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USE OF CROWN ETHERS IN GAS CHROMATOGRAPHY

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SUMMARY

Two new kinds of crown ethers, 4,4-dipentadecyl- or 4,3'-dipentadecyldibenzo-30-crown-10 and 3-pentadecylbenzo-15-crown-5, were coated on glass capillary columns and fused-silica capillary columns, and their chromatographic characteristics studied. The polarity, selectivity and stability of the crown ethers were characterized. The rôle of the crown ether ring in separating solutes is also mentioned.

INTRODUCTION

Crown ethers or macrocyclic polyethers, which were first introduced by Pedersen[1], have the ability to form stable complexes with metal cations. They are interesting organic compounds and have found wide applications in chemistry, especially in analytical chemistry. They can be used as solvent extraction reagents for the separation and isolation of metal ions, as components in membranes for ion-selective electrodes and as a component of the stationary and mobile phases in liquid chromatography. A very important review on the applications of crown ethers in analytical chemistry has been written by Kolthoff[2].

Blasius *et al.*[3] and Cram and co-workers[4] first reported the use of crown ethers in chromatograpy. Since then this usage has developed greatly, especially in liquid chromatography. Chromatographers have just began to pay attention to them in gas chromatography (GC) and there have been a few articles[5–9] concerning the application of crown ethers in GC. Li[5,6] used packed columns coated with dibenzo-24-crown-8, dibenzo-18-crown-6 and other crown ethers to separate hydrocar bons, alcohols, amines and other compounds. Graphitized thermal carbon blacks modified with crown ethers can also be used to separate hydrocarbons, aromatic compounds and halides, etc.[7]. Fine *et al.*[8] coated crown ethers including polymers with crown ether groups on glass capillary columns and characterized their chromatographi c properties. 18-Crown-6-substituted polysiloxane was synthesized and used as a stationary phase by Lee and co-workers[9].

Two new kinds of crown ethers indicated in Fig. 1 have similar structure and

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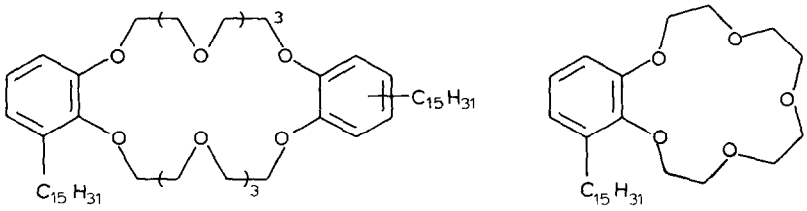

DSU30C10
m.p. 51°C–52°C

SU15C5
m.p. 49°C–50°C

Fig. 1. Structures of crown ethers used in this study.

each has three different functional groups: long apolar alkyl, easily polarizable benzene ring and polar polyether ring. Thereby they were expected to have strong abilities in separating different classes of organic compounds. They were both coated on glass and fused-silica capillary columns and their chromatographic characteristics were studied.

EXPERIMENTAL

A Model SP-2305 gas chromatograph (Beijing Analytical Instrument Factory, China) equipped with a capillary split injection system, flame ionization detector and integrator was used. Glass tubing with 7 mm O.D. and 3 mm I.D. (Beijing Glass Experimental Factory, China) was drawn into capillary columns (0.29 mm I.D.) by using a Model GDM-1B glass drawing machine (Shimadzu, Japan). Prior to drawing, the tubes were rinsed with chromic acid, water, methanol and acetone and then dried. Glass capillaries were filled to 80–90% of their lengths with 20% hydrochloric acid, sealed at both ends and then heated at 170°C overnight. The ends were opened and the columns were rinsed with diluted hydrochloric acid (pH 3), methanol and acetone, and then dried at 200°C under a stream of nitrogen. The columns were coated dynamically with hexamethyldisilazane. Then the ends were sealed and the columns were heated at 400°C for 4 h. The ends were opened and the columns were rinsed with dichloromethane, methanol and acetone. The columns were dried at 150°C for 2 h. Fused-silica columns (0.22 mm I.D.; Yongnian Optical Fibre Factory, China) were purged with nitrogen at 170°C for 6 h before coating. Glass and fused-silica capillary columns were then statically coated at room temperature with stationary phase solutions in pentane. Each column was conditioned at 100, 150 and 190°C for 1 h, respectively.

