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Gas chromatographic characterization of the adsorption properties of the natural adsorbent CACMM2

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Abstract

The adsorption behavior of *n*-pentane, *n*-hexane, *n*-heptane, benzene and cyclohexane on the natural adsorbent CACMM2 at 60°C was studied by use of gas chromatography. The variation of the differential enthalpy of adsorption and the entropic factor were determined and are similar than those obtained on such non-specific adsorbents as dehydroxylated silica. Retention of alkanes depends mainly on the boiling point. The separation of the mixtures pentane–benzene, pentane–cyclohexane, hexane–benzene, hexane–cyclohexane, heptane–benzene and heptane–cyclohexane is achieved in 1 min. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

One year ago a novel natural adsorbent designated as CACMM1 [1] was extracted from a cactus [2]. This material is characterized by a low surface area (32 m²/g) and a peculiar particle and pore size distribution [3], but presents considerable adsorption of water vapor, as well as of organic vapors and of solutes in water solutions [4]. Owing to this adsorption capacity, it is a very attractive material for the design of new adsorbents and stationary phases.

Adsorption isotherms allow the evaluation of the adsorption capacity of diverse vapors by a solid in terms of the intermolecular interactions between the adsorbate and the adsorbent. Gas chromatography is a powerful tool to achieve this information. With this method, the material under investigation is used as

the adsorbent and is placed in a chromatographic column. This transforms the solid in a stationary phase, whose separation properties can also be tested.

The method of elution by characteristic points [5] has been used to derive isotherm data from the gas chromatographic peaks assuming ideal chromatography. Today, for this purpose, the chromatograph is interfaced to a computer for digital acquisition of the peak profile. In this way silica based adsorbents [6] packed in 15 m open tubular quartz columns have been studied. However, the classical peak maxima method [7] allows the isotherm construction for adsorbents in short packed columns when efficiency is not high. Gas chromatography has also shown advantages in the study of the surface chemistry of adsorbents like pyrocarbon silicas [8], and aminated silochroms [9] and stationary phases by means of retention volume measurements.

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2. Experimental

2.1. Column

CACMM2 with particle size 300 μm was dried at 100°C in air and packed in a 50 cm \times 2 mm I.D. glass column. Specific surface area (11 m²/g) of this sample was obtained from the BET method applied to the nitrogen adsorption isotherm at 77 K assuming the conventional value of 0.162 nm² for the cross section area of the N₂ molecule at that temperature.

2.2. Chemicals

Benzene, cyclohexane, the C₅–C₁₅ *n*-alkanes, 2,2,4-trimethylpentane, diethyl ether, methyl ethyl ketone purchased from Merck were used without further purification and injected not diluted.

2.3. Equipment

A Varian series 2800 gas chromatograph equipped with a thermal conductivity detector was used in this work. Column temperature was varied according to the measurement carried out. Detector and injector were maintained at 100°C. A strip chart recorder adjusted at 10 mV was connected to the detector.

2.4. Carrier gas

Before runs the adsorbent was preconditioned at a certain temperature for 12 h in N₂ flow. The column was evaluated in terms of its efficiency by measuring at 80°C the height equivalent to a theoretical plate (HETP) at different gas (N₂) average flow-rates in the interval 10–60 cm³/min. Benzene with a capacity factor measured in this column $k=1.3$, was used as test compound. This served for the construction of a typical Van Deemter curve [10], which showed a minimum value for the optimum carrier gas flow of 25 cm³/min used throughout the work. The interrelationship between temperature and HETP showed a constant plateau up to 80°C at carrier gas average flow-rate of 22 cm³/min.

