研究快报

GAS CHROMATOGRAPHIC STUDY ON THE INCLUSION PROPERTIES OF CALIX[4]ARENE DERIVATIVES*

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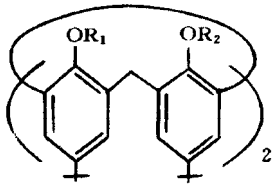
Abstract The inclusion properties of two kinds of derivatized calix[4]arene were studied with gas chromatography. Homologous series of aromatics, alcohols and halogenated hydrocarbons were used as solutes. It was found that inclusion compounds are formed between C[4]A and benzene, toluene, methanol, ethanol, dichloromethane and chloroform and between C[4]B and methanol, dichloromethane and chloroform.

Key words gas chromatography, calix[4]arene derivatives, inclusion property

1 Introduction

Calixarenes, which are macrocyclic compounds containing cavities of molecular sized dimension, have attracted much interest in the history of host-guest chemistry. As the third generation host compounds followed cyclodextrins and crown ethers, their inclusion properties have been mainly studied in solid state. There is little information about their properties in gaseous phase.

Gas chromatography, a direct and powerful technique in determining the intermolecular interaction under gas-liquid or gas-solid condition, has been applied to the study on the inclusion properties of the basic, unsubstituted calixarene series[1,2]. However, the column efficiency, column temperature and the precision of the results were greatly limited because of the poor solubility and high melting point of the parent compounds. Recently, we synthesized calix[4]arene derivatives[cone 5, 11, 17, 23-tetra-tert-butyl-25, 27-bis(isopropylcarbamoyl methoxy)-26, 28-diundecenyloxy calix[4]arene and partial cone 25, 27-dibutoxy-5, 11, 17, 23-tetra-tert-butyl-26, 28-diundecenyloxy calix[4]arene] with good lipophilicity, low melting points and fixed conformations(Fig. 1). Using them as selective components of stationary phases with OV1701, we got high column efficiencies and wide range of operating temperature. In this paper we tried to study their inclusion properties on the basis of the retention behavior of selected homologous series in order to clarify the interaction mechanism in chromatographic separation process and thus to take it as a guide in the synthesis of such new selective stationary phases.



C[4]A | R_1: $CH_2CONHCH(CH_3)_2$; R_2: $(CH_2)_9CH{=}CH_2$

C[4]B | R_1: *t*-Bu; R_2: $(CH_2)_9CH{=}CH_2$

Fig. 1 The structure of C[4]A and C[4]B

2 Experimental

2.1 Synthesis

5, 11, 17, 23-tetra-tert-butyl-25, 27-bis(isopropylcarbamoyl-methoxy)-26, 28-diundecenyloxy calix[4]

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arene(C[4]A) was synthesized according to the references[3,4]. The ^{1}HNMR spectrum showed it existed in a cone conformation.

25, 27-dibutoxy-5, 11, 17, 23-tetra-tert-butyl-26, 28-diundecenyloxy calix[4]arene(C[4]B) was synthesized as in the reference[4]. It possessed a partial cone conformation as indicated by its ^{1}HNMR spectrum.

2.2 The preparation of fused silica capillary columns and their gas chromatographic procedure

C[4]A-OV1701 column(13.5m × 0.25mm i.d.) and C[4]B-OV1701 column(12m × 0.25mm i.d.) were statically coated with 0.5% *W*/*V* solution of calixarene derivatives and OV1701(50∶50) in dichloromethane at 33℃. OV1701 column(15m × 0.25mm i.d.) was prepared in the same manner. The evaluations were carried out on a GC-7A gas chromatograph (Shimadzu, Japan) with a flame ionization detector. Retention times of the analytes were measured at 10℃ intervals in the temperature range of 80-120℃ to determine thermodynamic parameters. Correlation coefficients of $\ln k'$ versus $1/T$ plots were higher than 0.996.

3 Results and discussion

The introduction of undecenyl group on the basic calix[4]arene may greatly improve the lipophilicity of the compounds. To gain a better coating efficiency, we mixed them with OV1701. The column efficiencies of C[4]A-OV1701 and C[4]B-OV1701 at 120℃ for naphthalene were 3138 and 4602 plates/m, respectively. Fig. 2 and Fig. 3 illustrate the retention behaviors of different homologous series at 110℃ on calix[4]arene derivative stationary phases. The effect of the polysiloxane component(OV1701) in the stationary phase was eliminated by using the difference in the capacity ratios(d*k*) between C[4]A(or B)+ OV1701 and pure OV1701.

