In this study, the chromatographic characteristics of dibenzo-18-crown-6 (DC18C6), dibenzo-24-crown-8 (DB24C8) and dicyclohexano-24-crown-8 (DCH24C8) were compared.

EXPERIMENTAL

A Hewlett-Packard Model 5880A gas chromatograph equipped with a level 4 integrator and computing system and a flame ionization detector was used. Aldrich-grade crown ethers were used for making the stationary phases. The crown ethers (DB18C6, DB24C8 and DCH24C8) were coated on Chromosorb W AW DMCS (80–100 mesh) at concentrations of 3%, 10% and 20%. The coated supports were packed in stainless-steel columns (1.8 m × 3 mm O.D.). The maximum operating temperatures for the stationary phases were first established using thermogravimetry and differential scanning calorimetry (DSC) and the phases were then tested chromatographically by the method of Pulsipher *et al.* [18]. Nitrogen was used as the carrier gas at a flow-rate of 30 ml min⁻¹. The polarities of DB24C8 and DCH24C8 were measured at 120°C and that of DB18C6 at 180°C.

The column void volume was determined by the iterative method of Guardino *et al.* [19]. The efficiency of the crown ether columns was determined at 170°C and compared with that of Carbowax 20M. The selectivities of the crown ethers were characterized by injecting positional isomers of cresol, nitrochlorobenzene, chloroaniline, chlorophenol, dimethylphenol, nitrophenol and nitroaniline.

RESULTS AND DISCUSSION

Phase transition and thermal stability studies

The specific retention volume (V_g) for the test compound *p*-toluidine was calculated at 10°C intervals and a graph of $\log V_g$ versus $10^4/T$ was plotted for *p*-toluidine on DB18C6 and DCH24C8 columns (Fig. 1). There is no phase transition in DCH24C8, as indicated by the straight line. The temperature range from T_1 (140°C) to T_2 (153°C) is the transition range for DB18C6 as determined by GC. At temperatures below T_1 , solute retention will depend essentially on adsorption processes, but as the temperature is raised above T_1 , the stationary phase starts to melt and it attains the liquid state at T_2 . At the latter temperature the retention of solutes is due to partition. This temperature matches the phase transition temperature obtained by DTA. Fig. 2 shows the plot of $\log V_g$ versus $10^4/T$ for acetonitrile on DB24C8. The phase transition temperature obtained from the graph (104°C) is in good agreement with that obtained by DSC (107.5°C). DB24C8 becomes a true liquid at 104°C.

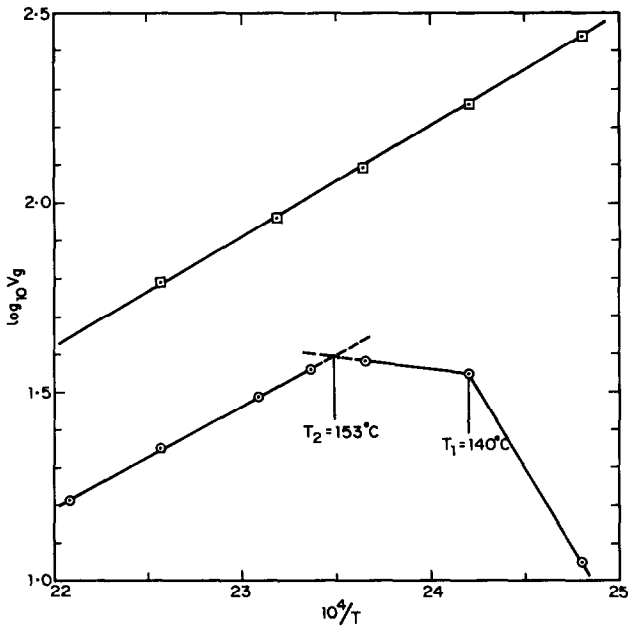


Fig. 1. Plots of \log (specific retention volume) against inverse of absolute temperature for *p*-toluidine on (○) 10% DB18C6 and (□) 10% DCH24C8 columns.