The crown ethers were obtained from the Department of Environmental Science, Wuhan University, China. All other chemicals used for characterization were analytical reagent grade.

RESULTS AND DISCUSSION

Table I shows the characteristics of the crown ether capillary columns. It indicates that fused- silica columns have higher column efficiencies than glass capillary columns though the former were not deactivated.

The selectivity and polarity of the crown ethers are expressed by McReynolds

TABLE I
CHARACTERISTICS OF CROWN ETHER CAPILLARY COLUMNS USED IN THIS WORK
Test compound: 1-octanol.

Column No.	*Column size (L × I.D.)*	*Type of capillary*	*Stationary phase*	*Column efficiency (n/m)*
1	17 m × 0.29 mm	Glass	DSU30C10	1860
2	10 m × 0.22 mm	Silica	DSU30C10	2750
3	20 m × 0.22 mm	Silica	DSU30C10	2680
4	16 m × 0.29 mm	Glass	SU15C5	1580
5	10 m × 0.22 mm	Silica	SU15C5	2550
6	20 m × 0.22 mm	Silica	SU15C5	2770

constants, 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 and $r = t'_R\ (n+1)/t'_R(n)$. These parameters and the average polarity shown in Table I were obtained at 120°C.

The average polarity for the crown ethers is much lower than that of PEG-20M, owing to their long apolar alkyl groups and benzene. However, the b value for the crown ethers is higher than that of SE-30, indicating that the crown ethers are very convenient for separating apolar compounds. As Fig. 2 shows, the slope of the plot of log t'_R *vs.* carbon number of homologous alcohols on DSU30C10 is higher than on PEG-20M, implying that DSU30C10 has higher selectivity for alcohol than PEG-20M does. 18-C-6 substituted polysiloxase has an higher selectivity for nitrogencontaining polycyclic aromatic compounds than has a polar stationary phase[9], but there is no appreciable difference in the interaction of biphenyl with the crown and Carbowax 20M becaus biphenyl is too large to fit in the cavity of the crown ether ring. The selectivity of crown ethers depends mainly on the relative size of the solute and the crown ether cavity, the type, number and placement of hetero atoms and the conformational flexibility of the crown ether ring.

Crown ethers have special selectivity, especially for aromatic compounds and their derivatives, amines, anilines, etc.[7]. The two crown ethers are versatile gas chromatographic stationary liquids. They give excellent separations of organic

TABLE II
SELECTIVITY AND POLARITY OF THE CROWN ETHERS USED
X′ = Benzene, Y′ = butanol, Z′ = 2-pentanone, U′ = nitropropane, S′ = pyridine.

Stationary phase	*McReynolds constants (I)*					*Mean*	*b*	*r*
	X′	*Y′*	*Z′*	*U′*	*S′*			
DSU30C10	82	116	128	213	166	141.0	0.272	1.903
SU15C5	121	218	165	242	195	188.2	0.273	1.877
SE-30[10]	15	44	53	64	41	432.4	0.2495	1.766
PEG-20M[10]	322	536	368	572	510	461.2	0.2235	1.673

