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USE OF GAS CHROMATOGRAPHY FOR A STUDY OF CROWN ETHERS

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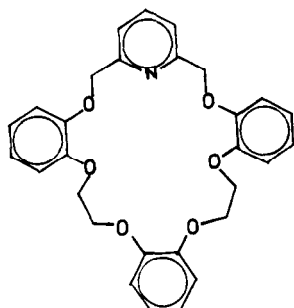
SUMMARY

The inclusion properties of dibenzo-18-crown-6 and the recently described tribenzopyridine-21-crown-7 were studied gas chromatographically. Substances potentially capable of interacting with the cavities of the above crown ethers (alkanes, alcohols, amines) were used as the sorbates. It was found that inclusion compounds are formed with lower members of the homologous series of *n*-alcohols, whereas amines interact through hydrogen bonding.

INTRODUCTION

Studies of various crown ethers have indicated that substitution on the basic skeleton affects their physical properties and inclusion selectivity^{1–6}. Peripheral substituents influence the shape of the space within the crown ether and the overall lipophilicity of the system, which is manifested in an increased selectivity toward guest molecules. The inclusion selectivity is also affected by the basicity of the heteroatoms.

Whereas crown ethers have often been employed in liquid chromatography for selective separations, as components of either the stationary or the mobile phase, their use in gas chromatography has so far been rare. Graphitized carbon black and Carbochrome have been modified by dibenzo-18-crown-6 and dinitrobenzo-18-crown-6 and used as stationary phases for the separation of *n*-alkanes, aromatic hydrocarbons and chlorinated compounds⁷. This modification leads to a lowering in the number of non-specific interaction sites and in the energy of interaction and thus to a shortening of the retention times with preservation of the original elution order. Crown ethers deposited on Firebrick have been used for separation of dichloro-



Tribenzopyridine-21-crown-7

phenols⁸. Capillary columns with crown ethers chemically bonded to polymers have also been employed⁹.

The present paper is concerned with dibenzo-18-crown-6 [DB(18)C-6], whose inclusion properties have been studied and whose selectivity has been utilized in various liquid chromatographic separations¹⁰⁻¹⁶, and with the recently described tribenzopyridine-21-crown-7 [TBP(21)C-7] which has not yet been used in chromatography¹⁷.

EXPERIMENTAL

The measurements were carried out on a Chrom 5 gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia). The stationary phases were prepared by dissolving the crown ethers in dimethylformamide, depositing them on Gas Chrom Q (60-80 mesh) and evaporating the solvent at 50°C and a decreased pressure (10-20

TABLE I

RETENTION DATA FOR ALKANES, ALCOHOLS AND AMINES ON DB(18)C-6, TBP(21)C-7 AND SOLID SUPPORT

$t_{\text{column}} = 70^\circ\text{C}$, flow-rate 6.7 ml N₂/min.

Compound	B.p. (°C)	Solid support		DB(18)C-6		TBP(21)C-7	
		t'_R (s)	$\log r_{12}$	t'_R (s)	$\log r_{12}$	t'_R (s)	$\log r_{12}$
Pentane	36.1	1.2	0	1.3	0	1.2	0
Hexane	69.0	2.2	0.263	2.2	0.228	2.3	0.283
Heptane	98.0	4.1	0.534	4.2	0.509	4.9	0.611
Octane	125.7	7.4	0.790	8.6	0.821	7.9	0.818
Nonane	150.8	13.2	1.041	12.3	0.976	15.9	1.122
Decane	174.1	19.7	1.215	20.8	1.204	24.0	1.301
Undecane	195.0	36.3	1.481	35.3	1.434	40.8	1.531
Dodecane	216.0	50.1	1.621	51.8	1.600	65.6	1.738
Cyclohexane	81.0	2.9	0.383	2.9	0.348	3.0	0.398
Isoheptane	90.0	3.4	0.452	3.2	0.391	3.6	0.477
Isooctane	99.3	4.3	0.554	4.2	0.509	4.5	0.574
Methanol	64.7	64.3	1.729	378.4	2.464	344.2	2.458
Ethanol	78.5	72.5	1.781	308.9	2.376	527.5	2.643
<i>n</i> -Propanol	97.2	85.1	1.851	237.6	2.262	375.8	2.496
<i>n</i> -Butanol	117.3	109.4	1.960	162.9	2.098	326.7	2.435
<i>n</i> -Pentanol	138.0	120.2	2.001	136.2	2.020	229.8	2.282
<i>n</i> -Hexanol	158.0	139.4	2.065	175.0	2.129	267.2	2.348
<i>n</i> -Heptanol	177.0	175.1	2.164	232.8	2.253	372.8	2.492
<i>n</i> -Octanol	194.0	204.2	2.231	301.5	2.365	420.6	2.545
2-Propanol	82.4	62.3	1.715	65.2	1.700	80.5	1.827
2-Butanol	108.0	83.8	1.844	88.4	1.835	90.6	1.878
2-Pentanol	132.0	102.6	1.932	105.5	1.909	110.4	1.964
Butylamine	77.8	308.5	2.410	841.3	2.811	892.8	2.871
Cyclohexylamine	134.5	384.8	2.506	983.9	2.879	1074.4	2.952
Diethylamine	56.3	299.4	2.397	633.8	2.688	645.9	2.731
Dipropylamine	110.0	345.3	2.459	649.0	2.698	680.6	2.754
Triethylamine	90.0	314.2	2.418	256.9	2.296	289.8	2.383

