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Synergistic Effect in Mixed Capillary Gas Chromatographic Stationary Phases Containing Heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and Dibenzo-18-crown-6

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Abstract: Fused-silica capillary columns containing heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and dibenzo-18-crown-6 were prepared. By studying the selectivity of mixed stationary phases for some solute pairs, as well as comparing with the heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and the dibenzo-18-crown-6 used as individual stationary phase, the synergistic effects were observed. These effects were affected by the column temperature, mixed ratio and linear velocity of carrier gas.

Keywords: Gas chromatography; mixed stationary phase; synergistic effect; heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin; dibenzo-18-crown-6.

The crown ether has high selectivity for the separation of polar position isomers and cyclodextrin stationary phases for the separation of chiral compounds and positional isomers. Recently our research group has shown the existence of synergistic effect in some mixed gas chromatographic stationary phases with special selectivity[1-3]. Noticing the similar molecular structure of cyclodextrins and crown ether as well as their difference in molecular recognition, we mixed heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and dibenzo-18-crown-6 and used it as the stationary phase for capillary gas chromatography to see whether there is also a synergistic effect in this cyclodextrin-crown ether system.

The synthesis of heptakis (2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin was achieved by our group. Dibenzo-18-crown-6 and SE-54 were chromatographic grade reagents. All the compounds tested were of analytical reagent grade. Columns (Yongnian Optical Fibre Factory, Hebei, China) were statically coated, as listed in **Table 1**. The chromatographic measurements were carried out on a Model GC-9A gas chromatography (Shimadzu Corporation, Japan) equipped with a flame-ionization detector (FID). The carrier gas was nitrogen at a linear velocity of 11.2~11.6 $cm.s^{-1}$. The injection split ratio was 80:1.

Table 1. The Stationary Phases of Open Tubular Columns

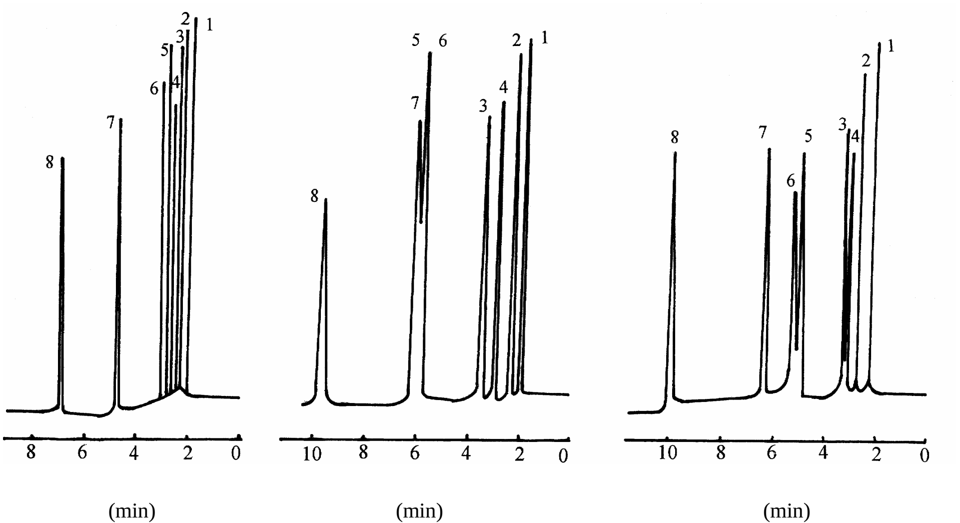
No.	Column	Stationary phases	Ratio
1	CD	*β*-CD	
2	G	dibenzo-18-crown-6（in SE-54）	
3	CD-$G_{2:1}$	*β*-CD + dibenzo-18-crown-6（in SE-54）	2:1
4	CD-$G_{1:1}$	*β*-CD + dibenzo-18-crown-6（in SE-54）	1:1
5	CD-$G_{1:2}$	*β*-CD + dibenzo-18-crown-6（in SE-54）	1:2

Dibenzo-18-crown-6 : SE-54 = 1:2

Table 2. Characteristics of three capillary columns

Column	Column dimension (m × mm)	Film thickness (μm)	k	Temp. (^{o}C)	Opt. linear velocity (cm s^{-1})	Colum efficiency Plates.m^{-1}	Compound tested
G	11 × 0.25	0.28	2.28	120	12.8	4627	Dodecane
CD	11 × 0.25	0.28	1.56	140	14.9	1302	Octanol
CD-$G_{1:1}$	11 × 0.25	0.28	2.10	130	12.9	2833	Dodecane

Figure 1. The performance of column CD, G, CD-$G_{1:1}$ tested by using the Grob test mixture at 140 ℃. 1=decane, 2=undecane, 3=octanol, 4=nonanal, 5=2,6-dimethylphenol, 6=2,6-dimethylaniline, 7=methyldecanoate, 8=methylundecanoate.



Column G (u=12.6cm.s^{-1}) Column CD (u=12.5cm.s^{-1}) Column CD-$G_{1:1}$ (u=12.5cm.s^{-1})

Table 2 summarizes the characteristics of the columns CD, G and CD-$G_{1:1}$. It shows that the film-forming property of the stationary phases and the performance of the column are not very poor. The Grob's test mixture was also separated (in **Figure 1**) and the elution sequence and retention characteristics of the peaks on the mixed stationary phase were different from the results obtained on either individual stationary phase. This cannot be explained by the simple addition of the retention characteristics of mixed gas chromatographic stationary phases. It shows that the interaction mechanism of the mixed stationary phase with some guest molecules has been changed.

