The Effect of Water Vapour on the Cyclodextrin–Solute Interaction in Gas–Solid Chromatography

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Abstract. The effect of water vapour on the interaction between the solutes and a cyclodextrin was studied chromatographically in a gas/solid system. It has been shown that all the sorbates capable of forming inclusion complexes with α-CD are affected by the presence of water, in contrast to the sorbates that do not interact with α-CD, which are unaffected. The measurements were carried out with the cyclodextrin deposited on a solid carrier (Chromosorb W) and with water vapour contained in the mobile phase. Some advantages of this system have been demonstrated for an analytical application.

Key Words. Sorbate-cyclodextrin interaction, Effect of water vapour, Gas-solid chromatography, Analytical applications.

1. Introduction

Cyclodextrins (CDs) have recently found use as stationary phases in gas-solid chromatography (GSC) [1–8, 12–14] and in gas-liquid chromatography (GLC) [8–11], because of their selective separation capability. Their application to separations of stereoisomers (alkenes, pinenes) and positional isomers of aromatics (xylenes, trimethylbenzenes) has been found to be very advantageous. The inclusion process, which underlies selective separations, is, with cyclodextrins, also affected by the presence of water. It is well known that cyclodextrins form crystal hydrates and that the water of crystallization participates in the formation of inclusion complexes [15]. On the formation of an inclusion complex, the water molecules included in the CD cavity are liberated preferentially. This liberation is further enhanced under the dynamic conditions of gas chromatography. It can thus be assumed that water also plays an important role in the equilibrium processes between CD and a guest (sorbate) in the gaseous state.

  To evaluate the intensity of the effect of water on the inclusion process, the conditions were modelled, so that the mobile phase consisted of an inert carrier gas saturated with water vapour, whereas a cyclodextrin represented a solid stationary phase. The use of mixed mobile phases consisting of water vapour in an inert gas has been known in gas chromatography for rather a long time [16, 17] and it is still utilized [18]. The water vapour present in the carrier gas affects the properties of the mobile phase (polarity, viscosity), as well as those of the stationary phase (interaction of the water vapour with the sorbent active sites). With cyclodextrins, the water

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enclosed in the cavities has also the function of a 'catalyst' of the inclusion complex formation. Therefore, it could be expected that the presence of water vapour in the carrier gas might not only affect the surface of the stationary phase, but also cause substantial changes in the formation of the inclusion complex, i.e. in the equilibration between the sorbate and the inclusion compound.

2. Experimental

α- and β-CD (Chinoin, Budapest) were deposited on Chromosorb W (60–80 mesh) from a dimethylformamide solution. The CD content in the stationary phase was determined from the results of organic elemental analysis and amounted to 4.75% wt. for α-CD and 7.32% wt. for β-CD. Columns 1200 mm long, 3 mm I.D., were used.

The chromatographic measurements were carried out on a CHROM 41 instrument (Laboratorní Přístroje, Prague, Czechoslovakia) with a flame ionization detector (FID). Mixed mobile phases were obtained by including a thermostatted water-saturator in the carrier gas stream. The measurements were carried out at water vapour pressures of 1.33, 2.97, and 6.50 kPa, corresponding to 0.8, 1.7, and 4.3% wt., respectively. The water vapour content in the carrier gas was determined gravimetrically, by absorption in $Mg(ClO_4)_2$. The carrier gas flow rate was 60 ml/min and the column temperature was 80 °C. Dilute vapours of the samples were injected with a Hamilton 10 µl syringe.

