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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

3.1.1. *Thermodynamic Properties of the Inclusion Process in the Gas-Solid 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

the guest in the gaseous state and the host (cyclodextrin) in the solid phase, which have permitted the calculation of the thermodynamic quantities. The relationship describing the dependence between a principal chromatographic characteristic (reduced retention volume V'_{RA}) and thermodynamic quantitites (the changes in the enthalpy, ΔH_i, and the entropy, ΔS_i,)

$$\log V'_{RA} = -\frac{\Delta H_i}{2.3\,RT} + \frac{\Delta S_i}{2.3\,R} + \log n_H j\,,$$

where n_H is the number of moles of the host and j is a correction factor for the pressure gradient along the column, enables one to obtain these quantitites from the dependence of V'_{RA} on $1/T$.

The results of extensive measurements with various types of sorbates (alkanes, alcohols, aromatics, hydrocarbon halogen derivatives), carried out dynamically (GSC) and statically in closed systems, are being treated and will be published separately. Even now it is possible to draw some general conclusions:

(1) The Gibbs energies for *n*-alkanes on α-CD (~ 84 kJ mol^{-1}) are about 30 kJ mol^{-1} higher than those on the β-CD phase (~ 52 kJ mol^{-1}). This difference is in agreement with the assumption that the potential energy of the inclusion complex is higher in the narrow cavity of α-CD than in β-CD.

(2) Comparison of the enthalpies for *n*-alkanes and alcohols yields a difference that roughly corresponds to the hydrogen bond energy. The difference in the enthalpies for alkanes (hexane, heptane, octane) and alcohols (1-propanol, 1-butanol, 1-pentanol), ΔH_i, is roughly 15 kJ mol^{-1}.

(3) The entropy change dependence on the number of carbon atoms in the alkane molecule confirms the assumption of a localized interaction of the guest molecule with the CD cavity; for a higher number of carbon atoms the entropy decrease is smaller.

(4) The change in the Gibbs energy, reflecting the contributions from the enthalpic and entropic terms, is determined by the entropy for *n*-alkanes, i.e., the change in the Gibbs energy increases with the increasing number of carbon atoms.

(5) The change in the Gibbs energy for *n*-alcohols is dependent on the number of carbons in the molecule and is linear from $n = 3$. The relatively larger values obtained for methanol are related to its nontypical interaction with the cyclodextrin cavity in which the small methanol molecule is oriented nonsymmetrically [19] and thus must be subject to intense thermal motion. Similar results have been obtained in other chromatographic measurements [15].

(6) It follows from the dependences of the thermodynamic quantities on the polarizability and molar volume of the sorbate (guest) molecules that ΔG is proportional to these quantities in a homologous series. For halogen derivatives and aromatics the dependence for β-CD can be approximated by a straight line, while steric hindrances are observed with the phases containing α-CD, depending on the volume and shape of the interacting molecules which affect the selectivity of the separation process. This dependence is especially important for aromatic hydrocarbons but can also be found with, e.g., the xylene isomers and other positional isomers with roughly equal molar volumes, where pronounced differences in the Gibbs energies have been found.

3.1.2. *Comparison of the Results in Dynamic and Static Systems*

In dynamic systems, e.g., during the chromatographic process, inclusion complexes of CD are formed temporarily and are probably in equilibrium with the guests bound outside the CD

cavity by weak physical interactions. To quantify the inclusion complexes formed, measurements were carried out in a closed system (in saturated vapours of the guest molecules, to which CD was exposed for at least 12 h), followed by gas chromatographic determination after thermal decomposition or dissolution in water. The equilibrium constants, K_{eq} (or K_f = formation constant), were calculated from the equation,

$$K_{eq} = \frac{n_A^{(H)}}{n_H - n_A^{(H)}} \cdot \frac{RT}{p_A}$$

where $n_A^{(H)}$ and n_H are the numbers of moles of substance A included in the host cavities and of the host, respectively, and p_A is the guest partial pressure in the gaseous phase, and were one or two orders of magnitude lower than the equilibrium constants of the inclusion complexes formed in the liquid (aqueous) phase. This difference is apparently caused by the solvation energy involved in the inclusion in the liquid phase that substantially contributes to the total interaction energy. The occupation of the CD cavities, expressing the stoichiometry, approaches the value of unity for molecules capable of forming inclusion complexes.

