Gas chromatographic study of the inclusion properties of dibenzo-24-crown-8 ether

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ABSTRACT

The inclusion properties of dibenzo-24-crown-8 ether were studied in gas–solid chromatography (GCS) and gas–liquid chromatography (GLC) systems. Substances potentially capable of interacting with the cavity of the crown ether —homologous series of alkanes, alcohols, ethers, aromatics and halogenated hydrocarbons— were used as the sorbates and solutes. It was found that inclusion compounds are formed with methanol, ethanol, dichloromethane, trichloromethane, 1,2-dichloroethane, diiodomethane and the aromatic nucleus of aromatics under conditions used in the GSC system and with dichloromethane, trichloromethane, 1,2-dichloroethane, diiodomethane and the aromatic nucleus of aromatics in the GLC system.

INTRODUCTION

Crown ethers, which are macrocyclic polyethers, are primarily used for selective binding of metal cations in order to transfer the cations into non-polar media. However, many crown ethers also form inclusion compounds with organic molecules [1,2].

This study of the inclusion properties of dibenzo-24-crown-8 ether (DB-24-C-8) (Fig. 1) is a continuation of the previous work [3], in which the formation of inclusion compounds of dibenzo-18-crown-6 and tribenzopyridine-21-crown-7 ethers with lower *n*-alcohols was demonstrated under gas chromatographic conditions. The use of DB-24-C-8 ether in gas chromatography is rare [4,5].

The aim of the present work was to study the inclusion properties of crown ethers with a cavity size of 0.3 × 0.6 nm [6], which is large enough for the inclusion of simple organic molecules.

EXPERIMENTAL

The stationary phases for gas–solid chromatography (GSC) were prepared by dissolving the crown ether in N,N-dimethylformamide, coating Chromosorb W (60–80 mesh) with this solution and evaporating the solvent at 55°C *in vacuo* (10–20 Pa). The stationary phase obtained, containing 8% (w/w) DB-24-C-8 ether, was used to fil micropacked glass columns (1.6 m × 1 mm I.D.). The stationary phas-
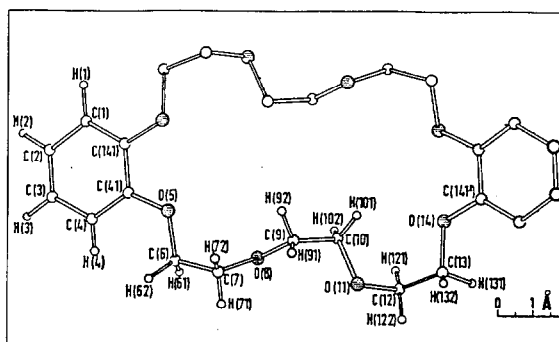

Fig. 1. Crystal structure of the molecule of dibenzo-24-crown-8 ether. The centrally symmetrical atoms are denoted by a superscript I. (according to Ref. 4).

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es for gas–liquid chromatography (GLC) were prepared by separately dissolving the crown ether and methylsilicone gum SE-30 in chloroform, mixing the two solutions, coating the mixture on Chromosorb W (CHS) 60–80 mesh and evaporating the solvent at 55°C under atmospheric pressure. The stationary phase thus obtained, containing 8% DB-24-C-8 ether and 4% SE-30 (w/w, CHS), was used to fill a micropacked glass column (1.5 m × 1 mm I.D.).

The measurements were carried out on a CHROM 61 gas chromatograph equipped with a flame ionization detector (Laboratorní přístroje, Prague, Czechoslovakia). The column temperature was 70°C and the flow-rate of the nitrogen carrier gas was 6.7 ml/min. Head-space sample injection was used, with Hamilton microsyringes. All the substances used were of analytical reagent purity.