3. Results and Discussion

3.1. THE EFFECT OF WATER VAPOUR ON THE SORBATE RETENTION

As is demonstrated by the results summarized in Tables I and II, introduction of water vapour into the carrier gas led to a decrease in the retention times of all the sorbates, compared with those obtained in the dry carrier gas. An analogous decrease in the retention times when using water vapour in the carrier gas was also described in e.g. the paper by Guillemin and Millet [18]. The authors employed much higher water vapour contents (above 10%) and classical adsorbents (silica gel, alumina, porous polymers). With cyclodextrins, a perceptible decrease in the retention occurs even for 0.8% water vapour in the carrier gas. This phenomenon can be explained by partial adsorption of water molecules on the stationary phase surface, in a similar manner to common adsorbents. However, the experimental results, especially those obtained with α-CD as the stationary phase (Table I), indicate an effect on the equilibrium in the formation of the sorbate–cyclodextrin inclusion complex, in favour of the free guest. A great excess of water vapour over the sorbate apparently leads to competitive inclusion of water molecules and thus to faster desorption of the guest.

The dependence of the retention times of various sorbates on the water vapour pressure in the carrier gas, obtained for α-CD, can be formally classified into three groups, on the basis of the curve shape, characteristic of certain groups of substances:

1. Linear dependences with permanent decrease.
2. Hyperbolic dependences with a faster decrease at lower water vapour pressures.
3. Dependences with a very small dependence of the sorbate retention times on the water vapour concentration in the carrier gas.

Table I. Corrected retention times of sorbates on α-CD and their dependence on the water vapour in the carrier gas

Water vapour pressure (kPa)		0	1.33	2.97	6.50
Substance	b.p.($^{\circ}$C)		t_R'(s)		
n-Pentane	36.2	26	–	–	–
n-Hexane	69.0	205	123	72	25
n-Heptane	98.5	980	630	405	153
Cyclopentane	50.0	38	–	9	–
Cyclohexane	78.0	293	151	66	21
Methylcyclohexane	101.0	560	223	100	32
2,2,3,3-Tetramethylbutane	106.5	6	5.5	5	4.5
3-Methylheptane	115.5	1430	890	570	235
2,4-Dimethylheptane	133.5	170	83	44	15
2,2,4-Trimethylhexane	126.0	10	–	5	–
cis-3-Methyl-3-Hexene	94.0	278	168	118	52
trans-3-Methyl-3- Hexene	93.3	21	56	31	10
Cyclohexene	83.0	230	–	34	–
Benzene	80.1	66	38	22	6
Toluene	110.8	154	87	46	13
Ethylbenzene	136.2	685	426	249	84
n-Propylbenzene	159.2	–	–	838	325
Isopropylbenzene	152.4	160	69	36	24
sec-Butylbenzene	173.0	193	89	46	28
tert-Butylbenzene	169.0	35	27	21	18
o-Xylene	144.0	68	21	10	6
m-Xylene	138.8	137	63	33	15
p-Xylene	138.5	1080	605	356	126
1,2,3-Trimethylbenzene	176.1	27	20	16	12
1,3,5-Trimethylbenzene	164.7	20	16	12	9
1,2,4-Trimethylbenzene	169.4	136	56	30	17
o-Diethylbenzene	183.4	36	28	22	17
m-Diethylbenzene	181.0	776	437	263	87
m-Diisopropylbenzene	203.2	97	76	63	49
Diisopropylbenzene	210.3	128	95	75	56
Methanol	64.6	62	21	11	9
Ethanol	78.0	58	27	17	13
1-Propanol	97.0	134	66	43	28
2-Propanol	82.4	71	44	29	19
1-Butanol	117.7	520	251	172	97
Isobutanol	108.0	300	129	103	54
1-Pentanol	137.0	1550	1200	790	400

The dependences for alkanes and cycloalkanes are given in Figure 1 and are linear for n-alkanes; 2,4-dimethylheptane alternates between the first and second type, the second type is characteristic of cycloalkanes and the third type was found with 2,2,3,3-tetramethylbutane.