The study of the dynamic and static systems results in the finding that the inclusion into the CD cavity from the gaseous phase is a specific physical process in which steric properties of molecules participate in a similar way as in inclusion from solutions. The intensity of interaction is determined by the magnitude of the van der Waals forces, accompanied by hydrogen bonding with some guest types.

3.1.3. *Inclusion Properties of Cyclodextrins and Their Methylated Derivates*

The ability of CDs to form inclusion compounds can be influenced by their modification or building into polymers. The changes in the inclusion properties are given by [4]:
(1) A change in the CD cavity depth; (2) a decrease in the accessibility of the cavity owing to a spatial hindrance represented by the substituent; (3) the electric charge on the substituent that increases the strength of the bond with the oppositely charged guest; (4) the formation of very stable complexes of dimeric or polymeric CDs with bulky guests, in which two or more CD rings correspond to a single guest molecule; (5) an increased rigidity of the conformation of inclusion compounds of polymeric CDs, which may contribute to an increased complex stability.

In gas chromatography, variously esterified CD derivatives [20,21] have so far been used in which, however, the separation mechanism does not depend on inclusion. Polyurethane resins containing α- or β-CD [7], utilize hydrophobic interactions depending on the CD inclusion properties, as well as a π-electron interaction or hydrogen bonding. A polyurethane resin with a chemically modified cyclodextrin (6-deoxy-α- or β-CD) exhibits a substantially increased retention of some substances, compared with unmodified CDPU, caused by an increase in the hydrophobicity of the CD cavity from which primary hydroxyl groups were removed.

Our previous work [6] verified that α- and β-CD in the solid phase are capable of selective interaction with sorbates in the gaseous phase. We have also found in this system that the main steric effect is accompanied by other interactions, especially with polar substances, the most important being the effect of the CD hydroxyl groups. Therefore, methylated derivatives of α- and β-CD were prepared and their chromatographic properties compared with those of the parent compounds. The preparation of methylated α- and β-CD was based on the work of Casu *et al.* [17,18]. The preparations obtained were checked by TLC, IR spectroscopy and

by the determination of the active hydrogen and it was found that they were methylated to two thirds (complete methylation was not attained even when using other procedures), in positions 2 and 6 which are more readily accessible than the less reactive hydroxyl group in position 3.

The cyclodextrins and their methylated derivatives were deposited (10% w/w) on Chromosorb W (60–80 mesh) from a dimethylformamide solution, covering the support completely. The specific surface areas of the resulting stationary phases, measured by the thermal desorption method, were 1.4–2.0 m^2/g; hence the effect of the surface area need not be considered in the treatment of the retention data. *n*-Alkanes, branched alkanes, aromatic hydrocarbons and alcohols were used as sorbates. The results obtained for compounds with various structures and geometries are demonstrated in the following figures.

The large differences found for alkanes on α- and β-CD (Figures 1 and 2) are in agreement with the differences in the host cavity sizes, and in the guest dimensions. While on β-CD no great difference was found in the retention of linear and branched alkanes, a side group on the main chain is a great obstacle to inclusion into the α-CD cavity; e.g., the retention of

