Journal of Chromatography A, 1343 (2014) 167–173

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Separation performance of cucurbit[8]uril and its coordination complex with cadmium (II) in capillary gas chromatography

Tao Sun [a], Ningning Ji [b], Meiling Qi [a,*], Zhu Tao [b,*], Ruonong Fu [a]

[a] Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials and School of Chemistry, Beijing Institute of Technology, Beijing 100081, China
[b] Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China

ARTICLE INFO

Article history:
Received 18 January 2014
Received in revised form 30 March 2014
Accepted 31 March 2014
Available online 12 April 2014

Keywords:
Cucurbit[8]uril
Coordination complex
Stationary phase
Capillary gas chromatography

ABSTRACT

Here we report the investigation of using cucurbit[8]uril (CB8) and its coordination complex with cadmium (II) (CB8-Cd) as stationary phases for capillary gas chromatography (GC). The prepared capillary columns of CB8 and CB8-Cd stationary phases achieved column efficiency of 2200 plates/m and 1508 plates/m, respectively, and showed weak polarity based on the measured McReynolds constants. Their separation performance was investigated by GC separation of mixtures of different types while a commercial column was used for comparison. The CB8 stationary phase achieved high resolution for a wide range of analytes from nonpolar to polar while the CB8-Cd stationary phase exhibited good separation mainly for nonpolar to weak polar analytes. The CB stationary phases differ from the commercial one in terms of retention behaviors and resolving ability due to their different molecular interactions with analytes. Moreover, energy effect on the retention of analytes on CB8 and CB8-Cd stationary phases was examined, showing that retention on CB8 column was determined mainly by enthalpy change for polar analytes and by both enthalpy change and entropy change for weak polar analytes whereas retention on CB8-Cd column was mainly controlled by entropy change. This work demonstrates the great potential of CB8 and CB8-Cd stationary phases as a new type of GC stationary phases in GC analysis.

1. Introduction

Cucurbit[8]uril (CB8) is one of the family members of cucurbit[n]urils (CBs), which are glycoluril-based macrocyclic compounds of a rigid and symmetric structure bearing a hydrophobic cavity and two identical polar carbonyl fringe portals [1,2]. As shown in Fig. 1, CB8 possesses 16 carbonyl oxygen atoms, 16 methine and 32 methene protons surrounding the large cavity. Since each carbon is connected to two nitrogen atoms throughout the rings, the presence of two electron-withdrawing atoms increases the acidic character of the C—H protons and strengthens the corresponding H-bonding [3]. The unique structure offers CB8 superior molecular recognition properties that have attracted wide attention in supramolecular chemistry [4–8]. It can selectively interact with specific analytes *via* dipole–dipole and H-bonding interactions of the carbonyl groups and the methine/methene protons or *via* its hydrophobic cavity. Additionally, CB8 is characteristic of excellent chemical and thermal stability (>400 °C)[6]. In recent years, the coordination of CB8 with metal ions such as transition-metal ions and lanthanides has also received considerable attention [9–11]. Most recently, we reported the coordination complexes of CB8 with metal ions (Cd, Zn, etc.) and their potential in separation science as coatings for solid-phase microextraction [11]. The aforementioned structural features and physicochemical properties make CB8 and their coordination complexes ideal candidates as stationary phases for capillary gas chromatography (GC).

In fact, CB family used as GC stationary phases is rarely reported. Two reports are available for packed GC [12,13], in which perhydroxy-CB6 [12] and CB7 [13] were dissolved in concentrated hydrochloric acid and then coated onto white support as column packing for packed GC separations. Investigations on CBs for other chromatographic methods include using them as an additive in capillary electrophoresis [14,15], stationary phases in liquid chromatography [16,17] and fiber coating for solid-phase microextraction [18]. The reason for this can be mainly attributed to their poor solubility in ordinary organic solvents and chemical inactivity for derivatization. This also presents a great challenge for using CBs

* Corresponding authors. Tel.: +86 10 68912667/86 851 3620906; fax: +86 10 68914780.
E-mail addresses: mlqi2013@163.com (M. Qi), gzutao@263.net (Z. Tao).

http://dx.doi.org/10.1016/j.chroma.2014.03.084
0021-9673/

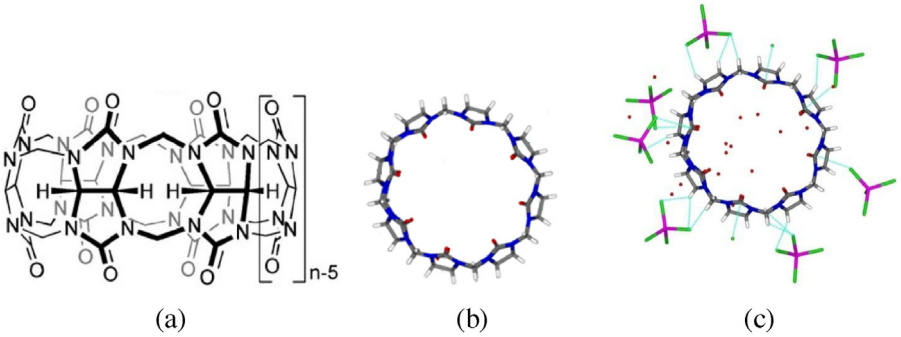

Fig. 1. Structures of (a) CB8 (n = 8, side view), (b) CB8 (top view) and (c) CB8-Cd (top view) stationary phases.

or their derivatives as stationary phases for capillary GC to achieve high-resolution separation performance. Most recently, CBs as stationary phases for capillary GC were reported by our research group [19,20].

