



ELSEVIER

Journal of Chromatography A, 864 (1999) 293–298

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Heats of adsorption of some organic compounds on β -cyclodextrin determined by gas–solid chromatography

Dezhi Sun^{a,b}, Jian Chen^{a,c}, Weimin Lu^a, Xiaoming Zheng^{a,*}

^a*Institute of Catalysis, Zhejiang University (Xixi Campus), 34 Tianmu Shan Road, Hangzhou, Zhejiang 310028, China*

^b*Department of Chemistry, Liaocheng Teachers' University, Liaocheng, Shandong 310028, China*

^c*Department of Chemistry, Zhejiang Normal University, Jinhua, Zhejiang, China*

Received 9 June 1999; received in revised form 14 September 1999; accepted 15 September 1999

Abstract

Isosteric adsorptive enthalpies have been derived from the temperature dependence of retention volumes determined by eluted pulse gas–solid chromatography. The heat data were obtained for systems using more than 20 organic liquids as adsorbates, and β -cyclodextrin as adsorbent. The experimental results have been discussed in the light of intermolecular force between molecules of adsorbate and adsorbent. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Heat of adsorption; Thermodynamic parameters; Cyclodextrin adsorbents; Adsorbents

1. Introduction

Cyclodextrins (CDs) are a family of macrocyclic oligosaccharides consisting of six (α -CD), seven (β -CD), eight (γ -CD) or nine (δ -CD) glucose units linked by $\alpha(1-4)$ interglucose bonds [1]. The molecules of them can accommodate guest molecules of suitable size in their central cavities [1,2], thereby forming inclusion complexes. Such an inclusion property has been utilized in both gas chromatography [3] and liquid chromatographic and capillary electrophoresis technologies, with CDs in both stationary and mobile phases [4–8]. Early in the 1980s, Koscielsky and Sybliska applied α - and β -cyclodextrins dissolved in formamide or ethylene glycol as stationary phases in gas–liquid chromatography for the resolution of isomeric dimethylcyclohexanes [9]. They found stereoselectivity

resulting from the inclusion of dimethylcyclohexanes in cyclodextrin. Krysl and Smolkova-Keulemansova thoroughly investigated the use of cyclodextrins in chromatography, and got excellent results that could be utilized for selective separation, pre-concentration and preparation of well-defined gaseous mixtures or solutions with low contents of the test substances [10]. To improve the effectiveness of the chromatographic separation, a comparison study was also carried out on cyclodextrin and liquid crystal stationary phases, and both materials were found to function as ordered media, with cyclodextrin inclusion complex formation predominant [11]. The above-mentioned literature studies show that interactions between the host (CD) molecules and various enclosed guest (adsorbate or solute) molecules are of great importance. When this type of interaction occurs, calorific effects should be observed. In the present work, retention volumes (V) of some alcohols, ketones, nitrohydrocarbons, benzene and

*Corresponding author.

methylbenzenes, and aromatic aldehydes have been determined on pure β -CD by eluted pulse gas–solid chromatography. The heats of adsorption (adsorption enthalpies, $\Delta H_{\text{ad}}^{\circ}$) of 23 adsorbates have been derived from the temperature dependence of the retention data. The thermodynamic data have shown again that the cyclodextrin can form host–guest adducts with some organic adsorbates, as it can in aqueous solution, and the central cave and the hydroxyl groups at the entrance of the cave can apply synergistic action on some adsorbate molecules.

2. Experimental

2.1. Chemicals

Chemically pure β -CD and all the liquid adsorbates were purchased from Shanghai Chemical Co. (Shanghai, China). β -CD was purified twice by recrystallization in distilled water, and oven-dried at 120°C. All the chemically pure liquids were purified by distillation or reduced pressure distillation, and the analytically pure ones were used as obtained.