2.5. Procedures

Adsorption isotherms of individual compounds

were obtained from isothermal runs at 60°C in the Henry region by the peak maxima method [6] injecting different volumes of the adsorbates (0.1–1.0 μl). Integration of the peak area and of the adsorption area [7] was performed manually by weighing. The mean value of three to five measurements was taken and had a 5% maximum error. Thermodynamic parameters were calculated readily from retention data of 0.1 μl injections, which gave broad but symmetrical peaks. For this purpose, retention times t_R of pure adsorbates were measured and transformed to specific retention volumes V_m in cm³/g by using the adjusted retention time t'_R , the flow-rate w and the mass packed into the column m by the known formula $V_m = (t_R - t_0)w/m$ [11]. Dead time was determined from the retention time for methane by extrapolation on the experimental graph $\log t_R$ vs. carbon atom number (C₁₃–C₁₈). Adsorption isosteres were obtained in the temperature interval 50–100°C from the graph of the logarithm of the retention volume V'_R versus reciprocal of the temperature at 10°C interval. Plotting $\ln V_m$ versus $1/T$ gave a straight line with the slope $\Delta H_{\text{ads}}/R$ being related to the differential enthalpy of adsorption and the intercept, to the entropic factor $\Delta S_{\text{ads}}/R$ [12]. All measurements are based on the average of at least three injections for each temperature. Separations of 8 model hydrocarbon mixtures were performed at 37°C and the sample size was 1 μl .

3. Results and discussion

First we will describe some results concerning adsorption for later application to systems of chromatographic interest. The adsorption of a series of compounds not significantly differing in the number of carbon atoms, but clearly having different structure and ability to undergo intermolecular interactions is a good approach of probing the adsorption characteristics of a new solid. Here gas chromatography allowed the determination of the adsorption isotherms of benzene, cyclohexane, *n*-hexane, *n*-pentane and *n*-heptane at 60°C in the initial region (Henry region) of the isotherm (Fig. 1). We observed first that as the number of carbon atoms in the *n*-alkane series grows, the adsorbed amount gradual-

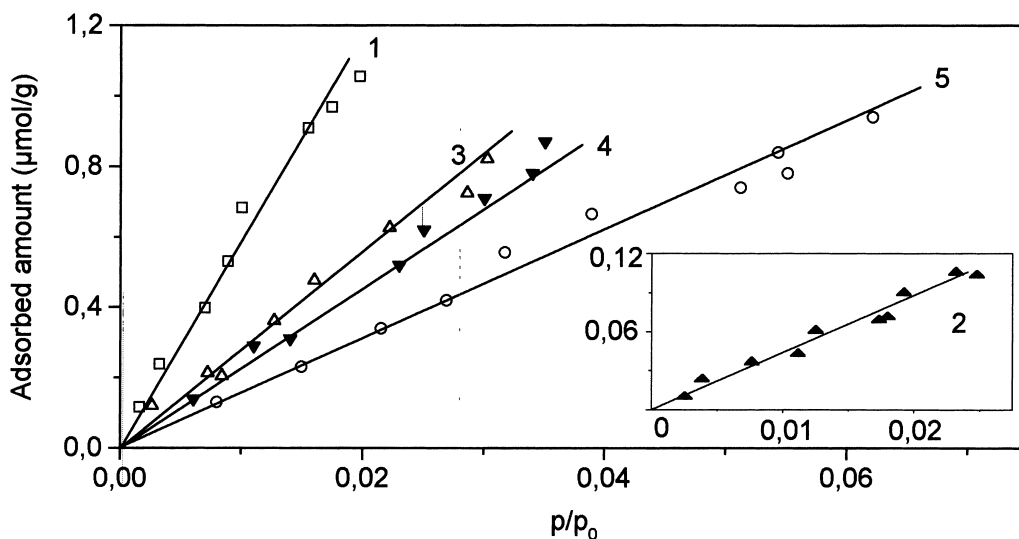


Fig. 1. Adsorption isotherms of *n*-pentane (1), benzene (2), *n*-hexane (3), cyclohexane (4) and *n*-heptane (5) on CACMM2 at 60°C.