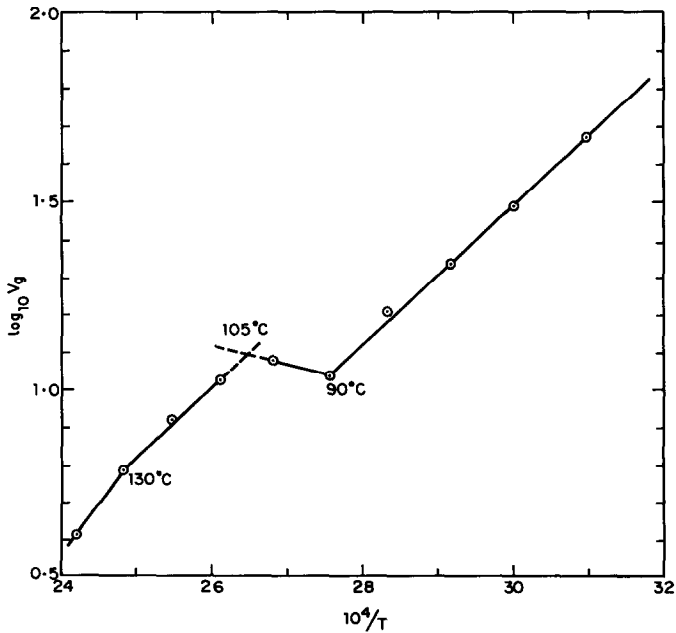


Fig. 2. Plot of \log (specific retention volume) against inverse of absolute temperature for acetonitrile on 10% DB24C8 column.

TABLE I

COMPARISON OF PHASE TRANSITION TEMPERATURES AND MINIMUM AND MAXIMUM OPERATING TEMPERATURES

Stationary phase	Temperature at which decomposition starts ^a (°C)	Maximum allowable temperature (°C)	Phase transition temperature (°C)	
			By DTA ^b	By DSC ^c
DB18C6	210	190	151	161.25
DB24C8	185	175	60	85
DCH24C8	199.5	180	80	107.5
			—	—

^a This temperature is determined by thermogravimetry.^b Differential thermal analysis.^c Differential scanning calorimetry.

The DB18C6 and DCH24C8 columns were first conditioned at 190°C for 4 h. The specific retention volume (V_g) for octadecane was then determined at 160°C. Subsequently stepwise conditioning was applied at 10°C intervals to establish whether there was any change in V_g . With 10% DB18C6 there was no change in the value of V_g whereas there was a 2.3% decrease in V_g for octadecane on 10% DB24C8 after conditioning at 190°C for 2 h. The 10% DB24C8 column was first conditioned up to 175°C and the specific retention volume for octadecane was then determined at 140°C. There was no change in V_g after stepwise conditioning of the column at 150, 160, 170 and 175°C.

Table I gives a comparison of the phase transition temperatures and maximum and minimum operating temperatures for the different crown ethers. A comparison of efficiencies in terms of total number of plates (N) and height equivalent to a theoretical plates (H) between various crown ethers and Carbowax 20M is shown in Table II.

Polarity and selectivity studies

McReynolds' constants (ΔI), retention indices (I), capacity factors (k') and average polarities of the various crown ethers together with the ΔI values for Carbowax 20M and tricresyl phosphate are given in Table III. The temperature for mea-

TABLE II

COMPARISON OF EFFICIENCY IN TERMS OF TOTAL NUMBER OF PLATES (N) AND HEIGHT EQUIVALENT OF THEORETICAL PLATES (H) BETWEEN VARIOUS CROWN ETHERS AND CARBOWAX 20M AT 170°C

Stationary phase	Octadecane		<i>o</i> -Nitrochlorobenzene		3,4-Dimethylphenol	
	N	$H(\text{cm})$	N	$H(\text{cm})$	N	$H(\text{cm})$
10% DB18C6	331	0.54	465	0.38	243	0.74
10% DB24C8	798	0.23	1611	0.11	1247	0.14
10% DCH24C8	836	0.22	1697	0.106	1979	0.09
Carbowax 20M	611	0.29	1527	0.118	2283	0.08

TABLE III

CAPACITY FACTORS (k'), RETENTION INDICES (I), McREYNOLDS' CONSTANTS (ΔI) AND AVERAGE POLARITY FOR THE McREYNOLDS' PROBES ON VARIOUS CROWN ETHERS ALONG WITH THE ΔI VALUES FOR CARBOWAX 20M AND TRICRESYL PHOSPHATE

Stationary phase	Parameter	McReynolds' probes					Average polarity
		Benzene	<i>n</i> -Butanol	2-Pentanone	Nitropropane	Pyridine	
DCH24C8	ΔI	153	333	194	331	291	260
	I	806	923	821	983	990	
	k'	1.31	2.47	1.43	3.40	3.55	
Tricresyl phosphate	ΔI	176	321	250	374	299	284
DB24C8	ΔI	286	454	366	544	607	452
	I	939	1044	993	1196	1206	
	k'	0.81	1.44	1.09	3.29	3.49	
Carbowax 20M	ΔI	322	536	368	572	510	462
DB18C6 ^a	ΔI	231	526	472	475	521	442
	I	1314	1558	1525	1580	1507	
	k'	0.56	2.57	2.09	2.95	1.87	