It has been known from the earlier papers [2, 6–8] that n-alkanes form very strong complexes with α-CD also under the conditions of gas chromatography, whereas voluminous molecules (2,2,3,3-tetramethylbutane) cannot interact with α-CD. Hence, it can be assumed that linear dependences are obtained for strongly interacting sorbates. With increasing concentration of water vapour in the carrier gas, inclusion

Table II. Corrected retention times of sorbates on β-CD and their dependence on the water vapour in the carrier gas

Water vapour pressure (kPa)		0	1.33	2.97	6.50
Substance	b.p.(°C)		t'_R (s)		
n-Hexane	69.0	9	–	3	–
n-Heptane	98.5	34	15	9	6
n-Nonane	150.5	467	195	124	82
Cyclohexane	78.0	37	22	16	11
Methylcyclohexane	101.0	60	32	22	15
2,2,3,3-Tetramethylbutane	106.5	255	112	74	63
3-Methylheptane	115.5	92	41	28	20
2,4-Dimethylheptane	133.5	193	84	55	40
2,2,4-Trimethylhexane	126.6	207	94	65	48
Cyclohexene	83.0	51	26	20	13
Benzene	80.1	59	33	22	14
Toluene	110.8	102	45	31	18
Ethylbenzene	136.2	282	118	77	45
n-Propylbenzene	159.2	880	373	231	133
Isopropylbenzene	152.4	626	304	187	118
sec-Butylbenzene	173.0	1240	600	369	234
tert-Butylbenzene	169.0	1370	735	485	315
o-Xylene	144.0	242	110	68	42
m-Xylene	138.8	202	82	52	32
p-Xylene	138.5	293	126	75	45
1,2,3-Trimethylbenzene	176.1	400	171	108	67
1,3,5-Trimethylbenzene	164.7	183	84	57	35
1,2,4-Trimethylbenzene	169.4	720	298	202	131
o-Diethylbenzene	183.4	536	234	139	98
m-Diethylbenzene	181.0	1150	495	304	183
Methanol	64.6	114	29	18	20
Ethanol	78.0	142	45	28	23
1-Propanol	97.0	518	182	122	82
2-Propanol	82.4	300	113	79	55
1-Butanol	117.7	1860	740	460	293
2-Butanol	98.0	877	336	219	138
Isobutanol	108.0	1380	595	400	274
tert-Butanol	83.0	593	232	159	110

of water is progressively more important and the retention of n-alkanes decreases. With the second group, the retention is strongly decreased even by low water concentrations. This concerns cycloalkanes, whose interaction with α-CD is complicated, in view of their conformational structures. It can be assumed from the experimental data that their interaction with the α-CD cavity is weaker and thus even low concentrations of water vapour in the carrier gas strongly shift the equilibrium in favour of the free sorbate. Sorbates with voluminous molecules that cannot be included into the α-CD cavity (2,2,3,3-tetramethylbutane) depend only negligibly on the water vapour content in the carrier gas and inclusion of water molecules has almost no effect on their retention.