2.2. Chromatographic conditions

A 2304-A chromatograph with a thermal conductivity detector was obtained from the Beijing Analytic Apparatus Factory (Beijing, China). Convenient flow-rates (15–20 cm³/min) were determined with a soap-bubble flow meter. Variations in the flow-rate were normally kept within $\pm 1\%$. The highly pure nitrogen (99.999%) was used as carrier gas. A 4.392-g amount of 60–80 mesh pure β -CD particles was packed in a stainless steel column (1000 \times 3 mm) as the adsorbent phase. The packed column had been aged for 24 h in flowing highly pure nitrogen at 260°C before determination of retention times. Inlet pressure (P_i) was controlled by a precision gas pressure stabilizer and determined by a precision pressure schedule (accuracy, ± 0.0005 MPa). The outlet pressure (P_r) was the atmospheric pressure, which was measured with a mercury atmospheric barometer. The range of ($P_i - P_r$) was from 0.02 to 0.06 MPa. So P_i was lower than 0.2 MPa and the gaseous phase was approximately ideal gas at the experimental temperatures.

The column temperature range over which the retention times were made was 50–210°C (pure β -CD solid was very stable in nitrogen at temperatures lower than 300°C). By thermostatic control of the column chromatography, steady temperatures with variations less than $\pm 0.2^\circ\text{C}$ were achieved. Liquid sample was pulse injected in the column at a size less than 0.0005 cm³, so as to establish the adsorption equilibrium state in the linear range (near to zero coverage) of the isotherm. Retention times (t_R) were recorded on a C-R6A Chromatopac instrument (Shimadzu, Japan) with time determining accuracy of ± 0.001 min. Every retention time used for the calculation of specific volume was the average value of five iterations.

Hold-up times (t_M) were calculated with Eq. (1) [12], based on a concept of zero carbon atom alkanes according to the retention times (t_R) of normal alkanes.

$$t_R = A + \exp(B + Cn + Dn^2) \quad (1)$$

where A , B , C , and D were adjustable parameters depending on the experimental conditions (column type, stationary phase, flow-rate, temperature, etc.); n was carbon number of alkane molecule and alkanes of $n=5-8$ were used; and finally $t_M = A + \exp B$ were obtained.

3. Results and discussion

3.1. From retention volumes to adsorption enthalpies

Specific retention volumes (V_g) should be calculated according to Eq. (2) [13,14].

$$V_g = \frac{j(273.2/T_r)(P_r - P_w)}{P_r} \cdot \frac{F_c(t_R - t_M)}{W} = \frac{V}{W} \quad (2)$$

where $j = 1.5[(P_i/P_r)^2 - 1]/[(P_i/P_r)^3 - 1]$ was the compressibility factor; since the experimental pressures were not high and the temperatures were not low, the carrier gas actually need no correction of non-ideality [15]; T_r was the temperature of the flow meter; P_w was the saturated vapor pressure of water at T_r ; F_c was the flow-rate of the carrier gas at T_r ; W was the mass of the adsorbent (β -CD) in outer

Table 1
Retention volumes $V = V_g W$ (cm^3) of some adsorbates on β -cyclodextrin

Adsorbate	Temperature (K)				
	336.7	342.7	351.7	362.7	375.7
Cyclohexane	0.313	0.277	0.264	0.272	0.246
Benzene	0.466	0.312	0.316	0.316	0.193
Toluene	1.835	1.138	0.878	0.562	0.382
Acetone	0.122	0.184	0.189	0.158	0.104
Butanone	0.632	0.364	0.334	0.281	0.191
Tetrahydrofuran	0.285	0.184	0.193	0.193	0.158
Dioxane	1.734	1.190	0.808	0.527	0.347
Cyclopentanone	3.860	3.738	2.468	1.586	0.870
Cyclohexanone	10.76	7.932	5.257	3.448	1.981
Nitromethane	2.626	1.449	1.225	0.7720	0.404
Nitroethane	3.417	2.473	1.629	0.953	0.488
2-Nitropropane	3.184	2.437	1.682	11.199	0.553
Methanol	0.856	0.676	0.668	0.602	0.540
Ethanol	0.896	0.545	0.457	0.351	0.206
1-Propanol	2.029	1.524	0.878	0.474	0.312
2-Propanol	0.856	0.606	0.367	0.281	0.224
1-Butanol	4.471	3.211	1.998	1.111	0.588
<i>p</i> -Xylene	4.221	3.562	2.767	2.090	1.533
<i>m</i> -Xylene	4.445	3.702	2.820	2.082	1.476
<i>o</i> -Xylene	5.297	4.370	3.320	2.420	1.616
2-Pentanone	1.867	1.647	1.383	1.124	0.887
Acetylacetone	4.708	3.966	3.109	2.639	1.722
Ethyl acetoacetate	17.92	17.09	111.98	7.941	5.042