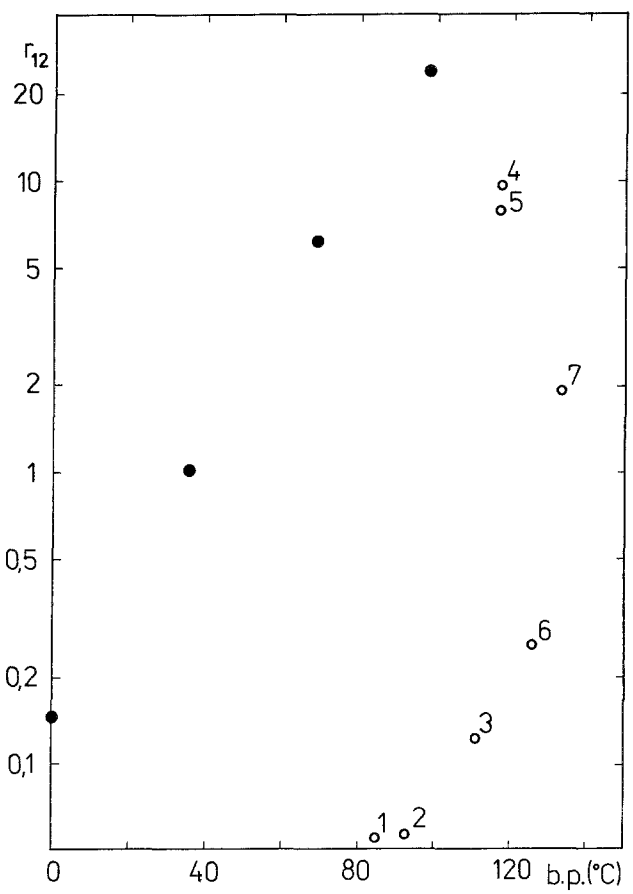

Fig. 1. Dependence of the relative retention on the boiling point for alkanes on α-CD. • – *n*-alkanes C_4–C_7, 1 – 3,3-dimethylpentane, 2 – 3-ethylpentane, 3 – 3,3-dimethylhexane, 4 – 3,4-dimethylhexane, 5 – 2-methylheptane, 6 – 2.2,4-trimethylhexane, 7 – 2,4-dimethylheptane.

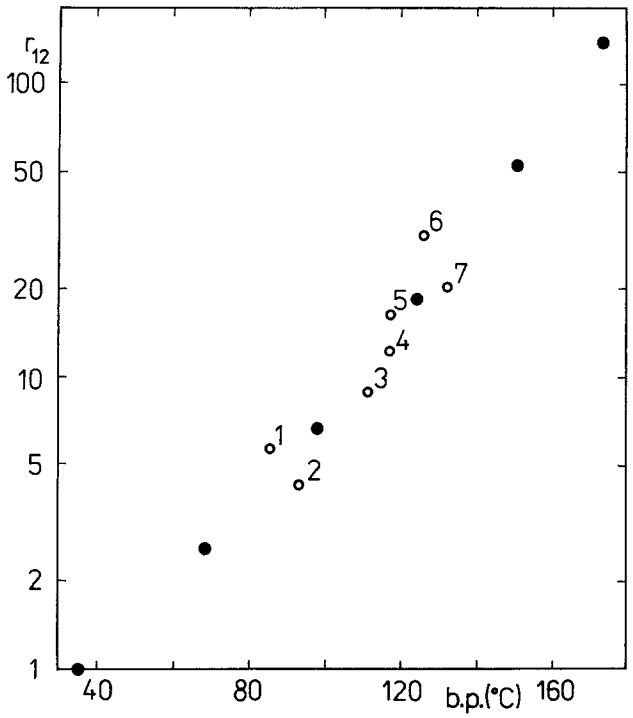

Fig. 2. Dependence of the relative retention on the boiling point for alkanes on β-CD. • – *n*-alkanes C_5–C_{10}; the other sorbates are the same as in Figure 1.

heptane is substantially higher than that of isomeric nonanes, even when the latter have higher boiling points; 2,2,4-trimethylhexane is less strongly retained than pentane. As these are nonpolar substances, the much greater retention of *n*-alkanes compared with that of branched alkanes can only be explained by the inclusion process. It follows from Figures 3 and 4 that methylation of the hydroxyl groups caused a decrease in the selectivity; the differences in the retention of *n*-alkanes and branched alkanes are less pronounced. As only dispersion forces are operative, these changes can only be explained by steric effects. The bulky methyl groups that replaced the hydrogen atoms originally present decrease the assessibility of the CD cavity. Therefore, only α-CD has practical importance for selective separation of this group of compounds.

In contrast to alkanes, pronounced stereoselectivity has not been found for the interaction of alcohols with α- and β-CD, even when the retention on α-CD is higher than that on β-CD (see Figures 5 and 6). In addition to the effect of the cavity size, hydrogen bonding between the alcohols and the cyclodextrin OH groups plays a major role in the interaction.

Methylation of the hydroxyl groups weakens the polar interaction between alcohols and cyclodextrins and the steric selectivity is again enhanced (Figures 7 and 8). Branched alcohols, being bulkier, are always retained less strongly than the corresponding linear alcohols; tertiary alcohols have the weakest retention. This effect is especially marked with Me-α-CD, but it is strong even with Me-β-CD. Methylated α-CD is suitable for separations of alcohols with similar boiling points, e.g., *tert*-butanol, *iso*-propanol and ethanol, or *tert*-pentanol, *sec*-butanol and propanol.

