

An inverse gas chromatographic study of the adsorption of alkanes on hydroxyapatite

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Saturated alkanes adsorption on synthetic well-crystallized hydroxyapatite was studied by the inverse gas chromatography method, at zero coverage. Hydroxyapatite was prepared from $\text{Ca}(\text{OH})_2$ and H_3PO_4 aqueous solutions by a slow titration technique. The powder was characterized by XR diffraction, surface area measurement, and chemical analysis. Adsorption of saturated alkanes was investigated in the temperature range 338–353 K, using a flame ionization detector, and nitrogen as a carrier gas. The gas/solid partition coefficients were calculated from the retention data as well as the standard thermodynamic functions of adsorption, ΔH_a^0 , ΔS_a^0 and ΔG_a^0 . Linear relationships between $\ln K$ and $1/T$ and between ΔG_a^0 and the number of carbon atoms in saturated alkanes were observed. The dispersive component of the surface free energy was calculated for the investigated temperature region. A possible analytical application of hydroxyapatite to *n*-alkanes separation is given. © 2000 Kluwer Academic Publishers

1. Introduction

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a major inorganic component of bones and teeth [1], and it is, together with fluoroapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, a widespread phosphate mineral in the earth crust, sediments and soil [2]. Physico-chemical and specially the surface properties of hydroxyapatite in contact with water solutions were intensively studied in medicine, stomatology, geochemistry, ecology etc. As found hydroxyapatite acts as a good and selective sorbent for many inorganic and organic molecules and ions. The major field of its application is in coprecipitation and sorption of heavy metals [1, 3–7], and radioactive species such as ^{90}Sr [8], but it is also applied as organic molecules sorbent, in liquid chromatography. It is used for separation and purification of proteins, nucleic acids, vitamins and pesticides [9–15].

There are no literature data on HAP as an organic molecules sorbent in gas chromatography. Inverse gas chromatography (IGC) or gas-solid chromatography (GSC) is a powerful method for solid surface studies [16, 17]. Adsorption on the surface of a solid can be determined either at finite or at zero surface coverage. Advantages of using IGC method at zero coverage are that it requires very small amounts of investigated adsorbates and that all observed phenomena come from adsorbate-adsorbent interactions while interactions between sorbate molecules themselves may be neglected. This technique was widely used in adsorption measurements, and surface characterization in the last decade. For example, surface properties of silicoaluminate glass fibers [18], alkaline earth-metal modified silica [19], silica gel [20], zeolites [21], activated carbon cloth [22], cork [23], was investigated by means of IGC.

The aim of our work was to investigate hydroxyapatite as a saturated alkane adsorbent, to find relations between retention data, number of carbon atoms, molecule geometry and working temperature, and to calculate surface free energy of hydroxyapatite and thermodynamic functions of adsorption.

2. Experimental procedure

2.1. Hydroxyapatite preparation and characterization

Hydroxyapatite was obtained from $\text{Ca}(\text{OH})_2$ and H_3PO_4 aqueous solutions, by slow titration method described elsewhere [24]. After washing, crystals were dried overnight at 105°C. Crystal structure of the synthesized material was determined by X-ray diffraction analysis using a Siemens-Kristalloflex diffractometer with $\text{Cu K}\alpha$ radiation. Specific surface area was measured by a single point nitrogen adsorption method using a Strohlein area meter. Stoichiometry of the sample was confirmed by determination of Ca/P ratio. Calcium concentration was measured by a Perkin Elmer 703 atomic absorption spectrophotometer and the concentration of phosphate as a blue phosphomolibdate complex at 690 nm was determined using a Perkin Elmer Lambda 1 A spectrophotometer.

2.2. Apparatus

A Perkin Elmer 8310B gas chromatograph with a flame ionization detector (FID) was used for the adsorption measurements and dry nitrogen as a carrier gas. The synthesized sample was sieved and a 0.16–0.20 mm fraction was used for further investigation. A

stainless-steel 25 cm long and 2.2 mm i.d. column was first cleaned with *n*-hexane, ethanol and acetone, and then packed with 0.6373 g of hydroxyapatite powder. After packing, the column was conditioned overnight at 523 K, while the nitrogen flow rate was $\sim 5 \text{ cm}^3 \text{ min}^{-1}$. The working temperature range was 338–352 K.