layer of the particles which was available for adsorption of solutes injected in the column. The depth of the layer is discussed in Section 3.2. Since only one packed column was used throughout our experiments, W was a constant. The retention volume $V = V_g W$ are collected in Tables 1 and 2. According to the literature [13,16], the plot of $\ln V_g$ versus $1/T$ yields a straight line whose slope is $-\Delta H_{ad}^{\circ}/R$ (Eq. (3)). Consequently, Eq. (3) is also correct:

$$\ln V = -\Delta H_{ad}^{\circ}/(RT) + \text{constant} \quad (3)$$

The $-\Delta H_{ad}^{\circ}$ data of 23 adsorbates calculated using Eq. (3) are shown in Table 3 along with the errors estimated with our earlier simple method [17]. The changes of retention volumes (V) of cyclohexane, benzene, acetone, butanone, and tetrahydrofuran with the change of column (phase equilibrium) temperature are so small (Table 1) in the whole studied temperature range that the adsorption enthalpies of the five adsorbates cannot be calculated with acceptable errors.

Most of the data in Table 3 might be interpreted in

Table 2
Retention volumes $V = V_g W$ (cm^3) of some higher boiling point oxygenous aromatic compound on β -cyclodextrin

Adsorbate	Temperature (K)					
	403.8	411.8	419.8	433.7	411.7	450.7
Benzaldehyde	3.729	2.890	2.016	11.660	1.107	0.975
<i>p</i> -Tolualdehyde	7.453	5.754	4.484	2.631	2.416	1.498
Methyl benzoate	6.394	5.701	3.434	2.811	1.937	1.480
Acetophenone	8.766	6.984	6.544	2.429	2.271	1.695
Propiophenone	10.71	9.614	5.837	5.588	3.834	2.723

Table 3
Standard heats of adsorption ($-\Delta H_{\text{ad}}^{\circ}$) of some adsorbates on β -cyclodextrin in the column

Adsorbate	$-\Delta H_{\text{ad}}^{\circ}$ (kJ/mol)	Error (kJ/mol)
Toluene	40.6	± 1.4
<i>p</i> -Xylene	27.4	± 0.6
<i>m</i> -Xylene	29.6	± 0.6
<i>o</i> -Xylene	30.5	± 0.4
Methanol	11.8	± 0.6
Ethanol	37.1	± 1.6
1-Propanol	52.1	± 2.6
2-Propanol	35.9	± 1.5
1-Butanol	54.5	± 1.8
Nitromethane	47.4	± 1.9
Nitroethane	52.0	± 1.6
2-Nitropropane	42.9	± 1.9
Dioxane	42.7	± 1.0
Cyclopentanone	46.6	± 1.4
Cyclohexanone	45.4	± 0.9
2-Pentanone	20.1	± 0.6
Acetylacetone	27.1	± 0.5
Ethyl acetoacetate	39.5	± 0.2
Benzaldehyde	43.6	± 1.1
<i>p</i> -Tolualdehyde	50.1	± 1.0
Methyl benzoate	47.8	± 0.7
Acetophenone	57.3	± 0.6
Propiophenone	42.8	± 1.2

the light of intermolecular force between β -CD and adsorbate. The unique molecular structure of the CD is very important to the interaction. β -CD molecules possess a hollow truncated cone and seven primary hydroxyl groups located on the narrower side of the cone and 14 secondary hydroxyl groups on the broader side. In aqueous solution systems, the cone-shaped inner cave can be regarded as a hydrophobic group, and the side hydroxyl groups are certainly hydrophilic [1,2]. There are still selective interactions between the inner cave and some lipophilic (apolar or weak polar) groups with adequate size, and those between the hydroxyl groups and some hydrophilic (polar) groups, although there is no water in solid–gas adsorption systems.