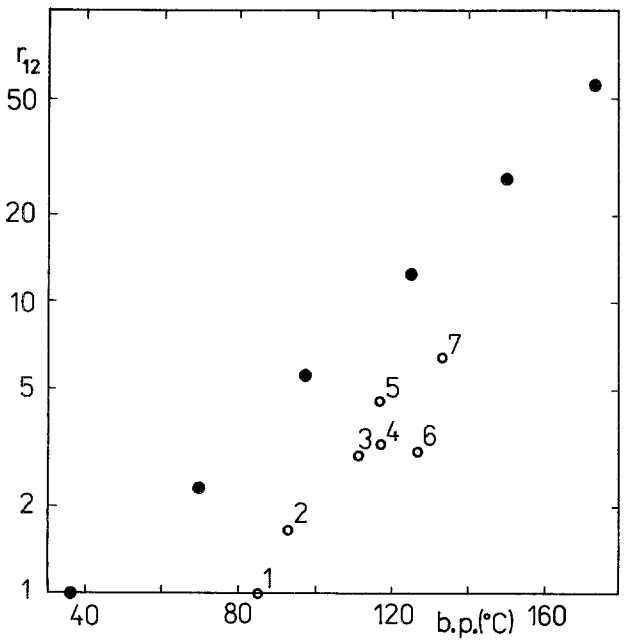

Fig. 3. Dependence of the relative retention on the boiling point for alkanes on Me-α-CD. ● – *n*-alkanes C_5–C_{10}; the other sorbates are the same as in Figure 1.

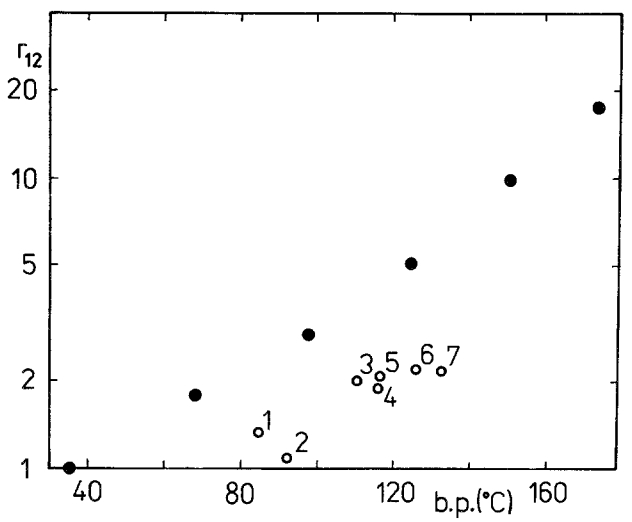

Fig. 4. Dependence of the relative retention on the boiling point for alkanes on Me-β-CD. ● – *n*-alkanes C_5–C_{10}; the other sorbates are the same as in Figure 1.

The retention data of aromatic hydrocarbons on α- and β-CD (Figures 9 and 10) again indicate an effect of the cavity size. Simple spatial assumptions permit prediction of the extent of interaction between CD and a guest. The effect of inclusion on the retention is most marked with positional isomers, e.g., *o*-, *m*-, *p*-xylenes and trimethylbenzenes. Isomers of xylene exhibit not only different retentions, but even different retention-orders on the two cyclo-