2.3. Adsorbates

Analytical grade saturated alkanes, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and cyclohexane, were chosen as adsorbates. Adsorption of these non-polar organic molecules on hydroxyapatite surface is due only to dispersive type of forces. The retention time of methane was measured for each column temperature and was assumed to be equal to the system dead-time. Analytical grade alkanes were injected, one at a time, by means of a $1 \mu\text{l}$ Hamilton microsyringe, in the smallest detectable amount of vapor. Each sorbat was injected at least three times, and the average retention times were used for further calculations. The carrier gas flow rates, measured with a soap bubble flow-meter, were in the range $18\text{--}22 \text{ cm}^3 \text{ min}^{-1}$. The ambient temperature, inlet and outlet (atmospheric) column pressure were also measured during the adsorption experiments. In order to examine the separation of saturated alkanes on hydroxyapatite, their mixture as vapor was injected at 343 K.

2.4. Calculations

The net retention volumes, V_N , were calculated using the equation:

$$V_N = (t_R - t_0)F_0(T/T_0)[(p_0 - p_w)/p_0]j \quad (1)$$

where t_R and t_0 represent the retention times of investigated alkane and unretained compound (methane) respectively, F_0 is the flow rate measured at room temperature T_0 , T is the column temperature, p_0 is the column outlet pressure (barometric), p_w is the water vapor pressure at T_0 , and j is the James-Martin correction factor for the gas compressibility. The gas/solid partition coefficients, K_s , were determined by dividing the net retention volume at given temperature by the total surface area of adsorbent in the column, A_s . A_s is derived by multiplication of the specific surface area of the adsorbent and the mass of the adsorbent in the column. The partition coefficients enabled us to calculate the thermodynamic data of adsorption. The standard differential enthalpy of adsorption, ΔH_d^0 , can be determined from the temperature dependence of K_s according to:

$$d(\ln K_s)/d(1/T) = -\Delta H_d^0/R \quad (2)$$

where R is a gas constant.

The standard free energy changes of adsorption, ΔG_a^0 , were calculated from the equation:

$$\Delta G_a^0 = -RT \ln(K_s p_{s,g}/\Pi_s) \quad (3)$$

where T is the column temperature, $p_{s,g}$ is the adsorbate vapor pressure in the gaseous standard state (101 kPa),

and Π_s is the surface pressure of the adsorbed gas in the standard adsorption state (0.338 mNm^{-1}).

The standard entropy changes of adsorption, ΔS_a^0 , can be calculated from the following relationship:

$$\Delta S_a^0 = (\Delta H_d^0 - \Delta G_a^0)/T \quad (4)$$

3. Results and discussion

X-ray diffraction and chemical analysis confirmed that pure well-crystallized hydroxyapatite (Fig. 1) with a Ca/P molar ratio of 1.67 was obtained. Specific surface area of the sample was $20.2 \text{ m}^2 \text{ g}^{-1}$.

The surface partition coefficients for all adsorbates at all column temperatures, as well as boiling points of each adsorbate are given in Table I.

The adsorption of *n*-alkanes increases with an increase in carbon atom number, as well as molar mass of adsorbate and its boiling temperature. The exception is cyclohexane, which boiling point is almost 12°C higher than the boiling point of *n*-hexane, yet all retention data for cyclic isomer show a weaker adsorption. The main reason for this phenomenon are the geometric properties of these two compounds. All six carbon atoms of *n*-hexane can approach a plane and interact with hydroxyapatite surface, while cyclohexane non-planar molecule can exist in the shape of a “boat” or a “chair” and only three or four carbon atoms are in the position for this interaction. Cycloalkanes are generally retained shorter than the corresponding normal alkanes in the gas-solid chromatography, but the converse is usually true in the gas-liquid chromatography [19]. Table I also shows a decrease in the adsorption