Some solute pairs were chosen as test samples for evaluation of the selectivity of the mixed stationary phase. **Table 3** lists separation factor (α) values for these compounds on column CD-G$_{1:1}$, CD and G. In general the α values measured on the column CD-G$_{1:1}$ should be between those obtained on columns CD and G. But the separations for chloroform/dichloromethane, methyl isobutyl ketone/2-pentanone, 2-pentanone/1-butanone, ethylbenzene/toluene， toluene/ benzene, 2,6-dimethyl aniline/*o*-methyl aniline on column CD-G$_{1:1}$ were greater than on column CD and G, and for benzene/cyclohexane, cyclohexane/hexane, 1,2-dichloroethane/chloroform, dichloro-methane/tertbutylchloride, *p*-chlorotoluene/*o*-chlorotoluene, *o*-methyl aniline/N,N-dimethyl aniline the separation was poores. It proved that the synergistic effect on the mixed stationary phase did exist.

The effect of the temperature and ratio of the stationary phases on synergistic effect was examined. These results could be expressed by plots of the separation factor (α) against the stationary phase ratio, depicted in **Figures 2** and **3**. It could be seen from the separation for 2-pentanone/1-butanone in **Figure 3** that the synergistic effect is more pronounced at higher column temperature.

Table 3. The separation factor (α) on column CD, column CD-G$_{1:1}$ and column G

Tempra-ture (℃)	Compounds tested	$^{\alpha}$ CD	$^{\alpha}$ CD-G (1:1)	$^{\alpha}$ G
60	benzene/cyclohexane	1.49	1.26	2.00
	cyclohexane/hexane	2.63	2.04	2.27
	1,2-dichloroethane/chloroform	1.11	1.08	2.04
	chloroform /dichloromethane	2.66	2.73	1.33
	dichloromethane /tert butyl chloride	1.92	1.41	2.38
80	cyclohexanone/methyl iso butyl ketone	4.44	4.26	3.50
	methyl iso butyl ketone/2-pentanone	1.46	1.52	1.46
	2-pentanone/1-butanone	2.04	2.27	2.00
	styrene/ethylbenzene	1.52	1.40	1.25
	ethylbenzene/toluene	2.00	2.09	2.00
	toluene/benzene	2.17	2.33	2.27
	o-xylene/*p*-xylene	1.23	1.23	1.20
100	*p*-chlorotoluene/*o*-chlorotoluene	1.04	1.03	1.07
140	*p*-cresol/*o*-cresol	1.33	1.27	1.07
	o-cresol/phenol	1.23	1.25	1.43
150	*n*-octanol/*n*-heptanol	1.73	1.59	1.45
	n-heptanol/cyclohexanol	1.26	1.26	1.30
	cyclohexanol/hexanol	1.22	1.20	1.10
	2,6-dimethyl aniline/*o*-methyl aniline	1.41	1.60	1.43
	o-methyl aniline/N,N-dimethyl aniline	1.41	1.23	1.56
	N,N-dimethyl aniline/aniline	1.04	1.19	1.79
	p-nitrotoluene/*o*-nitrotoluene	1.42	1.37	1.30

The synergistic effect of mixed stationary phase is affected by the linear velocity of carrier gas. Toluene/benzene and 2-pentanone/1-butanone were chosen as test samples. Their α values on the column CD-G$_{1:2}$ decreased with increasing linear velocity of carrier gas.

Figure 2. Plot of $\alpha_{toluene/benzene}$ *vs* G% on mixed stationary phases on Column CD, G, CD-$G_{2:1}$, CD-$G_{1:1}$ and CD-$M_{1:2}$ at 60℃, 70℃ and 80℃

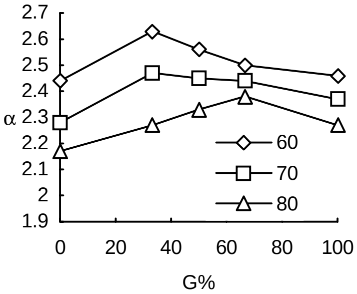
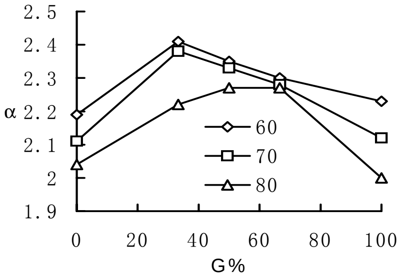


Figure 3. Plot of $\alpha_{2\text{-pentanone}/1\text{-butanone}}$ *vs* G% on mixed stationary phases on Column CD, G, CD-$G_{2:1}$, CD-$G_{1:1}$and CD-$M_{1:2}$ at 60℃, 70℃ and 80℃



We think that the synergistic effect is determined by the simultaneous action of β-CD and crown ether on the solute molecules. In their interaction mechanism the supramolecular power plays an important role. It can be assumed that the largest synergistic effect is attained with maximum simultaneous action probability. This probability may depend on temperature, mixing ratio and linear velocity of carrier gas.

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