Aromatic hydrocarbons (Figure 2), benzene, ethylbenzene, p-xylene, follow the first type of dependence, in agreement with the concept of their inclusion, while the
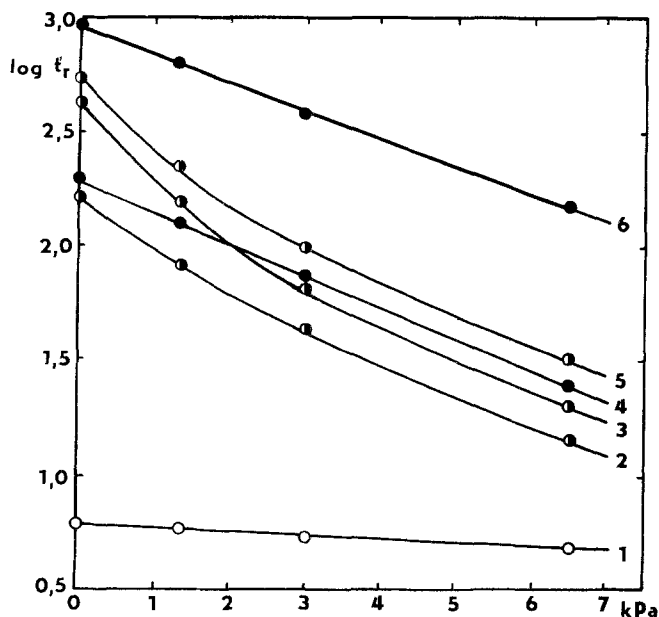
Fig. 1. A log t_R' dependence on the water vapour pressure (p) for alkanes and cycloalkanes on α-CD (● – first type, ◐ – second type, ○ – third type). 1 – 2,2,3,3-tetramethylbutane, 2 – 2,4-dimethylheptane, 3 – cyclohexane, 4 – n-hexane, 5 – methylcyclohexane, 6 – n-heptane.
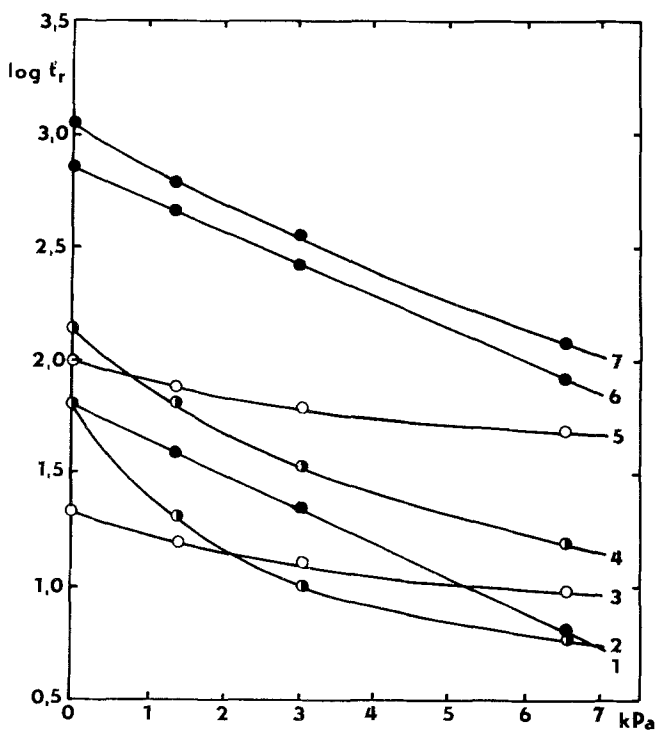

Fig. 2. A log t_R' dependence on the water vapour pressure (p) for aromatic hydrocarbons on α-CD. (● – first type, ◐ – second type, ○ – third type). 1 – benzene, 2 – o-xylene, 3 – 1,3,5-trimethylbenzene, 4 – m-xylene, 5 – m-diisopropylbenzene, 6 – ethylbenzene, 7 – p-xylene.

second type of dependence has been found for *o*- and *m*-xylene. The retention times of *m*-diisopropylbenzene and 1,3,5-trimethylbenzene are virtually independent of the water vapour content in the carrier gas.

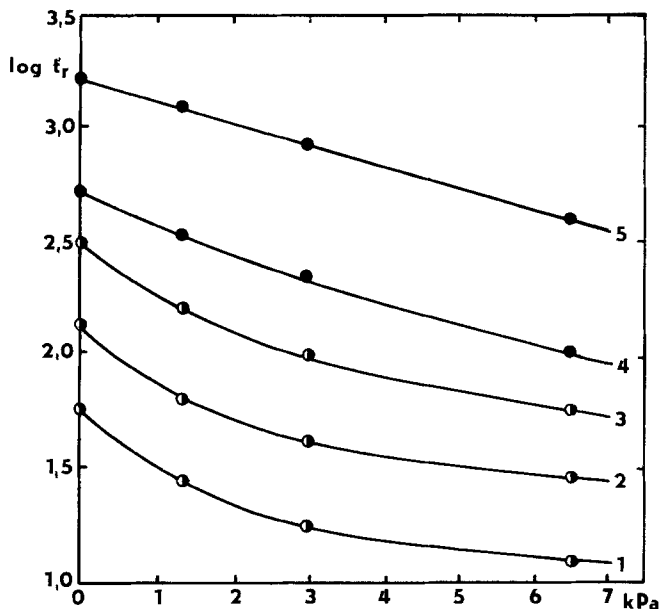The first type of dependence was obtained for the alcohols (Figure 3) 1-butanol