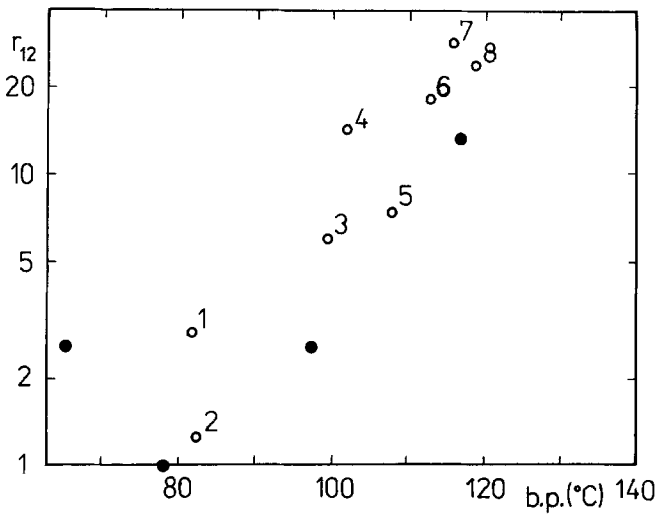

Fig. 5. Dependence of the relative retention on the boiling point for alcohols on α-CD. • – alcohols C_1–C_4, 1 – *tert*-butanol, 2 – *iso*-propanol, 3 – *sec*-butanol, 4 – *tert*-pentanol, 5 – *iso*-butanol, 6 – 3-methyl-2-butanol, 7 – 3-pentanol, 8 – 2-pentanol.

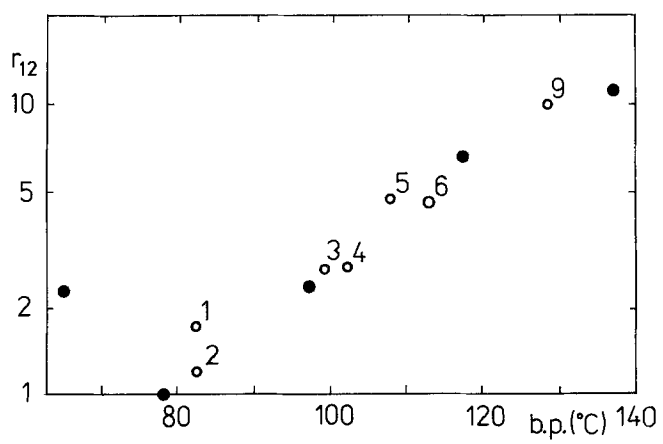

Fig. 6. Dependence of the relative retention on the boiling point for alcohols on β-CD. • – *n*-alcohols C_1–C_5; 1–6 as in Figure 5, 9 – *iso*-pentanol.

dextrins. Greater differences are again found on α-CD, where the elution order is *o*-, *m*- and *p*-isomer, while the *o*-isomer is most strongly retained on β-CD. With trimethylbenzenes, the elution order is 1,3,5 < 1,2,3 < 1,2,4-trimethylbenzene on both α- and β-CD. The most voluminous symmetrical isomer is least strongly retained by the two phases and its elution time is less than that of benzene. It can be concluded that the inclusion of the benzene ring into the CD cavity is essential for the retention of aromatic hydrocarbon isomers. An increase in the molecular volume and bulky substituents prevent inclusion of the benzene ring.

Methylation of the two cyclodextrins leads again to changes in the retention of the test substances. With β-CD the selectivity of the separation of positional isomers increases and

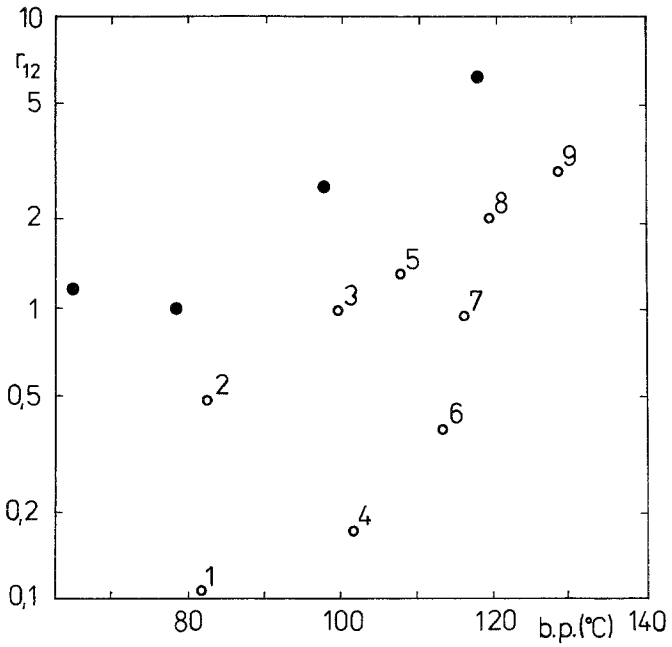

Fig. 7. Dependence of the relative retention on the boiling point for alcohols on Me-α-CD. ● – *n*-alcohols C_1–C_4; 1–8 as in Figure 5, 9 – *iso*-pentanol.

