Chromatographic Study of the Inclusion Properties of Cyclodextrins: Study of Inclusion from the Gaseous Phase

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Abstract. The ability of cyclodextrins to form inclusion compounds with substances in the gaseous phase was studied chromatographically. Chromatographic measurements enabled the mechanism of the inclusion process to be clarified and have shown that other forces, mainly hydrogen bonding, play a role in the process in addition to the geometric properties of the interacting substances. These facts are expressed in terms of the changes in the chromatographic quantities and of the changes in the thermodynamic characteristics that are derived from the former quantities. The selective properties of cyclodextrins have been utilized in separations of substances that are otherwise separated with difficulty (xylenes, diethylbenzenes, trimethylbenzenes, etc.).

Key words: α- and β-cyclodextrins, methylated cyclodextrins, inclusion from gaseous phase, gas chromatographic investigation.

1. Introduction

The ability of cyclodextrins (CDs) to selectively interact with a great variety of substances, depending on the shape and size of their molecules, provides a number of possible applications in the field of chromatographic methods and separations on laboratory or industrial scales [1–4].

The use of substances capable of forming inclusion compounds as selective separating phases has been studied in many laboratories the world over. The use of zeolites is sufficiently well known (although the process of inclusion is not emphasized as the principal interaction type with these substances), as well as the use of bentonites, urea, thiourea, and desoxycholic acid in gas chromatography and extensive studies of the use of Werner complexes in liquid chromatography [5].

It has been demonstrated, especially in recent publications, that the use of cyclodextrins in chromatography has some advantages over the other host substances, e.g., the ability to form inclusion compounds not only as crystalline substances, but also as inclusion complexes in solution. Further, CDs retain inclusion properties even in the form of polymers, can be used as selective chemically modified phases and variously chemically modified native CDs. These potentialities have recently been outlined and thus the number of publications dealing with the application of CDs as stationary or mobile phases in the chromatographic process [4] have increased. Many publications give interesting analytical results that often have not been unambiguously interpreted from the physicochemical point of view. The main reason is the
great diversity of the forces that can participate in the interaction as a result of the geometrical and chemical properties of cyclodextrins or their polymers.

The separation of various types of chemically similar substances on the basis of structurally selective interactions is further enhanced by the multistep chromatographic process. The papers published so far demonstrate that chromatography not only solves many interesting specific analytical problems, but is becoming a very powerful and valuable method for the study of inclusion phenomena.

The research carried out at our Department contributes to the solution of these questions. As relatively little attention has so far been paid to inclusion from the gaseous phase, we have mainly concentrated on a more detailed study of the interactions in the gas-solid system, with CDs representing the solid phase. We have assumed that the physical forces participating in the formation of inclusion complexes can be better evaluated in this system because of the absence of interactions with the solvent. We have carried out both chromatographic, i.e., dynamic, measurements and static measurements, from which some principal thermodynamic data were obtained on the inclusion process from the gaseous phase [14]. In view of the great complexity of the interactions involved in the separation process we chemically modified (methylated) basic CDs in order to suppress the polarity of the original CDs and thus to suppress the contribution from hydrogen bonding [15]. To obtain a complete picture of inclusion from the gaseous phase, we compared, in cooperation with workers of the Polish Academy of Sciences, these results with those obtained in the gas-liquid system, where CDs formed a component of the liquid stationary phase [9]. The study of the interactions of CDs with sorbates in the gaseous state was complemented by measurements in aqueous solutions [16]. On the basis of the results obtained we attempted to explain the separation processes and to outline the possibilities of their practical use.

2. Experimental

α- and β-CDs were obtained from Chinoin (Budapest, Hungary). The stationary phases for the GSC measurements were prepared by coating Chromosorb W (80–100 mesh) or Celite (80–120 mesh) with different amounts (% w/w) of α- or β-CD from a dimethylformamide solution. After removing the solvent in vacuo at 95–100°C, the phase was packed into glass columns 2 or 3 mm i.d. and 100, 120, and 200 cm long. The columns were always conditioned at 90°C for at least 8 h. The samples were injected with Hamilton microsyringes. All the substances were of p.a. or reagent grade purity.

3. Results and Discussion

3.1. STUDY OF INCLUSION FROM THE GASEOUS PHASE IN THE GSC SYSTEM


The study of inclusion from the gaseous phase into the cyclodextrin cavity was based on the analogy with other types of host structures and on the present knowledge of the inclusion properties of CDs in aqueous media.

On the basis of these assumptions, a model has been developed for the inclusion from the gaseous phase and the gas chromatographic relationships have been applied to the system of