Fig. 3. A log t'_R dependence on the water vapour pressure (p) for alcohols on α-CD. 1 – ethanol, 2 – 1-propanol, 3 – isobutanol, 4 – 1-butanol, 5 – 1-pentanol (● – first type, ◑ – second type).
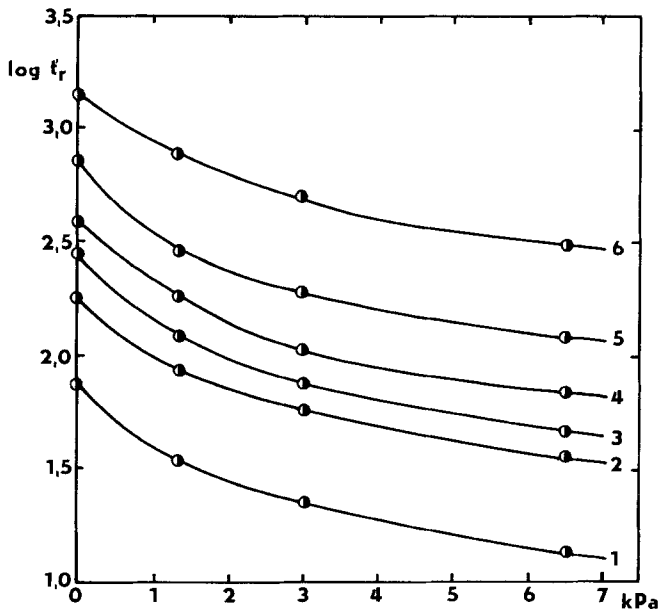

Fig. 4. A log t'_R dependence on the water vapour pressure for aromatic hydrocarbons on β-CD. (◑ – second type). 1 – benzene, 2 – 1,3,5-trimethylbenzene, 3 – ethylbenzene, 4 – 1,2,3-trimethylbenzene, 5 – 1,2,4-trimethylbenzene, 5 – *tert*-butylbenzene.

and 1-pentanol, whereas lower alcohols obeyed the second type. This finding is in agreement with the published data [19, 20] from which it follows that normal alcohols form progressively more stable complexes with increasing number of carbon atoms in the molecule (K_f for 1-pentanol is 210 M^{-1} and for 1-propanol only 20 M^{-1}).

The influence on the retention times of the test sorbates from water vapour cannot be explained in terms of the same concepts for β-CD. As follows from Table II, increasing water vapour pressure always leads to a decrease in the retention time, which, however, follows a different course from that obtained with α-CD. For positional isomers (xylenes, trimethylbenzenes) the elution order remains typical of interaction with CD over the whole range of the water vapour pressure. However, all the dependences (Figure 4) correspond to the second type, even for the substances with pronounced selectivity toward β-CD (aromatics) or for compounds with voluminous molecules, larger than the β-CD cavity.