RESULTS AND DISCUSSION

The formation of inclusion compounds of DB-24-C-8 ether was studied with homologous series of alkanes, alcohols, ethers, aromatics and halogenated hydrocarbons. The steric effects on the retention of these substances were found from the dependence of the logarithm of the capacity ratio on the boiling temperatures or the volumes of the test molecules. The effect of the pure supporting material was considered. The effect of the methylsilicone component (SE-30) in the GLC stationary phase was eliminated by using the difference in the capacity ratios (dk) between the phase used (SE-30 + DB-24-C-8) and pure SE-30. The results obtained were critically evaluated by comparing the size of the DB-24-C-8 ether cavity with the sizes of the solute molecules.

Retention behaviour of alkanes and alkenes

The alkane and alkene homologues are eluted in order of their boiling temperatures. Dispersion interactions predominate; with alkenes, interactions between the π-electrons of the multiple bond and the electron-deficient $-CH_2-CH_2-$ groupings of the polyether ring in the crown ether also play a role. No steric preference was observed.

Retention behaviour of alcohols

In the GSC system, the values for methanol and

ethanol deviate considerably from the log k versus boiling temperature linear dependence in the n-alcohol homologous series (Fig. 2). The dependence of log k on the polarizability of the solutes also indicates an increased retention of the two substances (Fig. 3). A comparison of the sizes of the molecules and the DB-24-C-8 ether cavity demonstrates that methanol and ethanol are included into the DB-24-C-8 ether cavity in the GSC system. Higher alcohols are not included, but their retention behaviour is affected by the position of the hydroxyl group in the chain. The presence of the multiple bond in alkenols exerts no substantial influence on their retention, as hydrogen bonding between the alcohol hydroxyl group and the electron-donor oxygen atoms in the polyether ring remains the predominating interaction. The coating of the relatively active surface of Chromosorb W with the crown ether eliminates the specific interaction sites in the surface, which leads to a perceptible improvement in the column efficiency in separations of alcohols and also of many other polar substances.

In contrast to the GSC system, the GLC system exhibited no steric preference in the retention of homologous alcohols.

Retention behaviour of ethers

Acyclic homologous ethers are eluted in order of their boiling temperatures in GSC. Cyclic tetrahydrofuran is more retained, and the stereochemistry of this molecule suggests possible inclusion in the DB-24-C-8 ether cavity.

The ethers behave similarly in the GLC system. However, information about the system (especially about the DB-24-C-8 ether structure in the SE-30 medium) is not sufficient for deciding whether inclusion is the predominating factor in increased retention of cyclic ethers.