ly decreases. Cyclohexane adsorption isotherm occupies an intermediate position between *n*-hexane and *n*-heptane, while benzene is stronger adsorbed than *n*-hexane. Table 1 shows Henry and Freundlich adsorption constants. We can observe low Henry constant values, but the adsorption pattern for the molecules containing six carbon atoms corresponds to the interaction presented by specific adsorbents like Silochrom [8] or large pore silica gels [13], where adsorption strength decreases in the order $C_6H_6 > C_6H_{14} > C_5H_{12}$. Freundlich's equation provided a good match ($R^2 \geq 0.95$) for the experimental adsorption data over the studied range. The results obtained for the constant n show that for cyclohexane all surface sites are equivalent ($n=1$), while for the other adsorbates, adsorption energies decrease with surface density ($n > 1$). From the temperature

Table 1

Henry (K_H) and Freundlich (K_F) adsorption constants of benzene, cyclohexane, *n*-pentane, *n*-hexane, *n*-heptane on CACMM2 at 333 K obtained from gas chromatographic data

Adsorbate	K_H ($\mu\text{mol}/\text{m}^2$)	R^2	K_F	n	R^2
C_5H_{12}	4.8	0.9921	$2.7 \cdot 10^{-2}$	1.2	0.9839
C_6H_6	3.7	0.9681	$4.9 \cdot 10^{-2}$	1.1	0.9653
C_6H_{14}	2.3	0.9937	$3.1 \cdot 10^{-2}$	1.2	0.9503
C_6H_{12}	2.2	0.9948	$6.3 \cdot 10^{-2}$	1.0	0.9890
C_7H_{16}	1.3	0.9867	$6.6 \cdot 10^{-2}$	1.1	0.9842

dependence of the retention volume (Fig. 2) we calculated thermodynamic adsorption properties of CACMM2. Table 2 shows that the differential enthalpy of adsorption rises with the growth of the adsorbate molecule and its magnitude is similar to the differential heat of adsorption obtained for fine and medium pore silica gels [13]. However, as it has been demonstrated in static measurements, the effect of pore narrowing does not affect the values of the heat of adsorption. Therefore, no conclusion about pore size of CACMM2 can be done as a result of these measurements and it will be reported elsewhere [3]. For three substances with identical number of carbon atoms (C_6H_6 , C_6H_{12} and C_6H_{14}) and similar boiling points as benzene and cyclohexane, the differential enthalpy of adsorption presents interesting results. Its magnitude is similar for hexane and benzene, where the first adsorbate is able to undergo only non-specific interaction, while the second can interact specifically. Here CACMM2 has a non-specific adsorbent [14] behavior, similar as dehydroxylated silica which presents heat of adsorption values of 8.8 kcal/mol and 8.6 kcal/mol for hexane and benzene, respectively at $\theta=0.5$ [15]. For benzene the ΔH_{ads} value is twice greater than that for cyclohexane although both adsorbates have the same boiling point. The same happens if one compares the magnitude of this thermodynamic parameter obtained