Herein we present the investigation of using CB8 and its coordination complex with cadmium (II) (CB8-Cd, Fig. 1) as stationary phases for capillary GC separation. To the best of our knowledge, this is the first report on using a coordination complex of CBs as GC stationary phase. The capillary columns of CB8 and CB8-Cd were statically prepared by using their suspensions in dichloromethane. For the prepared columns, column efficiency and McReynolds constants were measured and separation performance was investigated by GC separation of different mixtures (halogenated benzenes, PAHs, *n*-alkanes and bromoalkanes) and a complex mixture containing 21 analytes of great variety. Meanwhile, a well-recognized commercial column with comparable polarity was also used for comparison. In addition, energy effects on the retention of analytes were also investigated to get better understanding of their retention behaviors and separation mechanism.

2. Experimental

2.1. Chemicals and reagents

All the chemicals used in this work were of analytical grade. Benzene, pyridine, 1-butanol, 2-pentanone and 1-nitropropane were purchased from Alfa Chemical Company (Tianjin, China). Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene were from Aladdin Industrial Corp. (Shanghai, China). Glycoluril, paraformaldehyde and hydrochloric acid were purchased from the Beijing Chemical Reagent Company (Beijing, China). The analytes used for the evaluation of separation performance including *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromoheptane, 1-bromooctane, 1-bromodecane, 1,4-dibromobutane, 1,6-dibromohexane, 1,10-dibromodecane, 1,12-dibromododecane, chlorobenzene, bromobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,3-dichloropropane, 1,4-dichlorobutane, benzaldehyde, nonanal, 2-chloroaniline, methyl nonanoate, methyl decanoate, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and dichloromethane were purchased from Beijing Chemical Reagent Company (Beijing, China). All the analytes were dissolved in dichloromethane at 1 mg/mL. Fused silica capillary tube (0.25 mm i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Company (Hebei, China). A commercial HP-5MS capillary column (10 m × 250 μm, i.d.) purchased from Agilent Technologies was also employed for comparison.

2.2. Instrumentation

An Agilent 7890A gas chromatograph (Agilent Technologies, USA) equipped with a split/splitless injector, a flame ionization detector (FID) and ChemStation software was used. All the GC separations were performed under the following conditions: nitrogen of high purity (99.999%) as carrier gas at a flow rate of 1 mL/min, injection port at 300 °C, split injection mode at a split ratio of 30:1 and FID detector at 300 °C. A Shimadzu TGA-50H thermoanalyzer was used for thermogravimetric analysis (TGA) of the CB8 and CB8-Cd stationary phases. A JEOL JSM-7001F scanning electron microscope (SEM) (JEOL, Japan) was used for the morphological observation of the coated capillary columns.

2.3. Synthesis of CB8 and CB8-Cd stationary phases

The synthesis of CB8 was performed following refs. [20–22]. Briefly, glycoluril (71.4 g, 0.5 mol) and paraformaldehyde (30.1 g, 1.0 mol) were thoroughly mixed and added to a 500 mL round-bottomed flask. A concentrated HCl solution (110 mL) was then slowly added to the flask under rapid stirring at room temperature. Stirring was continued until the mixture turned into a gel. Then the mixture was heated to 100 °C, resulting in a rapid dissolution of the gel, and refluxed for 20 h and cooled down to room temperature. After the solution was concentrated to 50 mL and poured into 500 mL water, crystalline precipitate formed and was then filtrated. The obtained crystalline solid was further purified as follows. After the solid was successively washed with water and acetone and dried under vacuum, it was dissolved in a 40 mL HCl solution (4 mol/L) and stirred for 30 min and filtered. This process was repeated one more time. Then, the collected solid was successively washed with a 10 mL HCl solution and acetone and recrystallized in HCl solution (6 mol/L). The crystalline was washed with water, filtered and dried under vacuum. Finally, the CB8 product as white crystalline solid was obtained, which was confirmed by FT-IR and ^{1}H NMR in good agreement with the data in the references. The coordination complex of CB8-Cd was synthesized and characterized following our previously reported method provided in ref. [11]. The crystal structural analysis revealed that the 7$[CdCl_4]^{2-}$ anions were coordinated to a CB8 molecule (Fig. 1). Additionally, TGA tests for the CB8 and CB8-Cd stationary phases showed that the CB8 and CB8-Cd are thermally stable up to about 400 °C and 300 °C, respectively, on the basis of the temperature for 5% weight-loss.

2.4. Preparation of capillary columns

Suspensions of CB8 and CB8-Cd (0.25%, w/v) were individually prepared by dispersing 25 mg of CB8 or CB8-Cd in 10 mL of dichloromethane under ultrasonication for 5 min and were used