Retention behaviour of aromatics

It is evident from Fig. 4 that aromatics are more retained in the GSC system than with cyclohexane/cyclohexene. The sterically most likely cause of this behaviour is inclusion of the aromatic nucleus in the DB-24-C-8 ether cavity. Increased retention of o-xylene and decreased retention of p-xylene and p-ethyltoluene (Figs. 5 and 6) make it possible to estimate a probable steric arrangement of these molecules during interaction with DB-24-C-8 ether. Xy-
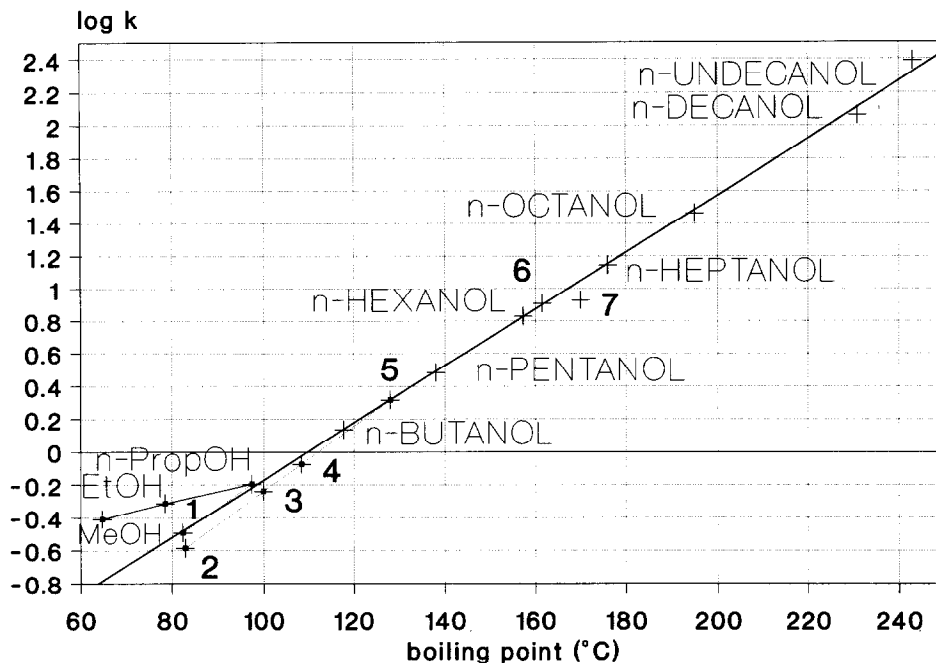
Fig. 2. Retention behaviour of alcohols in the GSC system: relationship between the logarithm of the capacity ratio and the boiling point. 1 = 2-propanol; 2 = *tert.*-butanol; 3 = *sec.*-butanol; 4 = isobutanol; 5 = isopentanol; 6 = cyclohexanol; 7 = methylcyclohexanol. MeOH = Methanol; EtOH = ethanol; n-PropOH = *n*-propanol.
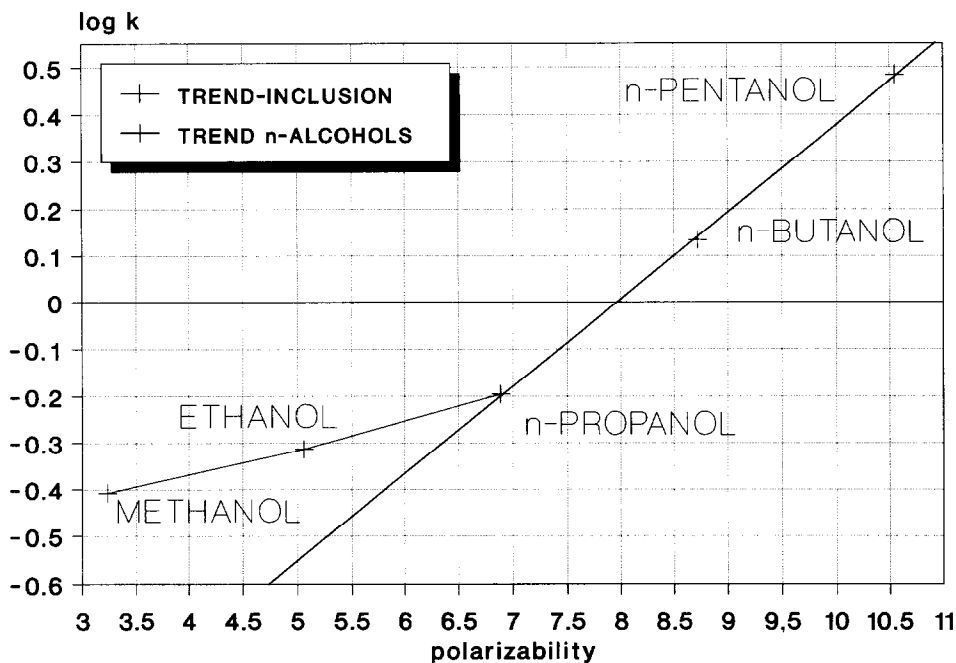