Tribenzopyridine-21-crown-7

Pa). This material, containing 10% (w/w) of a given crown ether, was packed in glass columns $1.2 \text{ m} \times 1 \text{ mm}$ I.D.

The crown ether DB(18)C-6 was obtained from the Laboratory of Adsorption and Chromatography, Moscow State University, and TBP(21)C-7 was provided by the Institute of Organic Chemistry and Biochemistry, University of Bonn.

The sorbates involved molecules of various structural types with various inclusion abilities (alkanes, alcohols, amines).

RESULTS AND DISCUSSION

The retention data for the test substances, obtained at 70°C on the stationary phases with DB(18)C-6, TBP(21)C-7 and on the pure support, are summarized in Table I. From the table and Figs. 1 and 2 in which the data are plotted for DB(18)C-6 and the pure support, respectively, non-polar alkanes are very weakly retained on DB(18)C-6 and are eluted in the order of their boiling temperatures irrespective of their structures.

Alcohols are bound much more firmly than alkanes on this phase because of hydrogen bonding. Methanol to butanol exhibit an anomalous behaviour. The significant increase in the retention of methanol can be explained by inclusion of the whole molecule in the DB(18)C-6 cavity. The retention decreases with increasing length of the *n*-alcohol chain, in agreement with decreasing stability of the complexes

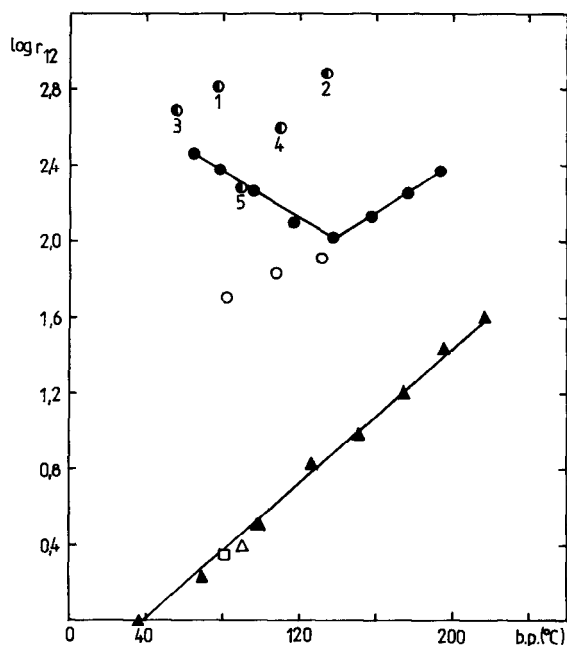


Fig. 1. Relationship between the relative retention and the boiling point on the solid support; $t_c = 70^\circ\text{C}$. ▲, *n*-alkanes (pentane to dodecane); □, cyclohexane; △, isoheptane and isoctane; ●, *n*-alcohols (methanol to octanol); ○, 2-propanol, 2-butanol and 2-pentanol; ⊙, amines (1 = butylamine, 2 = cyclohexylamine, 3 = diethylamine, 4 = dipropylamine, 5 = triethylamine).