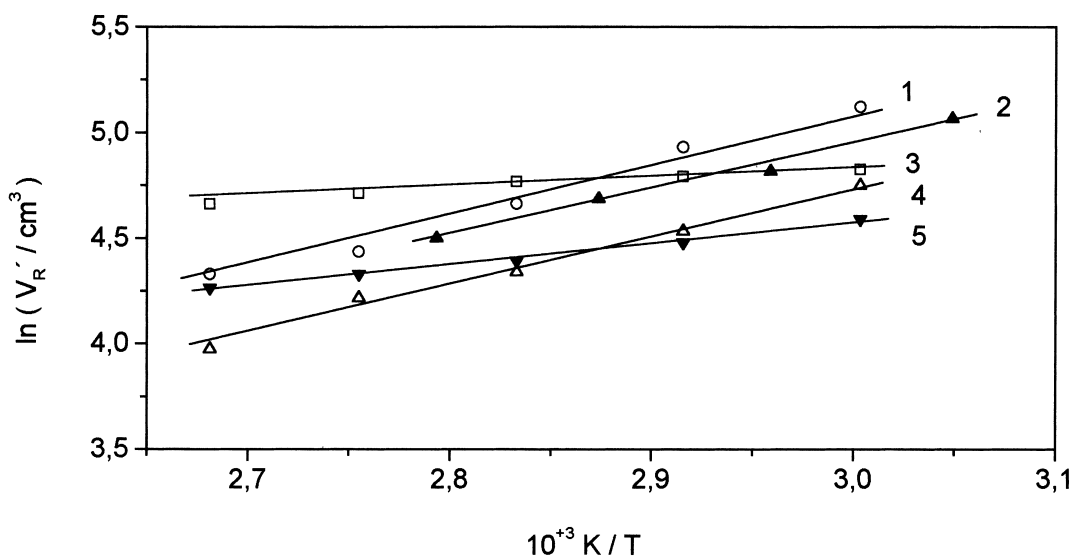


Fig. 2. Adsorption isosteres of *n*-heptane (1), benzene (2), *n*-pentane (3), *n*-hexane (4), and cyclohexane (5) on CACMM2.

for *n*-hexane and cyclohexane which present the same type of interaction. This points out that adsorption by CACMM2 depends also on the adsorbate structure.

Specific retention volumes V_m of a series of compounds were determined from chromatographic measurements. It can be seen from the results (Table 3) that V_m and k for the *n*-alkane homologous series grows (see Fig. 3, curve a) as the number of carbon atoms in the molecule increases, however, an additional methylene group does not produce a linear growth in the V_m value (see Fig. 3, curve b). It is evident from the values given in Table 3 that the retention of paraffins depends mainly on the boiling point. The capacity factor of toluene is four times higher than that of benzene, and on changing from toluene to ethylbenzene, k increases three times. This

shows that substitution in the ring is not equivalent to lengthening the chain in the *n*-alkanes.

The adsorption properties of CACMM2 towards

Table 2

Differential heat of adsorption and entropic factor of different adsorbates on CACMM2 determined by gas chromatography

Adsorbate	$-\Delta H_{\text{ads}}$ (kcal/mol) ^a	$\Delta S_{\text{ads}}/R$
C ₇ H ₁₆	5.2±1.0	-2.7±0.7
C ₆ H ₁₄	4.6±0.2	-2.2±0.7
C ₆ H ₆	4.3±0.2	-1.5±0.5
C ₆ H ₁₂	2.0±0.1	1.6±0.3
C ₅ H ₁₂	1.0±0.1	3.3±0.3

^a 1 cal=4.184 J.

Table 3

Specific retention volumes (V_m) and capacity factors (k) of different compounds relative to *n*-pentane obtained at 60°C on CACMM2

No.	Compound	V_m (cm ³ /g)	k
1	1-Octanol	48.7	62.7
2	Ethylbenzene	11.0	14.2
3	1-Pentanol	7.0	9.0
4	<i>n</i> -Octane	4.7	6.2
5	Toluene	4.3	5.1
6	1-Propanol	3.2	4.1
7	<i>n</i> -Heptane	2.0	2.7
8	2,2,4-Trimethylpentane	1.8	2.5
9	Ethanol	1.6	2.1
10	Diethyl ether	1.4	1.9
11	Acetonitrile	1.1	1.5
12	Methyl ethyl ketone	1.0	1.4
13	Cyclohexane	1.0	1.4
14	Benzene	1.0	1.3
15	Chloroform	1.0	1.3
16	Methanol	0.9	1.3
17	Tetrahydrofuran	0.9	1.2
18	Carbon tetrachloride	0.8	1.1
19	<i>n</i> -Hexane	0.8	1.1
20	Acetone	0.8	1.1
21	Ethylacetate	0.7	1.0
22	<i>n</i> -Pentane	0.7	1.0