Fig. 3. Retention behaviour of lower alcohols in the GSC system: relationship between the logarithm of the capacity ratio and the polarizability.
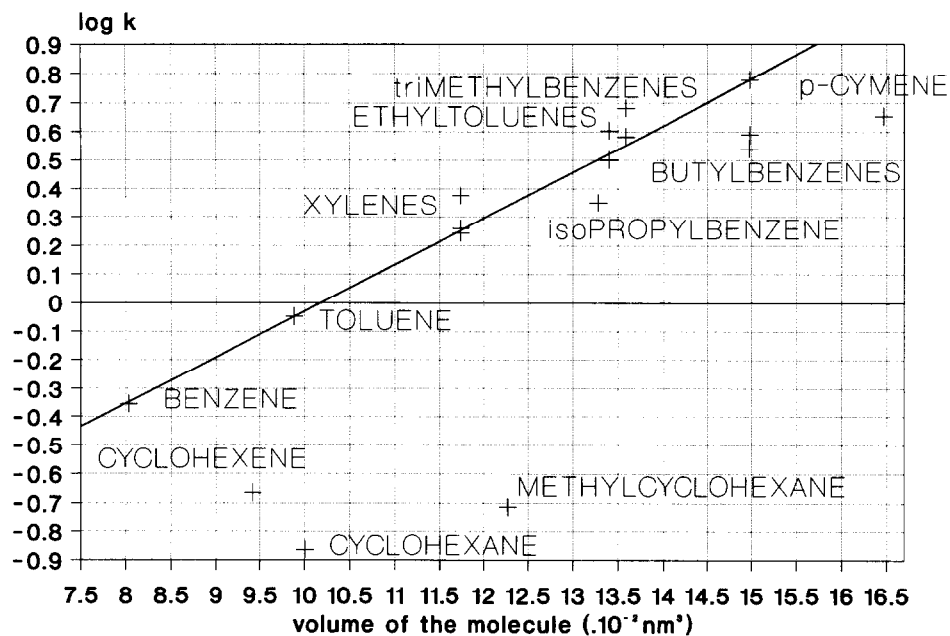
Fig. 4. Retention behaviour of aromatics in the GSC system: relationship between the logarithm of the capacity ratio and the volume of the molecule.
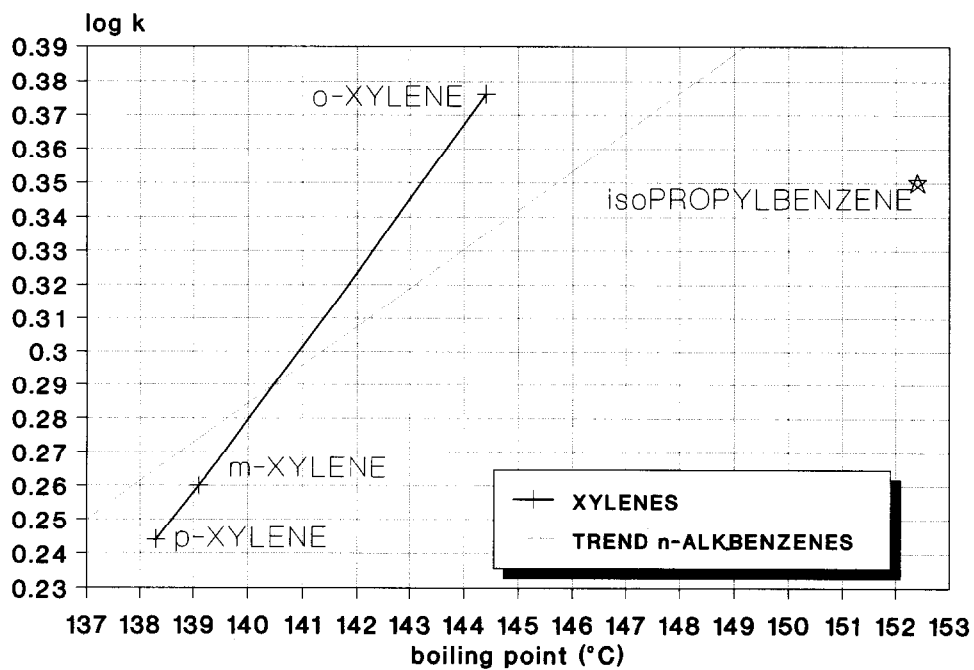