^aMcReynolds' constants for DB18C6 were determined at 180°C using high-temperature probes suggested by Vernon and Ogundipe [18], *i.e.*, *n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene and aniline.

surement of these values was 120°C for DCH24C8 and 180°C for DB18C6 (DB18C6 is a solid at 120°C). Test probes used at high temperature (*i.e.* 180°C) were *n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene and aniline, as suggested by Vernon and Ogundipe [20]. Comparison of the ΔI values shows that average polarity of DCH24C8 is similar to that of tricresyl phosphate and the latter retains ketones and nitro compounds more strongly. DB24C8 has an average polarity similar to that of Carbowax 20M and it retains proton-accepting compounds much more strongly whereas Carbowax 20M retains alcohols more strongly.

Since Ono [9] had reported the separation of dichlorophenol isomers on 20% DB18C6, we compared the selectivities of the crown ethers studied here with respect to dichlorophenols and similar compounds such as dimethylphenols, cresols, nitrophenols, nitrochlorobenzenes and chloranilines. DB24C8 has the largest ΔI value for nitro compounds and accordingly it gives the best separation of nitrochlorobenzene isomers, as is seen in Fig. 3. The analysis time is also much shorter (*ca.* 7 min) than that for the same separation on Carbochrome modified with DB18C6 (12 min) [14].

Previously we reported the determination of nitrochlorobenzene isomers on a 5% isopropylidenebisphenol diacetate column [21]. The separation of dimethylphenol isomers on the crown ether stationary phases is shown in Fig. 4. It was not possible to separate 2,4- and 2,5-dimethylphenol on any of the crown ethers and 2,3- and 3,5-dimethylphenol were only partially resolved. When the loading was increased to 20% the peaks became broad and the separation did not improve much. Separations of *o*-, *m*- and *p*-cresols and -chloroanilines were also tried, but without any success. When dichlorophenol isomers were injected onto the 10% DB18C6 column,

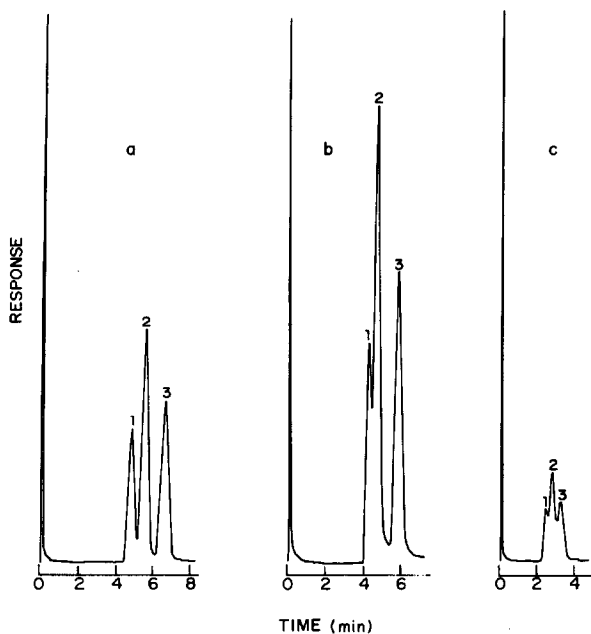


Fig. 3. Separation of nitrochlorobenzene isomers on various crown ethers at 170°C. Nitrogen flow-rate, 30 ml min⁻¹. Peaks: 1 = *m*-nitrochlorobenzene; 2 = *p*-nitrochlorobenzene; 3 = *o*-nitrochlorobenzene. (a) 10% DB24C8; (b) 10% DCH24C8; (c) 10% DB18C6.

