Synergistic Effect of PEG-20M and Heptakis(2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin Mixed Stationary Phase in Gas Chromatography

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In open tubular column gas chromatography, by investigating the chromatographic properties of the mixed stationary phase containing heptakis(2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and PEG-20M, as well as comparing with the heptakis(2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and the PEG-20M used as individual stationary phase, the synergistic effect was observed on this mixed stationary phase. This separation effects depend on temperature and mixing ratio.

Synergistic effect was first discovered in 1957 by Blake in the study of extraction of U(VI).[1] It is generally know that the rule of additivity for mixed stationary phase in GC is distinct. The investigation reported by our lab have shown the existence of synergistic effect in the side-chain crown ether polysiloxane and perethylated *β*-CD mixed stationary phase,[2] as well as in the mixed stationary phase consisting of *β*-CD and $AgNO_3$ or $TlNO_3$.[3] Cyclodextrins are cyclic molecules with cavity structure. It may form inclusion compounds with some molecules.[4] The polyethylene glycol 20M is an electron attractor.[5] The aim of the present paper is to further investigate this phenomenon on mixed stationary phase containing heptakis(2,3,6-tri-*o*-pentyl)-*β*-cyclodextrin and PEG-20M.

Fused silica capillary tubing (11m × 0.25mm i.d.), manufactured by the Yongnian Optical Fiber Factory (Heber Province, P. R. China), were purged with nitrogen at 240 ℃ for 4 h before static coating with 0.45% W/V dichloromethane solutions of single or mixed stationary phases. After the capillary column was filled with the dichloromethane solution, then one end of the capillary column was sealed and the other end was connected to a 0.07 ~ 0.08MPa vacuum line. Dichloromethane was gently evaporated at a constant 35 ℃ temperature. The columns which film thickness were about 0.28μm were conditioned finally at 160 ℃ for 6h. The open tubular columns used were listed in Table 1.

Table 1. The stationary phases of open tubular columns

No.	Column	Stationary phases	Ratio
1	CD	*β*-CD	
2	PEG	PEG-20M	
3	CD-$PEG_{2:1}$	*β*-CD+PEG-20M	2:1
4	CD-$PEG_{1:1}$	*β*-CD+PEG-20M	1:1
5	CD-$PEG_{1:2}$	*β*-CD+PEG-20M	1:2

The chromatographic measurements were carried out on a Shimadzu Model GC-9A Chromatography (Shimadzu Corporation, Japan) equipped with an FID. The carrier gas was nitrogen. The injection split ratio was 80:1. All the compounds tested were of analytical-reagent grade.

Column CD, PEG and CD-$PEG_{1:1}$ were used for the separation of benzene/cyclohexane, halogenated hydrocarbons, ketones and aromatics. The results of the separation expressed as relative retention (α) were given in Table 2. The most of α values on column CD-$PEG_{1:1}$ are not the simple arithmetic averages of the relative retention obtained on columns CD and PEG. For example, the separations for 1,2-dichloroethane/chloroform, styrene/ethylbenzene, toluene/benzene and *p*-nitrotoluene/*o*-nitrotoluene on column CD-$PEG_{1:1}$ are better than on column CD and PEG. Those separations reveal that there exist synergistic effect in the mixed stationary phase.

Table 2. The relative retention (α) on Column CD, CD-$PEG_{(1:1)}$ and PEG

Tempra-ture(℃)	Compounds tested	α_{CD}	$\alpha_{CD\text{-}PEG(1:1)}$	α_{PEG}
60	benzene/cyclohexane	1.49	3.25	4.71
	1,2-dichloroethane/chloroform	1.11	1.54	1.39
	chloroform /dichloromethane	2.66	2.50	1.97
	dichloromethane/tertbutylchloride	1.92	3.33	5.00
80	cyclohexanone/methylisobutylketone	4.44	4.36	2.20
	methylisobutylketone /2-pentanone	1.46	1.22	1.22
	2-pentanone/1-butanone	2.04	1.49	1.37
	styrene/ethylbenzene	1.52	3.89	2.17
	ethylbenzene/toluene	2.00	1.74	1.69
	toluene /benzene	2.17	2.27	1.79
	o-xylene/*p*-xylene	1.23	1.24	1.32
100	*p*-chlorotoluene/*o*-chlorotoluene	1.03	1.05	1.07
150	*p*-nitrotoluene/*o*-nitrotoluene	1.42	1.45	1.38