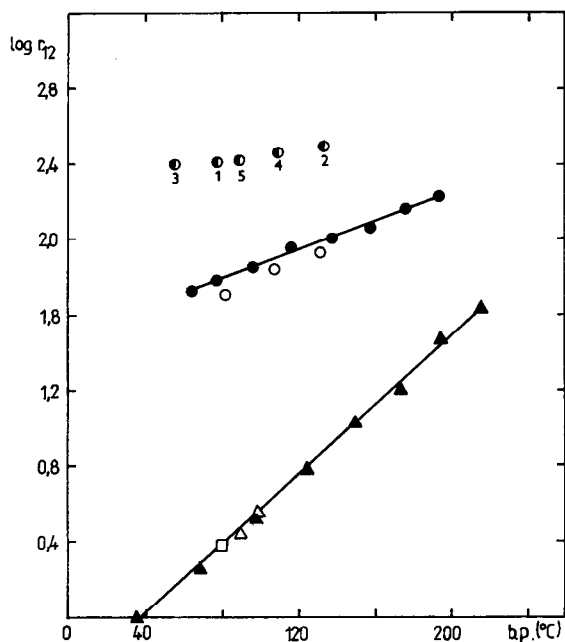


Fig. 2. Relationship between the relative retention and the boiling point on DB(18)C-6. Details as in Fig. 1.

between DB(18)C-6 and *n*-alcohols. The retention times of higher alcohols (*n*-pentanol to *n*-octanol) increase with increasing boiling temperatures. These alcohols form no inclusion compounds with DB(18)C-6, apparently due to the increasing non-polar character of the molecule. The selectivity of the crown ether for the lower members of the *n*-alcohol homologous series is also connected with the fact that DB(18)C-6 is capable of forming cage-shaped inclusion structures but cannot form channel structures as do some other host molecules. Branching of the alcohol chain is a steric hindrance for the formation of inclusion compounds and thus branched alcohols are eluted in the order of the boiling temperatures.

The amines studied in this paper (butyl-, cyclohexyl-, diethyl-, dipropyl- and triethylamine) are apparently not included and their retention is caused by hydrogen bonding. Primary amines, forming hydrogen bonds between the NH_2 group and the oxygen atoms of the crown ether, are retained most strongly. Complexes are probably formed, in which a single amine molecule is hydrogen bonded at each side of the crown ether ring. Secondary amines that can form only a weak hydrogen bond between the NH group and the crown ether oxygen atoms are eluted more rapidly. Triethylamine, incapable of hydrogen bonding, is eluted most rapidly and its retention time is identical with that observed on the pure support.

The experimental results obtained for TBP(21)C-7 (see Table I and Fig 3) are analogous to those for DB(18)C-6. Alkanes and branched alcohols are eluted in the order of the boiling temperatures.

The retention times of *n*-alcohols are, on the whole, higher than those obtained on DB(18)C-6, owing to hydrogen bonding between the pyridine nitrogen and the

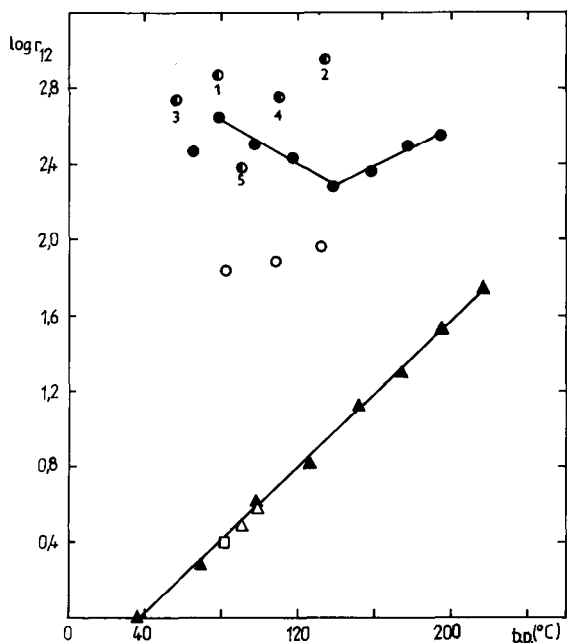


Fig. 3. Relationship between the relative retention and the boiling point on TBP(21)C-7. Details as in Fig. 1.

hydrogen of the hydroxyl group. Compared to the measurement with DB(18)C-6, ethanol is retained most strongly, as the TBP(21)C-7 cavity is larger. This finding is in agreement with the results for the formation of inclusion complexes in solution, when during crystallization from a methanol + ethanol mixture, ethanol is preferentially bound¹⁸. Methanol, propanol and butanol also exhibit significantly higher retention times than those corresponding to their boiling temperatures. The retention times of higher members of the homologous series again increase as a function of their boiling temperatures.

The elution order of the amines is again the same as on the phase with DB(18)C-6. Triethylamine is retained least, followed by secondary amines and the longest retention times are exhibited by primary amines. The retention times on the two phases are not very different. This confirms the assumption that the amines are not included in the crown ether cavities, as the increase in the cavity diameter does not lead to pronounced changes in the retention times.

The results obtained indicate that gas chromatographic measurements can significantly contribute to the evaluation of the properties of newly prepared crown ethers and to characterization of their interaction with various organic substances.

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