3.2. Heats of adsorption of benzene, toluene and xylenes

$-\Delta H_{\text{ad}}^{\circ}$ of toluene (40 kJ/mol) is not only larger than that of benzene, which is less than 20 kJ/mol

roughly estimated with the V values, but also larger than xylenes (~ 30 kJ/mol). Because the gas in the column is approximately ideal gas, the heat of adsorption ($-\Delta H_{\text{ad}}^{\circ}$) can express the strength of intermolecular force between adsorbate and adsorbent. So the thermodynamic data show that the intermolecular force of β -CD with toluene is larger than that of the cyclodextrin with xylenes as well as with benzene. The five aromatic hydrocarbons are all hydrophobic compounds. The intermolecular force occurred most probably when the molecule got into the molecular cave of the CD. The benzene molecule can entirely enter the cave, but it is too small to ‘fill up’ the cave, with 0.62 nm internal diameter and 0.79 nm height [18], because the diameter of benzene is only about 0.50 nm as estimated from bond lengths and angles [19]. In other words it can only interact with a local part of the cave. The two methyl groups of *m*- or *o*-xylene molecule might prevent the guest from entirely entering the host cave, because the width of *m*- and *o*-xylene reach about 0.52 nm, estimated with bond lengths and angles, which might result in a Van der Waals diameter longer than 0.62 nm; the *p*-xylene molecule might be too long (about 0.71 nm estimated from bond lengths and angles), and one of its methyl groups at the entrance of the cave partly destroys the intramolecular interactions between the hydroxyl groups of the host. So only the toluene molecule with 0.61 nm length and the same width of benzene as a guest is most adequate to the inner cave of β -CD. It is not surprising that toluene was utilized to precipitate selectively β -CD from enzymatic degradation products of a mixture of starch [1]. These thermal data of benzene and benzene derivatives as adsorbates indicate that the solid β -CD as adsorbent is in a layer-type packing structure, as described by Harata [20], because the $-\Delta H_{\text{ad}}^{\circ}$ value of *p*-xylene would larger than that of toluene, if the adsorbent were in a channel-type packing structure. Consequently, only a mono-layer of β -CD molecules is available for adsorption of solute molecules. The experimentally specific surface area of the CD particles in the column is only (20.7 ± 0.5) m²/g (determined in our laboratory on a Model 804 instrument from Carlo Erba (Italy) using nitrogen as molecule probe), which also shows that the solid β -CD is not in a channel-type packing structure.

3.3. Heats of adsorption of lower aliphatic alcohols, nitromethane and nitroethane

The data of the adsorption of lower aliphatic alcohols are interesting. $-\Delta H_{\text{ad}}^{\circ}$ of ethanol is 25 kJ/mol larger and 15 kJ/mol less than that of methanol and 1-propanol, respectively. Furthermore, $-\Delta H_{\text{ad}}^{\circ}$ of 1-butanol is only 2 kJ/mol larger than that of 1-propanol. An explanation might be obtained from the two types of intermolecular forces mentioned above. One is the so-called hydrophobic force, i.e., the aliphatic chain of a normal alcohol can get into the inner cave of the cyclodextrin molecule and attract the inside C–H bonds. The other comes from the interaction between the alcohol hydroxyl and the hydroxyl groups at the entrance of the cave. It is possible that an intermolecular hydrogen bond exists. We call the whole intermolecular force a type of synergistic interaction between molecules. The methanol molecule contains only a hydroxyl group and a methyl group, the latter is too short to get into the inner cave of the host when the intermolecular hydrogen bond exists. Hence the intermolecular force of methanol with β -CD is only the hydrogen bond, and of course is the weakest of the determined alcohols with the CD. From methanol to ethanol the intermolecular force changed from single hydrophilic force (maybe hydrogen bond) into a type of synergistic interaction containing both hydrophilic and hydrophobic forces between adsorbate and adsorbent molecules. So the heat of adsorption of ethanol is much larger than that of methanol. From ethanol to normal butanol, the hydrophobic (disperse) force between the aliphatic chain and the inside cave becomes stronger with the increase of carbon number. In addition, $-\Delta H_{\text{ad}}^{\circ}$ of 2-propanol is less than that of ethanol, which shows that the second hydroxyl may have less opportunity to form a hydrogen bond with the hydroxyl groups of the CD.