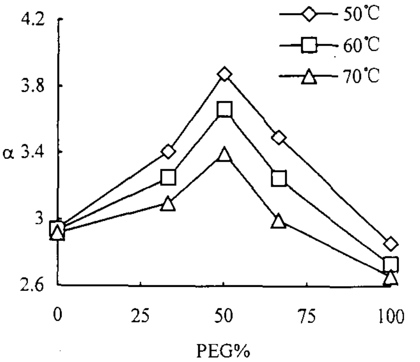

Figure 1. Plot of $\alpha_{1,2\text{-dichloroethane/ dichloromethane}}$ vs PEG% on mixed stationary phases on Column CD, PEG, CD-$PEG_{2:1}$, CD-$PEG_{1:1}$ and CD-$PEG_{1:2}$ at 50℃, 60℃ and 70℃.

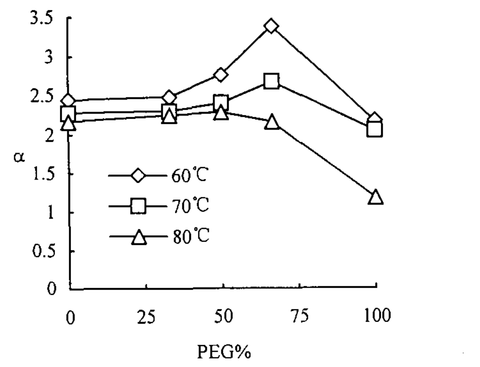

Figure 2. Plot of $\alpha_{toluene/benzene}$ vs PEG% on mixed stationary phases on Column CD, PEG, CD-PEG$_{2:1}$, CD-PEG$_{1:1}$ and CD-PEG$_{1:2}$ at 60℃, 70℃ and 80℃.

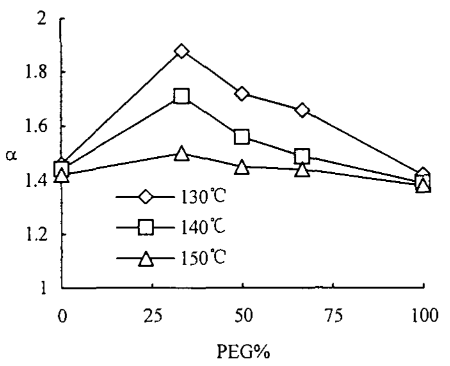

Figure 3. Plot of $\alpha_{p\text{-nitrotoluene/o-nitrotoluene}}$ vs PEG% on mixed stationary phases on Column CD, PEG, CD-PEG$_{2:1}$, CD-PEG$_{1:1}$ and CD-PEG$_{1:2}$ at 130℃, 140℃ and 150℃.

reveal that there exist synergistic effect in the mixed stationary phase.

Figure 1, 2 and 3 revealed the effect of mixing ratios and temperatures on the synergistic effect. They are expressed by plots of the relative retention (α) against the stationary phase ratios. When the temperatures are lower, the mixed stationary phase show stronger separation ability than either pure stationary phase.

On the whole, in the case of the separation of benzene/ cyclohexane, halogenated hydrocarbons, ketones and aromatics, the mixed stationary phase exhibits a synergistic effect. We assume that the synergistic effect is based on the intermolecular actions of the PEG-20M and special selectivity gas chromatography stationary phase β-CD to the solute molecules and the probability of simultaneous action of the mixed stationary phases to the solute pairs.[4, 6] This probability may be greater when the temperature is lower.

References and Notes

1 C. A. Blake, D. J. Crouse, C. F. Coleman, K. B. Brown, and A. D. Kelmers, *U. S. Atomic Energy Comm.*, ORNL-2172 (1957), *Chem. Abstr.*, **51**, 8391e (1957).
2 P. Jing, R. N. Fu, R. J. Dai, J. L. Gu, Z. Huang, and Y. Chen, *Chromatographia*, **43**, 546 (1996).
3 L. M. Yuan, R. N. Fu, S. H. Gui, X. T. Xie, R. J. Dai, X. X. Chen, and Q. H. Xu, *Chromatographia*, **46**, 295 (1997).
4 J. M. Lehn, "Supramolecular Chemistry: Concepts and Perspectives," VCH publishers (1995).
5 W. R. Supina, "The packed column in gas chromatography," Supeco. Inc. (1974).
6 L. M. Yuan, and W. J. Song, *He Huaxue Yu Fangshe Huaxue (journal of Nuclear and Radiochemistry)*, **12**, 180 (1990).