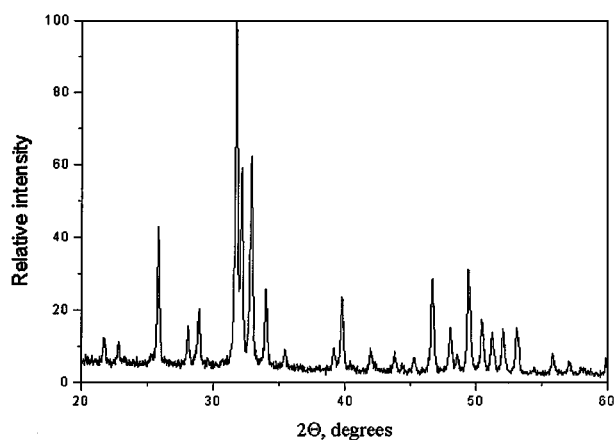


Figure 1 X-ray diffraction pattern of the hydroxyapatite obtained by slow titration method.

TABLE I K_s values ($\text{cm}^3 \text{ m}^{-2}$) at different temperatures for saturated alkanes adsorption on hydroxyapatite

Adsorbate	B.p. (K)	Column temperature (K)			
		338	343	348	353
<i>n</i> -pentane	309.4	0.68	0.46	0.40	0.33
<i>n</i> -hexane	342.2	2.07	1.44	1.25	0.91
<i>n</i> -heptane	371.6	7.47	4.81	4.33	3.00
<i>n</i> -octane	399.6	26.73	18.18	13.74	8.94
cyclohexane	354.6	1.56	1.12	—	0.73

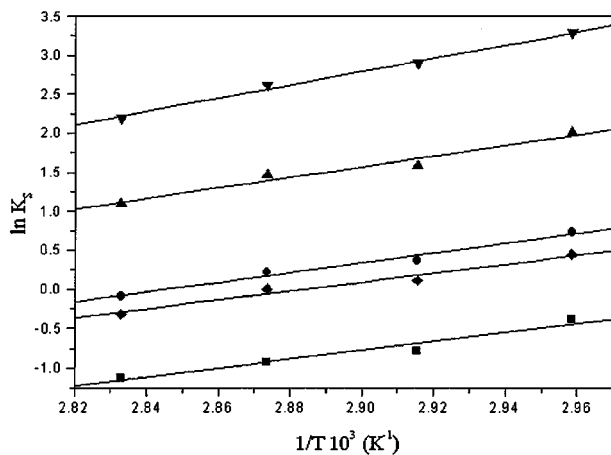


Figure 2 Plots of $\ln K_s$ vs. $1/T$ (K) for the adsorption of saturated alkanes on hydroxyapatite. ■ *n*-pentane, ● *n*-hexane, ▲ *n*-heptane, ▼ *n*-octane, ◆ cyclohexane.

of given adsorbates with a increase of column temperature (indication of non-specific interactions). Linear relationships between $\ln K$ and $1/T$ for the studied adsorbates are presented in Fig. 2.

The standard-state enthalpies of adsorption, at zero coverage, are obtained from plots of $\ln K_s$ against $1/T$, according to Equation 2. Standard free energy change and standard entropy change of adsorption were calculated from Equations 3 and 4. The obtained values of thermodynamic functions as well as of enthalpies of liquefaction, ΔH_L , are presented in Table II. According to the data given, ΔH_d^0 and ΔG_a^0 of the *n*-alkanes increase linearly with an increase in carbon atoms number. Adsorption enthalpies for all *n*-alkanes are ~ 1.7 times greater than the corresponding enthalpies of liquefaction. It is evident that *n*-hexane exhibits more negative ΔH_d^0 value than cyclohexane. The more negative the ΔH_d^0 and ΔG_a^0 , the greater the interaction between the adsorbate and the adsorbent.