3.2. THE EFFECT OF WATER VAPOUR ON THE SEPARATION PROPERTIES OF CD

A general phenomenon in the use of a carrier gas saturated with water vapour is shortening of the retention times of the sorbates and improvement in the shape of the elution curves. The shortening of the retention times of some little retained sorbates may adversely affect their separation. This is especially pronounced with substances that analogously interact with the CD cavity (benzene, toluene, cyclohexane, methylcyclohexane). A positive effect of water vapour can be observed in separations of
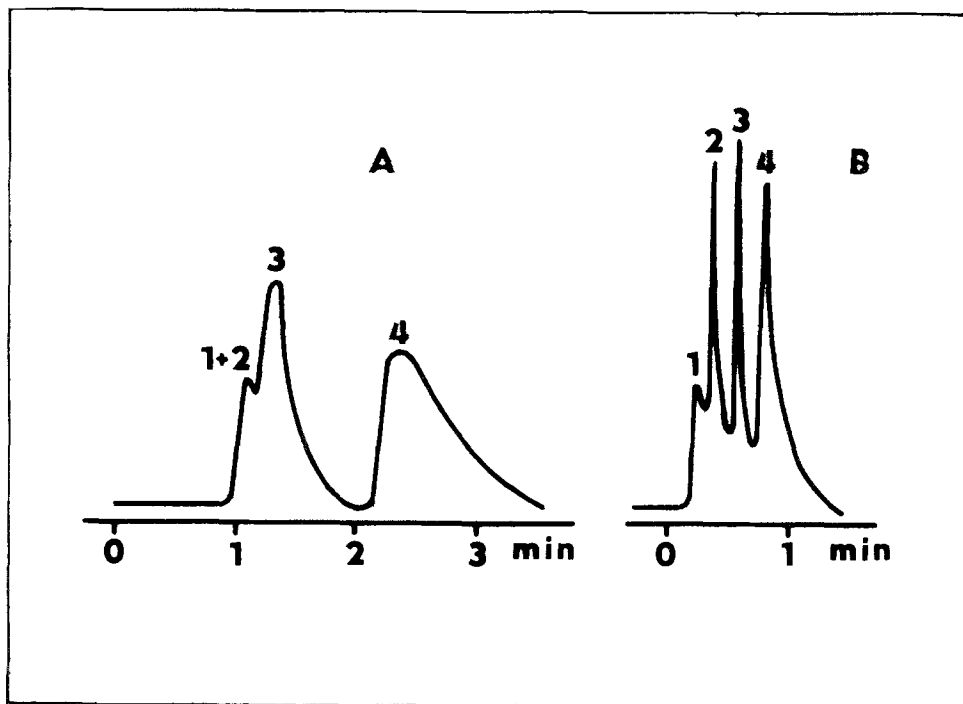