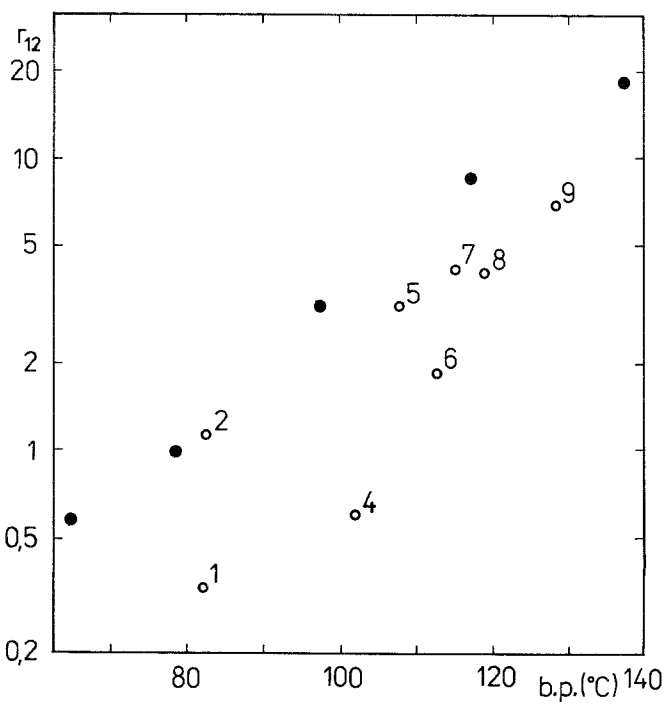

Fig. 8. Dependence of the relative retention on the boiling point for alcohols on Me-β-CD. ● – *n*-alcohols C_1–C_5, 1 – *tert*-butanol, 2 – *iso*propanol, 4 – *tert*-pentanol, 5 – *iso*-butanol, 6 – 3-methyl-2-butanol, 7 – 3-pentanol, 8 – 2-pentanol, 9 – *iso*-pentanol. 1, 2 and 4–8 as in Figure 5; 9 as in Figure 6.

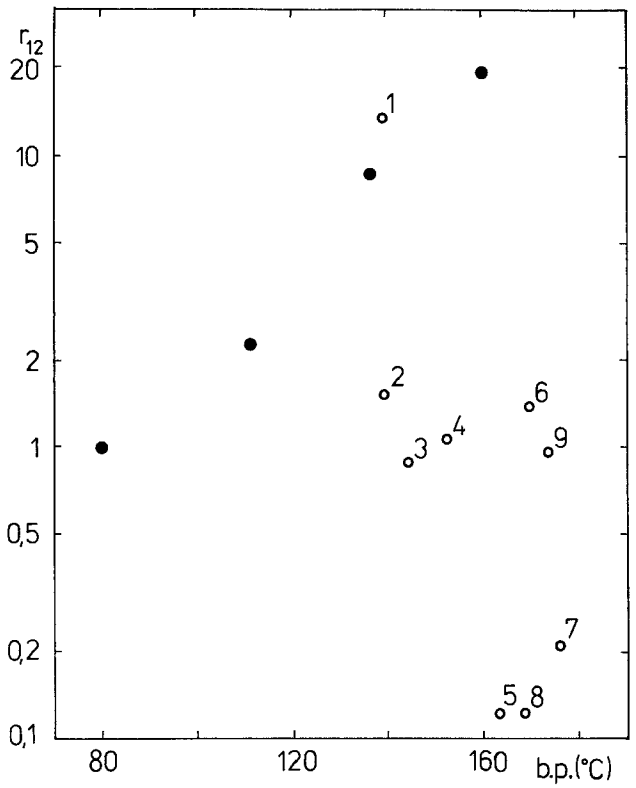

Fig. 9. Dependence of the relative retention on the boiling point for aromatic hydrocarbons on α-CD. • – benzene, toluene, ethylbenzene, *n*-propylbenzene, 1 – *p*-xylene, 2 – *m*-xylene, 3 – *o*-xylene, 4 – *iso*-propylbenzene, 5 – 1,3,5-trimethylbenzene, 6 – 1,2,4-trimethylbenzene, 7 – 1,2,3-trimethylbenzene, 8 – *tert*-butylbenzene, 9 – *sec*-butylbenzene.

