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Chromatographic study of the interactions of hydrocarbons with cyclodextrins and their derivatives in the gas–solid system

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ABSTRACT

Enthalpies were calculated from experimental temperature dependences of the retention data for selected alicyclic and aromatic hydrocarbons on α-, β- and γ-cyclodextrins and methylated α- and β-cyclodextrin. The sorbate–cyclodextrin phase interactions are discussed on this basis. The contributions of specific interactions, caused primarily by the formation of inclusion complexes, also follow from a comparison with data obtained on graphitized carbon black as a non-specific adsorbent.

INTRODUCTION

The selective properties of cyclodextrins that are contained in the separation system are increasingly being applied in gas and liquid chromatography [1–3]. The separation is based on the formation of inclusion compounds through host–guest interactions. Very good results have been obtained in separations of chemically similar substances, especially positional, geometric and optical isomers, but little attention has so far been paid to use of chromatographic measurements for characterization of the separation process form the thermodynamic point of view. Thermodynamic quantities for the formation of inclusion compounds have so far been determined mainly calorimetrically or the equilibrium constants were measured statically at various temperatures and the enthalpies were calculated from the temperature dependence [4]. Thermodynamic data can be obtained much faster and more readily from the temperature dependence of the specific retention volumes. This procedure has been employed widely to study solute interactions with various sorbents [5,6]. In addition to various types of carbonaceous sorbents, silica gels and aluminas, molecular sieves have also been studied chromatographically.

Molecular sieves belong among host structures capable of forming inclusion compounds, but the experimental data have not been interpreted from this point of view. This paper is a continuation of the first chromatographic study of the properties of cyclodextrins during inclusion of substances from the gaseous phase [7] and permits a study of host–guest interactions on the basis of the enthalpies obtained. As the guests, cyclic molecules of various sizes and polarities were selected. The hosts were cyclodextrins and their methylated derivatives.

EXPERIMENTAL

The measurements were carried out on a Chrom 41 gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia). The stationary phases were α, β- and γ-cyclodextrins (Chinoin, Budapest, Hungary) and their methylated derivatives, Me-α-CD and Me-β-CD (Me = methyl), prepared in our laboratory [8], deposited on Chromosorb W (60–80 mesh). The columns (120 cm × 2–3 mm I.D.) contained 4.75, 8.81, 5.00, 10 and 10% (w/w) of α-CD, β-CD, γ-CD, Me-α-CD and Me-β-CD, respectively. Retention data were obtained from 70 to 90°C in steps of 5°C. Cyclopentane, cyclohexane, cyclohexene, cycloheptane, benzene and toluene, all of analytical-reagent grade, were used as the sorbates.

RESULTS AND DISCUSSION

The specific retention volumes found for all the sorbates on the cyclodextrin stationary phases are summarized in Table I. From these data, using the relationship between log V_g and the reciprocal of the column temperature, the slopes of the temperature dependences were calculated by linear regression and the enthalpy changes were obtained form them, characterizing the energy of the sorbent–sorbate interactions. The results obtained are given in Table II. It follows from the data in Table II that the energy of interaction is correlated with the ratio of the sizes of the host cavity and the guest molecule.

With α-CD, the enthalpies for benzene and toluene are substantially different from those for other hydrocarbons, because these molecules have dimensions that fit best the size of the α-CD cavity and confirm the formation of an inclusion complex. The lowest enthalpy was found for cyclopentane, the molecule of which is too small compared with the α-CD cavity. No pronounced differences were found for the other sorbates, although the dimensions of cyclohexane and cyclohexene permit inclusion. The lower energy compared with aromatic hydrocarbons is due to the absence of polar interactions with the cyclodextrin hydroxyl groups.

The interaction of most sorbates, including aromatic hydrocarbons, with β-CD is weaker, owing to the larger β-CD cavity. On the other hand, the increased enthalpy for cycloheptane indicates the formation of an inclusion complex, as the dimensions of the molecule are close to those of the β-CD cavity. The differences in the enthalpies in the series of cyclohexane, cyclohexene and aromatic hydrocarbons are again connected with the molecular polarities. The same conclusions also hold for the interactions with γ-CD.