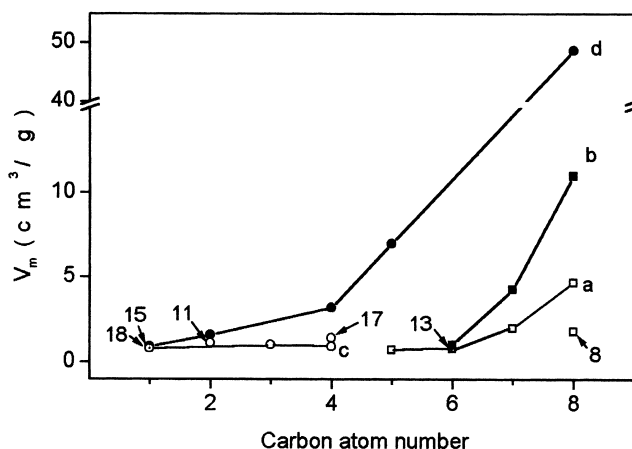


Fig. 3. Plot of V_m against the number of carbon atoms in the molecule for a series of *n*-alkanes (a), aromatic hydrocarbons (b), carbonyl group containing molecules (c) and alcohols (d). Points for other molecules are indicated with the line numbering of Table 3.

polar adsorbates has not been examined previously. In the series of alcohols we found that retention is much greater than the retention of the corresponding *n*-alkanes. From comparison of the V_m values of *n*-pentane and 1-pentanol or *n*-octane and 1-octanol it follows that the retention of polar adsorbates is higher than the retention of non-polar adsorbates having the same number of carbon atoms (see Fig. 3, curve d and a). This is due to the action of dispersion forces and additionally induction, orientation and hydrogen bonding forces. Thus it can be concluded, that the surface of CACMM2 supports also chemical groups able to undergo these specific interactions. The natural adsorbent CACMM2 has a component based on cellulose [1]. However, when one compares the relative retention of different alcohols on cellulose [16] and on CACMM2, one observes the opposite tendency, while other polar compounds such as acetonitrile, methylethylketone and tetrahydrofuran present the same behavior.

Finally, the separation abilities of CACMM2 was tested for a set of simple model mixtures. Although column efficiency was not high due in some extent to the high particle size, baseline separations of the mixtures C_5 – C_6 – C_7 alkanes and C_{13} – C_{14} – C_{15} alkanes (Fig. 4) were obtained using the CACMM2 as an analytical column. One advantage of the use of large adsorbent particles is that they can be used without causing an excessive pressure drop, which can compress low density solids packed in chromato-

graphic columns, as is the case of CACMM2. Other mixtures studied were pentane–benzene, pentane–cyclohexane, hexane–benzene, hexane–cyclohexane, heptane–benzene and heptane–cyclohexane (Fig. 5), where separation is achieved in 1 min as in the previous case. The retention of *n*-alkanes depends as

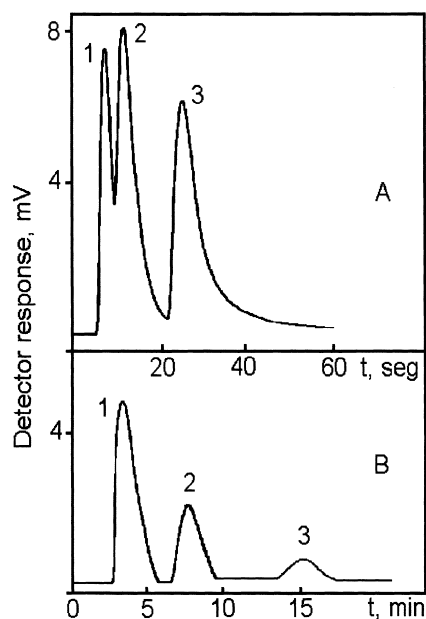


Fig. 4. Separation of model mixtures in a column packed with CACMM2. Mixture components: *n*- C_5 (1), *n*- C_6 (2), *n*- C_7 (3) alkanes in A and *n*- C_{13} (1), *n*- C_{14} (2), *n*- C_{15} (3) alkanes in B. Conditions are given in the text.