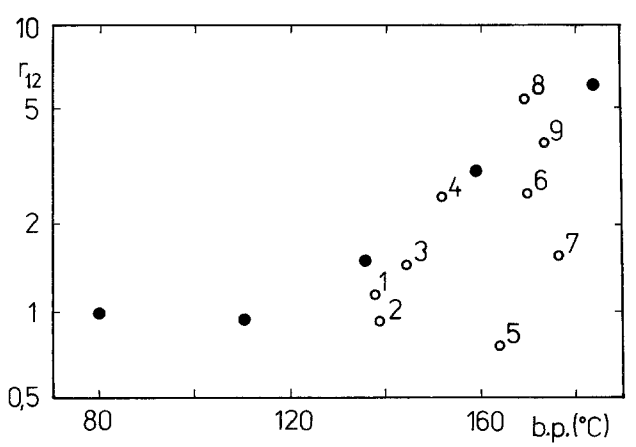

Fig. 10. Dependence of the relative retention on the boiling point for aromatic hydrocarbons on β-CD. • – benzene, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene; 1–9 as in Figure 9.

p-xylene is the most strongly retained of the xylene isomers. The situation with α-CD is similar. 1,3,5-Trimethylbenzene has a substantially shorter retention time than benzene. On the other hand, the selectivity decreases on methylated α-CD, due to steric hindrance; the differences in the retention of trimethylbenzene isomers are negligible. All these results indicate that the spatial arrangement is the predominating factor, and the contribution from specific interactions of the CD hydroxyl groups with the π-electrons of aromatic compounds is of secondary importance.

3.2. PRACTICAL USE OF THE CD INCLUSION PROPERTIES IN CHROMATOGRAPHY

The results obtained so far in the chromatographic study of CDs indicate certain advantages when they are used as stationary phases. A low efficiency, especially in GSC, is compensated by the advantage of the selectivity of the chromatographic process. A criterion often used to test the selectivity of various phases is the comparison of the relative retentions of the isomers, *m*- and *p*-xylene. Table I gives a survey of the separation efficiency for the two

Table I. Efficiency of separation of *m*- and *p*-xylenes on columns with various packings

Column type	Stationary phase	Column temperature (°C)	$V_{R_{p\text{-}x/m\text{-}x}}$	Number of plates
capillary	squalane	78	1.015	10^5
packed	Bentone 34 with a silicone phase	70	1.265	800
packed	$Ni(NCS)_2(4\text{-methyl-pyridine})_4$	80	2.60	90
packed	3.5% α-CD	100	3.80	30
capillary	4-methoxy-4′-ethoxyazobenzene (liquid crystal)	90	1.13	2.3×10^5

isomers on various stationary phases that exhibit selective inclusion interactions. For the sake of comparison, the values obtained with a highly efficient column containing a squalane stationary phase are also given. It is evident that the highest selectivity is attained on the column containing α-CD, although the plate number (determined for *p*-xylene) is the lowest, at the highest column temperature. There is a substantial difference in the selectivity even in comparison with Werner complexes which have been considered as being selective for aromatic substances. An interesting comparison can also be made with liquid crystals [22] which are again being intensively studied and used as stationary phases in capillary columns. Even in these cases, when the high efficiency of capillary columns is combined with the selective effects of liquid crystals, the selectivity is not as high as with α-CD (see Table I).

From the point of view of separation of various disubstituted benzene isomers, the works of Japanese authors [12, 13] are especially promising and deal with the use of CDs as stationary phases in liquid chromatography. Cyclodextrin was chemically bonded to polyacrylamide or silica gel and sometimes even further chemically modified. In all cases, positional isomers of disubstituted benzene derivatives were completely separated, mostly in the order, $o < m < p$-isomer, similar to our GSC measurements. Some exceptions have been encountered,

e.g., in the separation of dinitrobenzenes in a β-CD phase when the *o*-isomer is eluted last with a great delay, which is explained by the greater cross-section of the β-CD cavity and the possibility of hydrogen bonding stabilizing the inclusion complex. The liquid chromatographic separations confirm our GSC results.