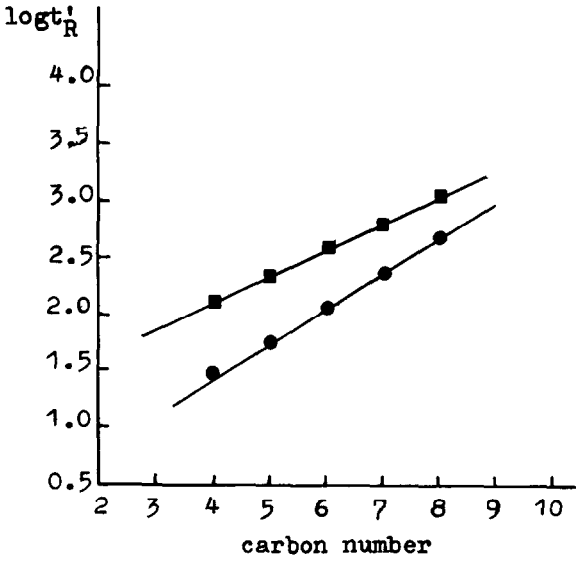

Fig. 2. Plot of log (adjusted retention time) against carbon number for homologous alcohols. (■) PEG-20M; (●) DSU30C10. Column temperature: 104°C.

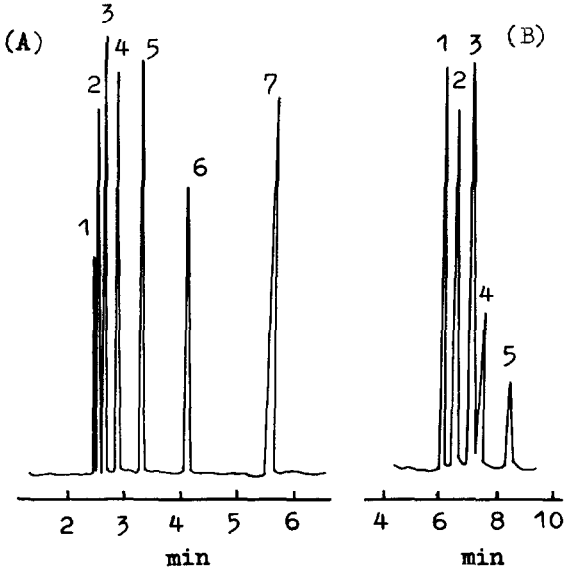

Fig. 3. Chromatogram of organic compounds with hydroxyl groups. (A) On column 1, carrier gas (nitrogen) flow-rate 13 cm/s, splitting ratio 1/100, at 132°C. Peaks : 1 = C_2H_5OH; 2 = n-C_3H_7OH; 3 = n-C_4H_9OH; 4 = n-$C_5H_{11}OH$; 5 = n-$C_6H_{13}OH$; 6 = n-$C_7H_{15}OH$; 7 = n-$C_8H_{17}OH$. (B) On column 6, carrier gas (nitrogen) flow-rate 15 cm/s, splitting ratio 1/100, at 194°C. Peaks: 1 = 2,6-; 2 = 2,4- and 2,5-; 3 = 3,5-; 4 = 3,4-; 5 = 2,3-dihydroxytoluene.