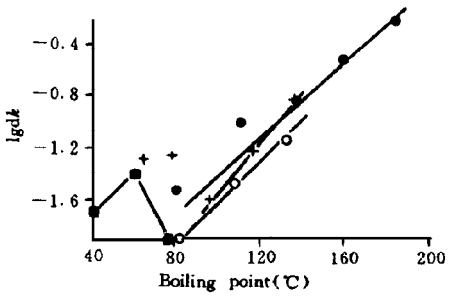

Fig. 2 Relationship between the logarithm of the difference in the capacity ratios (d*k*) of C[4]A+ OV1701 and pure OV1701 and the boiling point

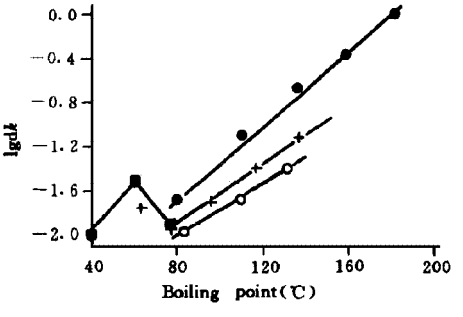

Fig. 3 Relationship between the logarithm of the difference in the capacity ratios (d*k*) of C[4]B+ OV1701 and pure OV1701 and the boiling point

● . aromatics (benzene, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene);
+ . *n*-alcohols (methanol, ethanol, *n*-propanol, *n*-butanol and *n*-pentanol);
○ . 2-propanol, 2-butanol and 2-pentanol;
■ . chloromethanes (dichloromethane, trichloromethane and tetrachloromethane).

It is evident that benzene and toluene are more retained on the C[4]A phase and it does not occur on C[4]B phase. The reason can be assumed that the conformation of calix[4]arene plays a crucial role for inclusion. It's relatively easier for CH_3(host)-π(guest) and CH_3(guest)-π(host) interactions in cone conformation than that in flattened partial cone on which electron clouds are not concentrated. This is in good agreement with the report of the reference[5].

The slope of alcohol homologous series is much larger than that of aromatics on C[4]A phase. This implies the decisive role of hydrogen bonding forces between OH group of alcohol and the imide group of the stationary phase. The strong interaction may also promote the inclusion of methanol and ethanol in the cavity of

C[4]A. But C[4]B can only encapsulate methanol molecules by dipole-induce dipole forces that are weaker than hydrogen bonding. Branched alcohols all eluted in the order of their boiling points due to the steric hindrance of the branched chain for the formation of inclusion compounds.

With regard to halogenated hydrocarbons, it can be easily found that the values of $\log|dk|$ of dichloromethane and trichloromethane all deviate significantly from linear dependences on C[4]A and C[4]B. This may be ascribed to the presence of CH-π interaction between the sorbate and the calixarene aromatic system which is considered as an important factor for the inclusion.

Further thermodynamic analysis results indicated that both configuration and polar effects contribute to the inclusion phenomena. When a solute is included, its $-\Delta H$ and $-\Delta S$ all become larger(Table 1). The decline of ΔS arise from the better fit of the analytes into the calix[4]arene cavity. On the other hand, the increase of $-\Delta H$ is realized owing to the stronger interaction between the host and guest. That is, the conformation and derivative groups of calixarenes all affect the retention behavior of analytes in the chromatographic separation process.

Table 1　ΔH^* and ΔS^{**} on OV1701, C[4]A-OV1701 and C[4]B-OV1701

Analyte	OV1701		C[4]A-OV1701		C[4]B-OV1701	
	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
Benzene	29.32	93.02	31.11	96.10	28.10	88.81
Toluene	32.42	95.59	36.62	103.62	31.51	90.81
Dichloromethane	27.76	99.03	36.42	120.01	29.77	102.27
Trichloromethane	30.28	99.81	40.08	121.91	33.24	104.80
Methanol	35.46	122.98	97.06	273.66	90.02	260.25
Ethanol	37.06	124.02	54.49	161.62	26.30	93.64

* The unit of ΔH is $kJ \cdot mol^{-1}$.

** The unit of ΔS is $J \cdot mol^{-1} \cdot K^{-1}$.

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气相色谱法研究杯芳烃衍生物的包结性能

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提　要　以苯系、醇系及卤代烃系列为探测物质, 用气相色谱法首次研究了两种杯[4]芳烃衍生物在气-液条件下的包结性能。结果表明: C[4]A 可与苯、甲苯、甲醇、乙醇、二氯甲烷及三氯甲烷形成包结物, 而 C[4]B 仅能与甲醇、二氯甲烷及三氯甲烷形成包结物。对其作用机理亦进行了初步探讨。

关键词　气相色谱法, 杯芳烃衍生物, 包结性能

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