In analytical evaluation, other properties of CDs must also be considered. An advantage in gas chromatography is the possibility of varying another experimental parameter, i.e., the temperature which strongly affects the CD separation properties and the time of analysis. GSC is advantageous in the speed of analysis when benzene derivatives (xylenes, diethylbenzenes and trimethylbenzenes) can be separated within seconds (see Figures 11–13), while GLC analysis requires [8,9] tens of minutes and liquid chromatography even up to one hundred minutes [12] (CD deposited on polyacrylic gels). This time has been considerably decreased by binding CD on silica gel and its acetylation [13]; the separation then also took only a few minutes. It seems that CDs chemically bonded to silica gel and possibly further modified on the hydroxyl groups will be the most suitable chromatographic material, which is also confirmed by our preliminary results, and recently documented by Armstrong and Hinze in an LC system [23].

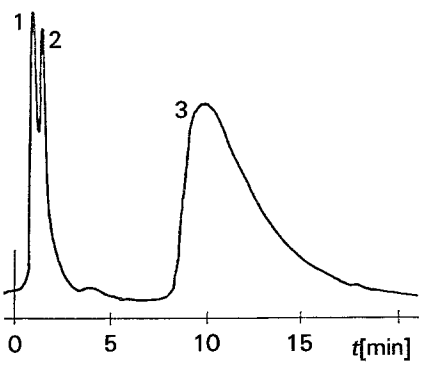

Fig. 11. Separation of a mixture of xylenes on α-CD at 90°C. (1) *o*-xylene, (2) *m*-xylene, (3) *p*-xylene.

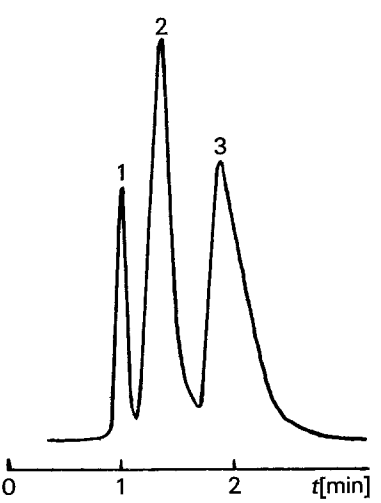

Fig. 12. Separation of a mixture of diethylbenzenes on β-CD at 90°C. (1) *o*-, (2) *m*-, (3) *p*-diethylbenzene.

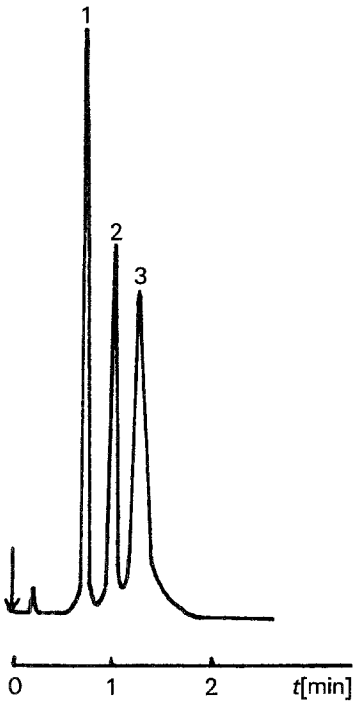

Fig. 13. Separation of a mixture of trimethylbenzenes on β-CD at 90°C. (1) 1,3,5-, (2) 1,2,3-, (3) 1,2,4-trimethylbenzene.

In this field there remains much work to be done on the optimization of the stationary phase properties on the separation conditions and on the unambiguous explanation of the complex separation mechanism in these systems.

The chromatographic study of inclusion from the gaseous phase has confirmed the ability of CDs to form inclusion complexes with known stoichiometry even with guests in the gaseous phase and this property can be used to stabilize the guest, store them and release them again into the gaseous or liquid phase [24]. By exposing a phase containing CD to substances with a known vapour tension it is possible to reproducibly prepare sufficiently stable inclusion complexes that dissociate at an elevated temperature or in aqueous solution and release the guests. This procedure makes it possible to prepare standard solutions of very low concentrations (e.g., 15 μg toluene/l). One of the many possibilities of the application of these complexes is the preparation of standards of gaseous substances for gas chromatographic analysis of trace concentrations of substances.

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