The results obtained for the methyl derivatives of cyclodextrins are in agreement with the assumptions that derivatization affects not only the polarity, but also the dimensions of the entrance to the cavity [8,9]. Methylation of α-CD causes a decrease in the diameter of the entrance down to a value close to the diameter of the cyclopentane molecule, hence the high value of the enthalpy of sorption. Analogously, methylation of β-CD decreases the cavity diameter down to a value corresponding to the α-CD cavity, which is confirmed by the almost identical enthalpies for alicyclic hydrocarbons. The decrease in the enthalpies for aromatic hydrocarbons is connected with a decrease in polar interactions due to replacement of the cyclodextrin hydroxyl groups by methyl groups.

TABLE I

SPECIFIC RETENTION VOLUMES V_g (ml g^{-1}), ON THE CYCLODEXTRIN PHASES

Substance	Column	Temperature (°C)				
		70	75	80	85	90
Cyclopentane	α-CD	28.00	24.55	21.51	18.35	15.20
	β-CD	18.22	16.41	14.31	12.41	10.22
	γ-CD	11.60	10.79	9.80	8.51	7.71
	Me-α-CD	164.89	135.13	103.99	74.35	54.60
	Me-β-CD	19.49	17.88	15.18	13.78	10.65
Cyclohexane	α-CD	46.20	40.02	32.90	27.70	21.85
	β-CD	40.10	35.02	29.99	25.49	20.73
	γ-CD	43.12	28.96	25.00	24.72	20.57
	Me-α-CD	43.00	37.25	31.63	26.05	20.53
	Me-β-CD	42.37	37.13	32.02	26.99	21.85
Cyclohexene	α-CD	60.02	51.58	45.53	35.40	27.20
	β-CD	54.44	47.12	40.02	32.72	25.56
	γ-CD	50.41	42.52	35.00	31.70	24.43
	Me-α-CD	57.78	49.58	41.30	33.10	26.98
	Me-β-CD	59.13	50.89	43.04	34.92	26.72
Cycloheptane	α-CD	54.73	47.44	40.20	32.92	25.60
	β-CD	149.71	123.50	97.44	71.26	45.14
	γ-CD	103.22	89.00	73.46	55.38	37.22
	Me-α-CD	52.99	45.76	38.62	31.56	25.32
	Me-β-CD	54.00	46.92	39.89	32.72	26.32
Benzene	α-CD	165.89	136.02	105.54	75.43	45.20
	β-CD	69.90	59.98	51.00	40.52	30.12
	γ-CD	55.70	48.69	40.70	32.60	25.53
	Me-α-CD	61.13	52.90	47.78	36.65	27.40
	Me-β-CD	152.98	126.79	100.53	74.47	48.20
Toluene	α-CD	182.97	150.83	118.60	84.46	49.30
	β-CD	107.72	92.64	76.52	59.25	42.00
	γ-CD	66.89	57.00	46.99	37.50	27.43
	Me-α-CD	70.68	60.12	48.98	38.64	28.53
	Me-β-CD	172.24	142.08	111.99	81.77	51.36

TABLE II

HEATS OF ADSORPTION OF HYDROCARBONS ON CYCLODEXTRINS

Sorbate	ΔH (kJ mol^{-1})[a]						Diameter of guest molecule (nm)
	α-CD	β-CD	γ-CD	Me-α-CD	Me-β-CD	GTCB [6]	
Cyclopentane	31.30	29.69	22.89	58.09	30.36	26.93	0.348
Cyclohexane	38.60	33.88	34.12	37.98	34.00	28.60	0.486
Cyclohexene	40.40	38.81	36.07	39.88	40.63	33.30	0.448
Cycloheptane	38.98	60.89	51.92	38.24	37.19	−	0.557
Benzene	65.88	42.91	40.56	44.75	58.72	36.20	0.443
Toluene	65.96	48.15	45.51	46.66	61.40	44.40	0.443[b]
Cavity diameter (nm) [10]	0.47–0.52	0.60–0.64	0.75–0.83				

[a] The correlation coefficients of the log V_g vs. T^{-1} linear dependences are 0.98–0.99, which corresponds to confidence limits of the determination of ΔH of ±5 kJ mol^{-1}.

[b] Without methyl side-group.

A picture of the contribution from specific interactions caused by the formation of inclusion complexes and polar interactions can be provided by a comparison of the enthalpies obtained for the test sorbates on a non-specific adsorbent, graphitized carbon black [6], which are also given in Table II. The enthalpies are higher in all instances when the formation of an inclusion complex can be assumed.

The results obtained confirm the formation of inclusion complexes in the gas–solid system and demonstrate the usefulness of their study and characterization by gas chromatography. As the thermodynamics of these systems are directly reflected in the retention data, initial information can be readily obtained from these data.

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