Fig. 5. Retention behaviour of xylenes in the GSC system: relationship between the logarithm of the capacity ratio and the boiling point. Alk. = Alkyl.
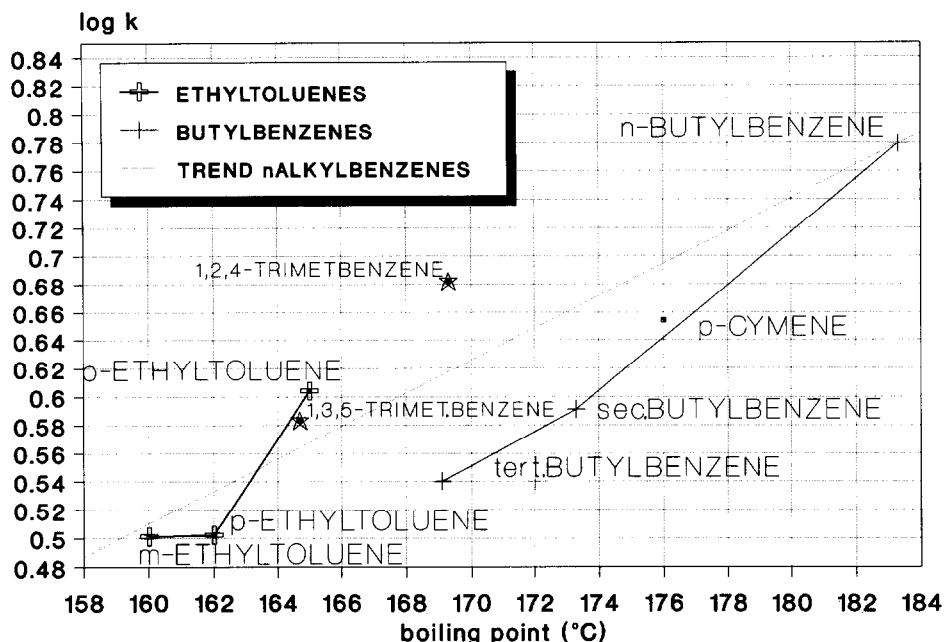
Fig. 6. Retention behaviour of ethyltoluenes and butylbenzenes in the GSC system: relationship between the logarithm of the capacity ratio and the boiling point. Met. = Methyl.

lenes and ethyltoluenes can, at least partially, enter the DB-24-C-8 ether cavity and thus form inclusion complexes. It is likely that the six-fold symmetry axis of the benzene ring in xylene (the guest) is oriented at right angles to the line connecting the aromatic rings of DB-24-C-8 ether (the host) and lies approximately in the plane of the polyether ring of DB-24-C-8 ether during the inclusion process. The π-electron system of the guest interacts with the electrophilic atom grouping at the C-9, C-10, C^I-6 and C^I-10 carbons (see Fig. 1). The electrophilic methyl/ethyl group interacts with the two strongly nucleophilic sites formed by the aromatic rings of DB-24-C-8 ether and the oxygen atoms O-5, O^I-14 or O-14, O^I-5. With this mutual orientation, inclusion is sterically easiest with the *ortho* isomer and the greatest steric hindrance is encountered with the *para* isomer (Fig. 7). The butyl derivatives of benzene interact in the same way, the electrophilic butyl chain interacting with the nucleophilic space around the DB-24-C-8 ether aromatic nucleus. The interaction is sterically easiest with the *n*-butyl chain and most difficult with *tert.*-butyl ones.

The mixture of acyclic (C_5–C_7), cyclic (C_6) and

aromatic (benzene, *o*-xylene, *p*-xylene, 1,3,5-trimethylbenzene and *n*-butylbenzene) hydrocarbon compounds was injected onto a DB-24-C-8 column on the GSC system at a column temperature 32°C and flow-rate of 6.0 ml/min. Separation of aromatic hydrocarbons from the acyclic and cyclic hydrocarbons was achieved.