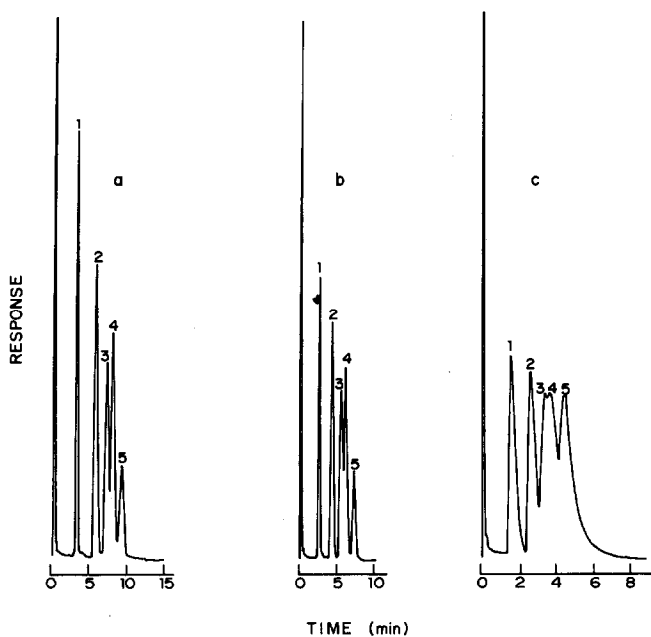


Fig. 4. Separation of dimethylphenols (DMP) on various crown ethers. Nitrogen flow-rate, 30 ml min⁻¹. Peaks: 1 = 2,6-DMP; 2 = 2,4 + 2,5-DMP; 3 = 2,3-DMP; 4 = 3,5-DMP; 5 = 3,4-DMP. (a) 10% DHC24C8 at 170°C; (b) 10% DB24C8 at 170°C; (c) 10% DB18C6 at 160°C.

post-tailing was observed. The retention times of these isomers depend on the amount injected. The DCH24C8 and DB24C8 columns gave symmetrical peaks but without any separation.

Nitrophenol and nitroaniline isomers were injected onto the 3% crown ether columns without any derivatization. *Ortho* isomers eluted immediately after the solvent peak whereas *meta* and *para* isomers were retained for a long time. The retention times of *p*-nitrophenol and *p*-nitroanilines are too long on DB24C8 and DCH24C8 at 170°C and 180°C, respectively, indicating that these molecules must fit well in the cavities of the crown ethers. The separation and analysis time for nitrophenols and nitroanilines on the 3% DB18C6 column is considerable and one can use a DB18C6 column for the direct analysis of nitrophenols (the coating can be even less, e.g., 1%). It is not necessary to derivatize the samples. The analysis of phenols is important owing to its practical applications in biochemical, clinical, forensic and wood chemistry and in food inspection and environmental pollution control. Table IV gives the retention indices of various positional isomers on the different crown ethers.

TABLE IV

RETENTION INDICES OF SOME POSITIONAL ISOMERS ON 10% CROWN ETHERS AT 170°C

Carrier gas, nitrogen at a flow-rate of 30 ml min⁻¹; injection temperature, 220°C; detector temperature, 250°C.

Solute	Stationary phase		
	DB18C6	DB24C8	DCH24C8
2,6-Dimethylphenol ^a	1741	1749	1593
2,5-Dimethylphenol	1858	1871	1724
2,4-Dimethylphenol	1858	1870	1721
2,3-Dimethylphenol	1919	1928	1767
3,5-Dimethylphenol	1935	1952	1789
3,4-Dimethylphenol	1976	1992	1820
<i>o</i> -Cresol	1785	1796	1593
<i>m</i> -Cresol	1858	1870	1655
<i>p</i> -Cresol	1849	1863	1651
<i>o</i> -Nitrochlorobenzene	1983	1968	1728
<i>m</i> -Nitrochlorobenzene	1918	1892	1661
<i>p</i> -Nitrochlorobenzene	1949	1927	1682
<i>o</i> -Chloroaniline	1835	1828	1640
<i>m</i> -Chloroaniline	2010	2011	1801
<i>p</i> -Chloroaniline	2005	2011	1796
<i>o</i> -Nitrophenol ^b	1839	1754	1761
<i>m</i> -Nitrophenol	2130	2647	2671
<i>p</i> -Nitrophenol	2183	2798	2804
<i>o</i> -Nitroaniline	2057	2335	2312
<i>m</i> -Nitroaniline	2124	2533	2504
<i>p</i> -Nitroaniline	2230	2816	2774

^a Dimethylphenols were injected at 160°C on DB18C6.

^b Nitrophenols were injected at 180°C on 3% DB18C6 and 3% DCH24C8 and at 170°C on 3% DB24C8.

CONCLUSIONS

The average polarities of DB24C8 and DCH24C8 are similar to those of Carbowax 20M and tricresyl phosphate, respectively. DB24C8 retains proton-accepting compounds much more strongly than Carbowax 20M. The efficiencies of DB24C8 and DCH24C8 are comparable to that of Carbowax 20M. Nitrochlorobenzene and dimethylphenol isomers are separated very well on DB24C8 and DCH24C8. DB18C6 can find applications in the direct analysis of nitrophenols and nitroanilines. The *para* isomers of nitrophenol and nitroaniline fit very well in the cavities of DB24C8 and DCH24C8, as is indicated by their long retention times on these crown ethers.

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