Fig. 5. Separation of alcohols on α-CD. Carrier gas flow rate, 60 ml/min. Column temperature, 80 °C. Fig. A – dry carrier gas (N_2); Fig. B – carrier gas with water vapour ($N_2 + H_2O$, $p_{H_2O} = 2.97$ kPa). 1 – methanol, 2 – ethanol, 3 – 2-propanol, 4 – 1-propanol.
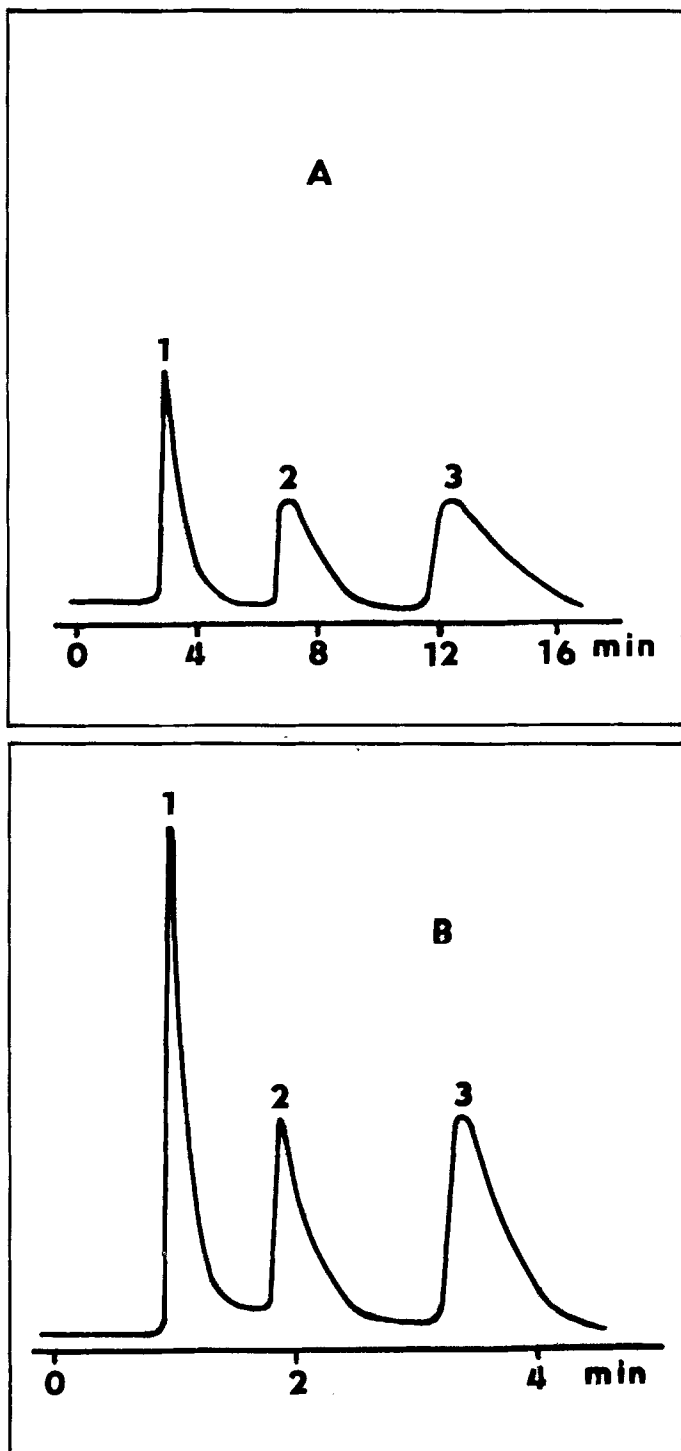
Fig. 6. Separation of trimethylbenzenes on β-CD. Carrier gas flow rate, 60 ml/min. Column temperature, 80 °C. Fig. A – dry carrier gas (N_2); Fig. B – carrier gas with water vapour ($N_2 + H_2O$), $p_{H_2O} = 2.97$ kPa. 1 – 1,3,5-trimethylbenzene, 2 – 1,2,3-trimethylbenzene, 3 – 1,2,4-trimethylbenzene.

substances that are strongly retained and thus produce broad, tailing elution curves (heptane, p-xylene, 1,2,4-trimethylbenzene).

The effect of water vapour in the carrier gas leading to shortening of the analysis and improvement in the separation can be demonstrated on a separation of lower alcohols on α-CD, depicted in Figure 5. It can be seen from the figure that saturation of the carrier gas with water vapour at a pressure of 2.97 kPa leads to a three-fold shortening of the analysis time and to separation of the two initial members of the homologous series.

With β-CD, advantages of saturation of the carrier gas with water vapour can be demonstrated on a separation of trimethylbenzenes (Figure 6). The three isomers are well separated even in the dry carrier gas, but the presence of water vapour shortens the analysis almost three-fold, while the separation efficiency is preserved.

4. Conclusion

The presence of water vapour in an inert carrier gas always affects the sorbate–cyclodextrin interaction. In contrast to analogous studies with sorbents such as alumina, silica gel and porous polymers, when the water vapour content in the carrier gas is 10% or more, a carrier gas (N_2) was used containing 1–5% water vapour. The general effect is a shortening of the retention times which occurs with CDs at water vapour contents as low as 0.5% and increases with increasing water vapour content. This effect is especially pronounced for sorbates whose structures correspond to the dimensions of the α-CD cavity. Analogous conclusions cannot be drawn for β-CD. A clarification of the contribution from the water vapour interaction with the cyclodextrin surface and the effect on its adsorption properties with respect to various types of sorbate is being studied further.

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