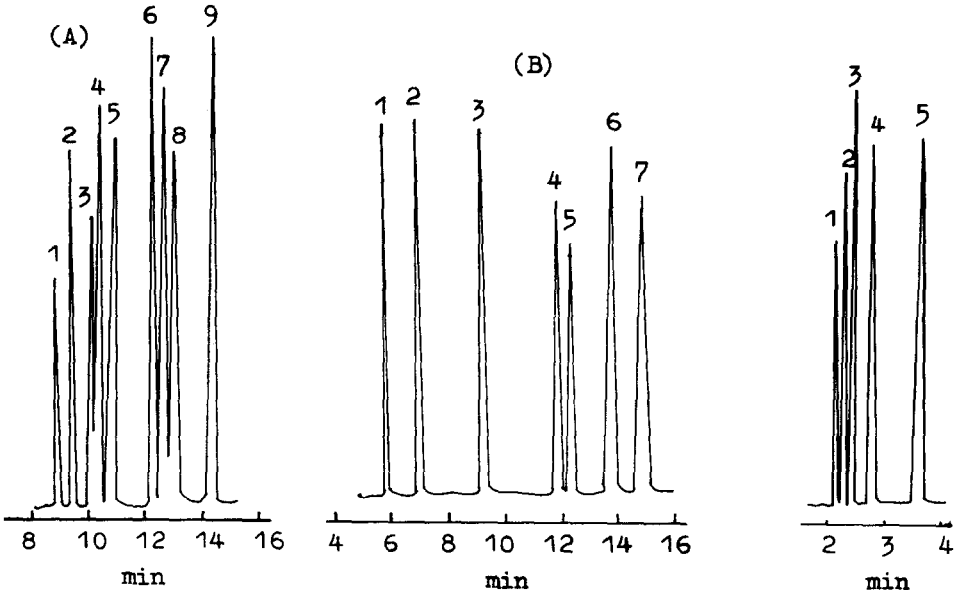

Fig. 4. Chromatogram of aromatic hydrocarbons (A) and their derivatives (B). (A) On column 5, carrier gas (nitrogen) fow-rate 13 cm/s, at 133°C. (B) On column 3, carrier gas (nitrogen) flow-rate 13 cm/s, at 128°C. Peaks: 1 = toluene; 2 = chlorobenzene: 3 = bromobenzene; 4 = *m*-dichlorobenzene; 5 = *p*-dichlorobenzene; 6 = *o*-dichlorobenzene; 7 = iodobenzene.

Fig. 5. Chromatogram of halohydrocarbons on column 4 at 132°C, carrier gas (nitrogen) flow-rate 13 cm/s, splitting ratio 1/100. Peaks: 1 = ethyl bromide; 2 = *n*-butyl chloride; 3 = *n*-butyl bromide; 4 = 1,3-dichloropropane; 5 = 1,4-dichlorobutane.

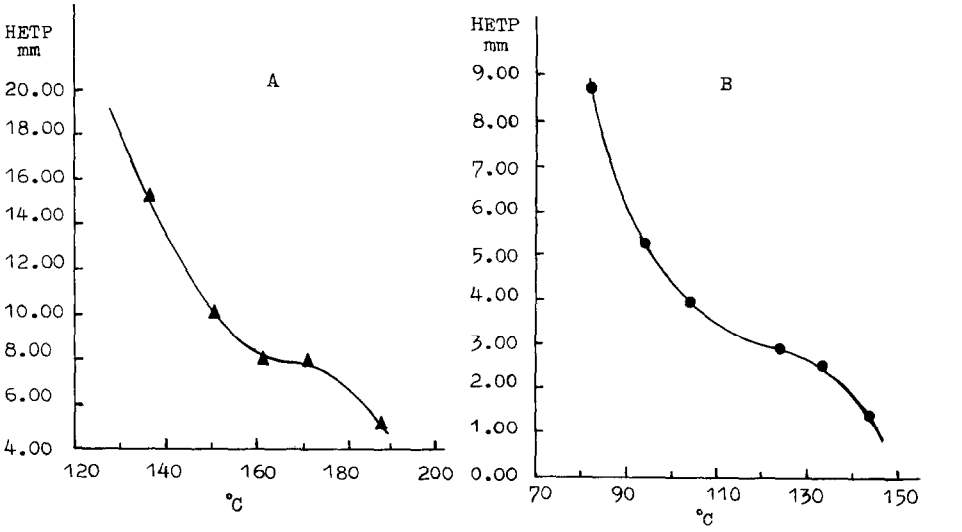

Fig. 6. Plot of HETP against temperature for *n*-octanol on column 5 (A) and *n*-tridecane on column 1 (B).

compounds with hydroxyl groups, without tailing (Fig. 3). This is due to the high efficiency and the deactivation of the residual silanol groups on the surface of the column walls by crown ethers rings. Apolar compounds such as alkanes, easily polarizable compounds such as aromatic hydrocarbons and their derivatives (Fig. 4) and moderately polar compounds such as halohydrocarbons (Fig. 5) were separated.