The $-\Delta H_{\text{ad}}^{\circ}$ difference between nitromethane and nitroethane is similar to that between methanol and ethanol, while the heats of adsorption show that interaction between the nitro group ($-\text{NO}_2$) and the hydroxyl groups of β -CD is stronger than that between the alcohol hydroxyl group and the hydroxyl group of β -CD. It is probable that the nitro group can interact with two hydroxyl groups simultaneously.

3.4. Heats of adsorption of cyclopentanone and cyclohexanone

$-\Delta H_{\text{ad}}^{\circ}$ of cyclopentanone and cyclohexanone are almost the same (46.6 and 45.5 kJ/mol), and evidently larger than that of 2-pentanone (20.1 kJ/mol). This indicates that the protruding oxygen atom of cyclopentanone or cyclohexanone can interact with the hydroxyl group at the entrance of the CD molecule cave, when the cycloalkane group is in the cave. It means that there is synergistic interaction between cyclopentanone/cyclohexanone and β -CD similar to that between 1-butanol and β -CD. However, the oxygen atom of 2-pentanone is located between two alkane groups. If the propyl group gets into the cave, the oxygen atom can hardly interact with the hydroxyl group of β -CD, due to disturbing of the methyl. Hence the interaction between 2-pentanone and β -CD is mainly the quite weak hydrophobic interaction.

3.5. Heats of adsorption of five oxygenous compounds containing benzoyl group

The heats of adsorption of five higher boiling point aromatic oxygenous compounds have been determined. $-\Delta H_{\text{ad}}^{\circ}$ of benzaldehyde (43.6 kJ/mol) is slightly larger than that of toluene. This shows that its polar and apolar groups ($-\text{CHO}$ and $-\text{C}_6\text{H}_5$) might synergistically interact with hydroxyl groups and molecular cave of β -CD. But the intermolecular force is not evidently larger than that between toluene and β -CD, due to the phenyl being not long enough. $-\Delta H_{\text{ad}}^{\circ}$ of *p*-tolualdehyde (50.1 kJ/mol) is evidently larger than that of benzaldehyde, which shows again that hydrophobic interaction between toluene and β -CD is stronger than that between benzene and β -CD.

Comparing the adsorption enthalpies of acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) with both methyl benzoate ($\text{C}_6\text{H}_5\text{COOCH}_3$) and propiophenone ($\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$), we find the following order:

$$\begin{aligned} &-\Delta H_{\text{ad}}^{\circ}(\text{C}_6\text{H}_5\text{COCH}_3) > \\ &-\Delta H_{\text{ad}}^{\circ}(\text{C}_6\text{H}_5\text{COOCH}_3) > \\ &-\Delta H_{\text{ad}}^{\circ}(\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3), \end{aligned}$$

which shows that the intermolecular force of β -CD

with acetophenone is the strongest one although the acetophenone molecule is the smallest of the three. It is worth noticing that the benzoyl group is the common radical of the three aromatic compounds. The oxygen atom of the acyl group can interact with the hydroxyl groups at the molecular cave of β -CD when the benzene ring of the benzoyl group is enclosed in the cave. It seems that both ethyl and methoxy groups hinder the interaction between the double bond oxygen atom and the hydroxyl groups of the CD. In other words, hydrophobic radicals of the guest molecule outside the host cave may partly destroy the synergistic interaction between the host and the guest molecules. The polar property of methoxy is stronger than that of ethyl, so the destroying action is weaker and the intermolecular force between methyl benzoate and β -CD is stronger than that between propiophenone and β -CD.