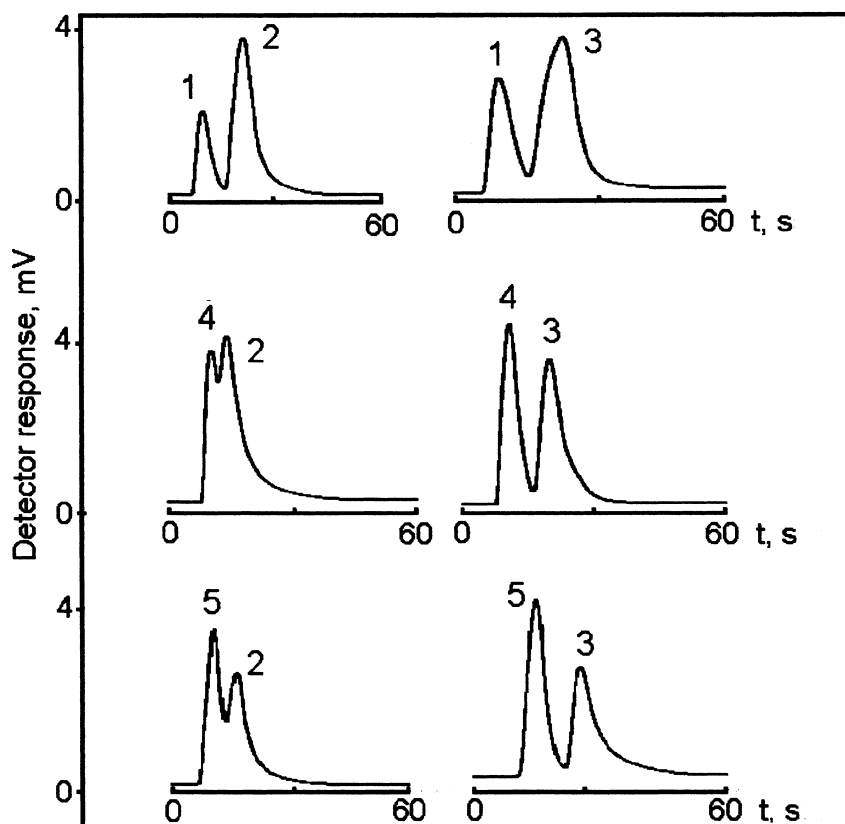


Fig. 5. Separation of model mixtures in a column packed with CACMM2. Mixture components: (1) *n*-pentane, (2) benzene, (3) cyclohexane, (4) *n*-hexane, (5) *n*-heptane. Conditions are given in the text.

would be expected on the number of carbon atoms in the molecule. The lowest *n*-alkane studied, pentane is separated from the next compound in the homologous series, hexane, with a selectivity of 1.8 (Table 4). Cyclohexane is eluted after *n*-hexane with resolution 1.2, but it cannot be separated from benzene.

Table 4

Selectivity (α) and resolution (R_s) of two-component hydrocarbon mixtures on the adsorbent CACMM2 at 32°C

Mixture	α	R_s
<i>n</i> -Pentane–cyclohexane	3.1	1.2
<i>n</i> -Pentane–heptane	3.0	2.1
<i>n</i> -Pentane–benzene	2.7	1.3
<i>n</i> -Pentane–hexane	1.8	0.5
<i>n</i> -Hexane–heptane	1.8	1.2
<i>n</i> -Hexane–cyclohexane	1.6	1.2
<i>n</i> -Hexane–benzene	1.4	0.4
<i>n</i> -Heptane–cyclohexane	1.6	1
<i>n</i> -Heptane–benzene	1.5	0.8

We observed different values of $\overline{\Delta H_{ads}}$ for the pair cyclohexane–benzene, although they have almost the same boiling point. Thus, the lack of resolution can be due to the low efficiency of the packed column together with the peak tailing effect.

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