The aromatic nucleus is also completely or partially included in the DB-24-C-8 ether cavity in the GLC system (Fig. 8). It can be assumed from the steric preference of *p*-xylene over the *ortho* and *meta* derivatives (Fig. 9) that methylsilicone medium probably favours interaction between the weakly electron-deficient methyl groups and the electron-
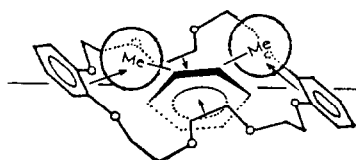

Fig. 7. Probable steric arrangement of inclusion complex of *o*-xylene and dibenzo-24-crown-8 ether (schematic).
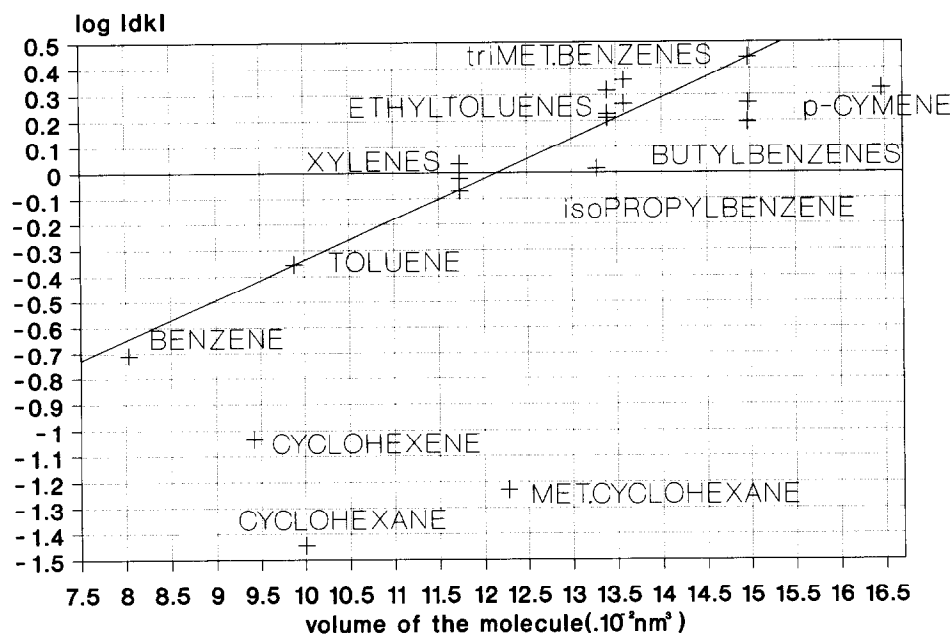
Fig. 8. Retention behaviour of aromatics in the GLC system: relationship between the logarithm of the difference in the capacity ratios (dk) of the phase used (SE-30 + DB-24-C-8) and pure SE-30 and the volume of the molecule.