4. Conclusions

Gas chromatography may be a convenient approach towards the determination of heats of adsorption of some types of adsorbates on β -cyclodextrin in a wide temperature range. The thermodynamic data can be used to estimate or compare the relative strengths of intermolecular forces between the adsorbent and various adsorbates, and to judge how the molecules of the adsorbate and the adsorbent interact. In this work, experimental thermal data have been explained in the light of important conclusions obtained from literature. Those are: (a) the β -CD molecule can form host–guest adduct with adsorbate molecule (guest) as it can in aqueous solution [9,10]. (b) As a strong intermolecular force between the host and the guest occurs when a type of synergistic interaction exists between them, namely, the inner cave and some hydroxyl groups of the CD molecule simultaneously interact with the apolar/hydrophobic and the polar/hydrophilic parts of the guest molecule [1,2,9–11,20]. Thermal data of benzene and benzene derivatives as adsorbates, as well as the experimentally specific surface area of the CD particles, indicate that the solid β -CD as adsorbent is

in a layer-type packing structure and only a monolayer of β -CD molecules is available for adsorption of solute molecules.

Acknowledgements

This work has been carried out with the financial assistance of the Natural Science Foundation of Zhejiang Province (China).

References

- [1] G. Wenz, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 803.
- [2] V. Zabel, W. Saenger, S.A. Mason, *J. Am. Chem. Soc.* 108 (1986) 3664.
- [3] S. Krysl, E. Smolkova-Keulemansova, *Chem. Listy* 79 (1985) 919 (in Czech).
- [4] J. Feurle, H. Jomaa, M. Wilhelm, B. Gutsche, M. Herderich, *J. Chromatogr. A* 803 (1998) 111.
- [5] P.D. Ferguson, D.M. Goodall, J.S. Loran, *J. Chromatogr. A* 768 (1997) 29.
- [6] M.D. Beeson, G. Vigh, *J. Chromatogr. A* 634 (1993) 197.
- [7] D.W. Armstrong, H.L. Jin, *J. Chromatogr. A* 462 (1989) 219.
- [8] P.D. Ferguson, D.M. Goodall, J.S. Loran, *J. Chromatogr. A* 745 (1996) 25.
- [9] T. Koscielsky, D. Sybliska, *J. Chromatogr.* 349 (1985) 3.
- [10] S. Krysl, E. Smolkova-Keulemansova, *J. Chromatogr.* 349 (1985) 167.
- [11] E. Smolkova-Keulemansova, L. Sojak, *Symp. Ser.* 342 (1987) 247.
- [12] R. Lebron-Aguilar, J.E. Quintanilla-López, J.A. García-Domínguez, *J. Chromatogr. A* 760 (1997) 219.
- [13] E.F. Meyer, *J. Chem. Educ.* 57 (1980) 121.
- [14] C. Sun, *The Principle and Technology of Gas Chromatographic Analyses*, Chemical Industrial Publishing House, Beijing, 1979, pp. 239–246 (in Chinese).
- [15] A.J.B. Cruickshand, B.W. Gainey, C.P. Hicks, T.M. Letcher, R.W. Moody, C.L. Young, *Trans. Faraday Soc.* 65 (1969) 1014.
- [16] R.L. Gale, R.A. Beebe, *J. Phys. Chem.* 68 (1964) 555.
- [17] D. Sun, J. Chen, W. Lu, X. Zheng, *J. Solution Chem.* 27 (1998) 1097.
- [18] J. Szejtli, *Chem. Rev.* 98 (1998) 1743.
- [19] Y.B. Yao, T. Jie, Y.M. Gao, *Handbook of Physicochemistry*, Shanghai Science and Technology Press, Shanghai, 1985, pp. 148–149.
- [20] K. Harata, *Chem. Rev.* 98 (1998) 1803.