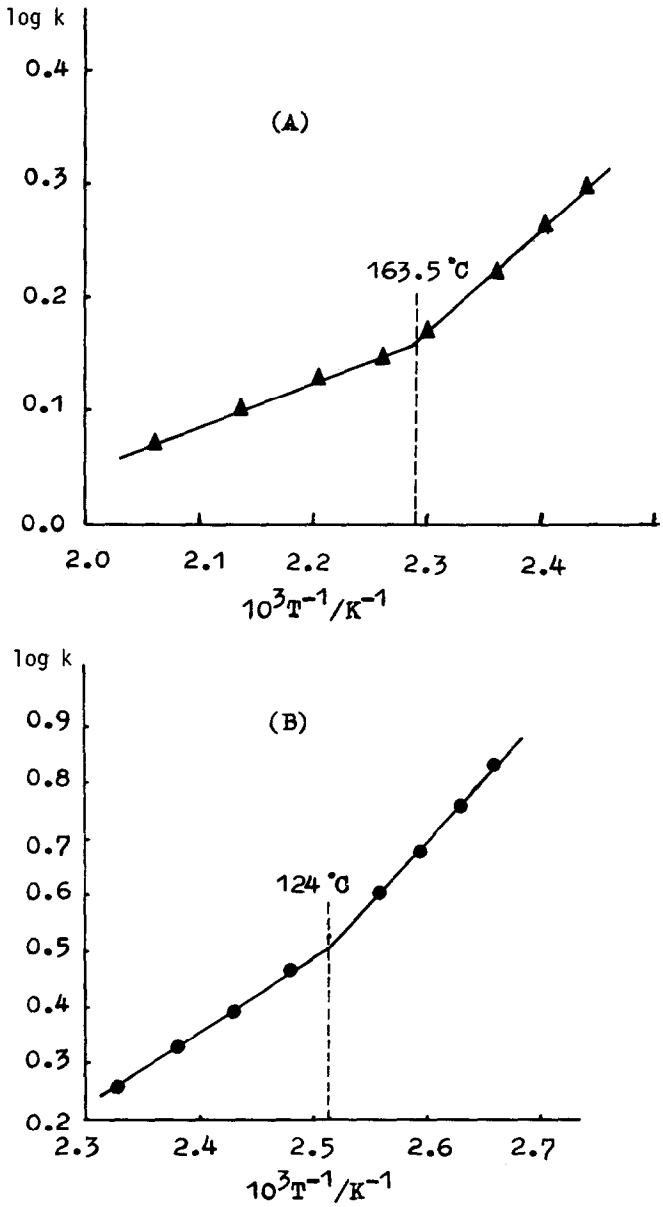

Fig. 7. Plots of log k against reciprocal absolute temperature for n-$C_{12}H_{26}$ with SU15C5 (A) and DSU30C10 (B) as the stationary phase. The transition temperature is indicated by the vertical dashed line.

To determine the effect of temperature on column efficiency, the height equivalent to a theoretical plate (HETP) was measured at different temperatures. Fig. 6 shows a plot of HETP *vs.* T for octanol and *n*-tridecane on the two crown ether columns. It is apparent that column efficiency increases with increasing temperature up to the temperature at which crown ethers begin to bleed obviously. Each curve has a turning point which implies that there is a liquid–liquid transition (see Fig. 7).

The maximum allowable operating temperature of the crown ether columns is relatively high, if their molecular weights are taken into account. The baseline is even when the column temperature is lower than 200°C. The capillary columns were used at about 200°C for 2 months without losses in column efficiency and capacity.

The minimum allowable operating temperature is low (about 50°C) as the crown ethers have low melting points. However, the column efficiency is rather low at this temperature.

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