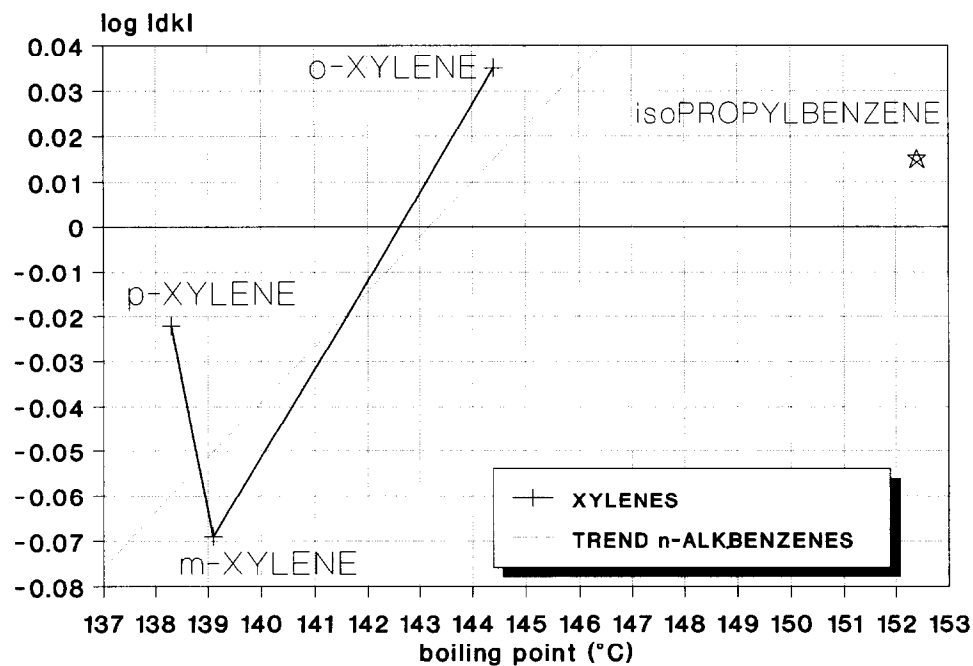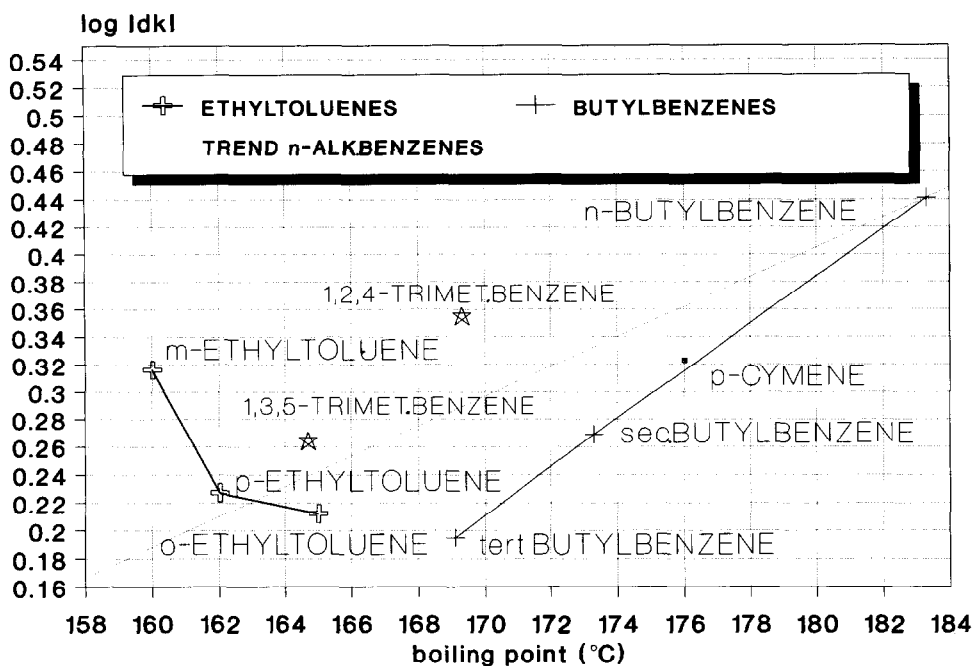Fig. 9. Retention behaviour of xylenes in the GLC system: relationship between log dk and the boiling point.

Fig. 10. Retention behaviour of ethyltoluenes and butylbenzenes in the GLC system: relationship between log dk and the boiling point.

donor areas of the benzene nuclei in DB-24-C-8 ether prior to complete inclusion of the xylene molecule in the DB-24-C-8 ether cavity. Under these conditions, the *para* position is the most favourable arrangement of the methyl substituents. The retention of ethyltoluenes and butylbenzenes in the GLC system can be seen in Fig. 10. The highest retention of the *meta* isomer can be caused by interaction of the alkyl substituents with the DB-24-C-8 ether benzene nuclei, as described above, which accompanies partial inclusion of the *m*-ethyltoluene benzene nucleus into the DB-24-C-8 ether cavity. This accompanying interaction is more likely with the *meta* isomers than with the para isomer, provided that the two interacting molecules have a suitable spatial arrangement. The group of butylbenzenes exhibits similar interactions to the GSC system.

Retention behaviour of halogen derivatives

Fig. 11 summarizes the retention behaviour of halogen derivatives in the GSC system. The compounds fall into two groups. The first group includes rather small molecules: dichloromethane, tri-

chloromethane, 1,2-dichloroethane and diiodomethane. The other group involves compounds with large molecules or long alkyl chains: tetrachloromethane, tetrachloroethane, *n*-heptyl-, *n*-octyl- and *n*-decylchloride. The compounds from the first group are retained substantially more strongly than those from the other group. This fact cannot be satisfactorily explained using only a purely electrostatic model of interaction. On the basis of a stereochemical study of these substances, the retention behaviour can be explained by inclusion of the molecules from the first group into the DB-24-C-8 ether cavity. The behaviour of halogen derivatives is identical in the GLC system.

CONCLUSION

The results obtained indicate that gas chromatographic measurement can significantly contribute to the evaluation of the properties of dibenzo-24-crown-8 ether and to the characterization of its interactions with various organic substances. Dibenzo-24-crown-8 ether can be classified among the
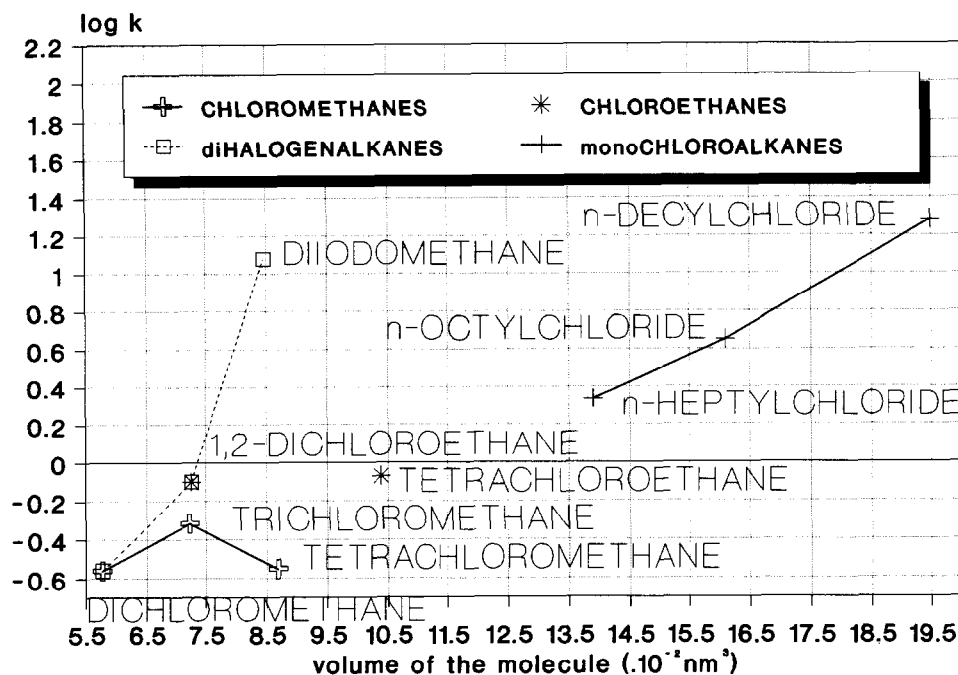
log k

Fig. 11. Retention behaviour of halogen derivatives in the GSC system: relationship between the logarithm of the capacity ratio and the boiling point.

substances whose specific spatial interactions with benzene derivatives can be used to study inclusion phenomena in gas chromatography. In contrast to α-cyclodextrin, dibenzo-24-crown-8 ether also specifically interacts with methanol and ethanol in GSC systems.

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