TABLE II ΔH_d^0 (kJmol⁻¹), ΔH_L (kJmol⁻¹), ΔG_a^0 (kJmol⁻¹), and ΔS_a^0 (JmolK⁻¹) values for investigated adsorbates with hydroxyapatite

Adsorbate	Column temperature (K)	$-\Delta H_L^a$	$-\Delta H_d^0$	$-\Delta G_a^0$	$-\Delta S_a^0$
<i>n</i> -pentane	338			14.92	92.6
	343	27.2	46.2	14.04	93.9
	348			13.83	93.1
	353			13.45	92.9
<i>n</i> -hexane	338			18.07	100.3
	343	31.4	52.0	17.31	101.0
	348			17.14	100.1
	353			16.45	100.6
<i>n</i> -heptane	338			21.67	103.6
	343	36.8	56.7	20.77	104.7
	348			20.73	103.3
	353			19.95	104.1
<i>n</i> -octane	338			25.25	134.5
	343	38.0	70.7	24.53	134.6
	348			24.07	134.0
	353			23.16	134.7
cyclohexane	338			17.28	90.5
	343	32.3	47.9	16.57	91.2
	353			15.79	90.8

^aFrom ref. [25].

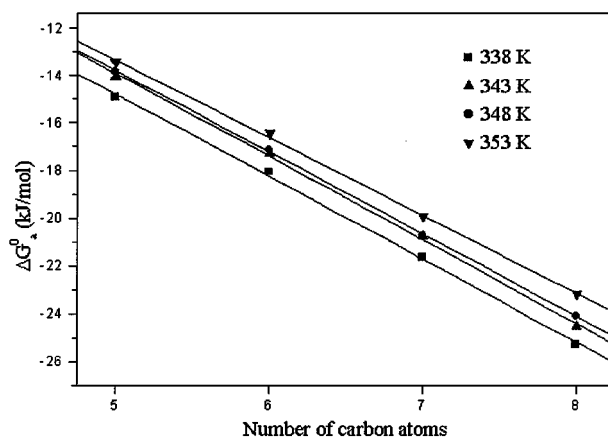


Figure 3 Plots of ΔG_a^0 versus *n*-alkane carbon number, at different temperature.

TABLE III The ΔG_{CH_2} and γ_s^d values for synthesized hydroxyapatite

Temperature (K)	338	343	348	353
ΔG_{CH_2} (kJmol ⁻¹)	-3.46	-3.49	-3.43	-3.26
γ_s^d (mJm ⁻²)	69.3	71.3	69.5	62.9

The standard free energy change of adsorption is the sum of dispersive and specific adsorbate/adsorbent interactions energies. Adsorption of *n*-alkanes occurs due to dispersive type of interactions only. The increment of adsorption energy corresponding to methylene group, ΔG_{CH_2} , may be obtained from the equation:

$$\Delta G_{CH_2} = -RT \ln(V_{N,n}/V_{N,n+1}) \quad (5)$$

where $V_{N,n}$ and $V_{N,n+1}$ are the net retention volumes for two *n*-alkanes having *n* and (*n* + 1) carbon number. ΔG_{CH_2} can also be derived from the plots of ΔG_a^0 versus carbon number, as a slope of these linear functions (Fig. 3).

Table III reports the ΔG_{CH_2} values for *n*-alkane series adsorbed on hydroxyapatite at various temperatures. Intermolecular interactions in an adsorbate/adsorbent system may be dispersive and specific corresponding to the dispersive, γ_s^d , and specific, γ_s^s , component of surface free energy, γ_s , of adsorbent

$$\gamma_s = \gamma_s^d + \gamma_s^s \quad (6)$$

Dorris and Gray [26] have used the incremental amount of free energy of adsorption, corresponding to the adsorption of one CH₂ group, to determine the dispersive component of surface free energy

$$\gamma_s^d = \Delta G_{CH_2}/4\gamma_{CH_2}N^2a_{CH_2}^2 \quad (7)$$

where γ_{CH_2} is the surface free energy of a solid containing only methylene groups, such as polyethylene ($\gamma_{CH_2} = 36.8 - 0.058 T(^{\circ}C)$ mJm⁻²), N is Avogadro's number, and a_{CH_2} is the cross-section area of an adsorbed CH₂ group (0.06 nm²).

The calculated γ_s^d values are reported in Table III. The γ_s^d value was found to increase with the temperature decrease from 353 to 348 K reaching a constant value (70.0 ± 1.1), in the temperature range from 348 to 338 K.

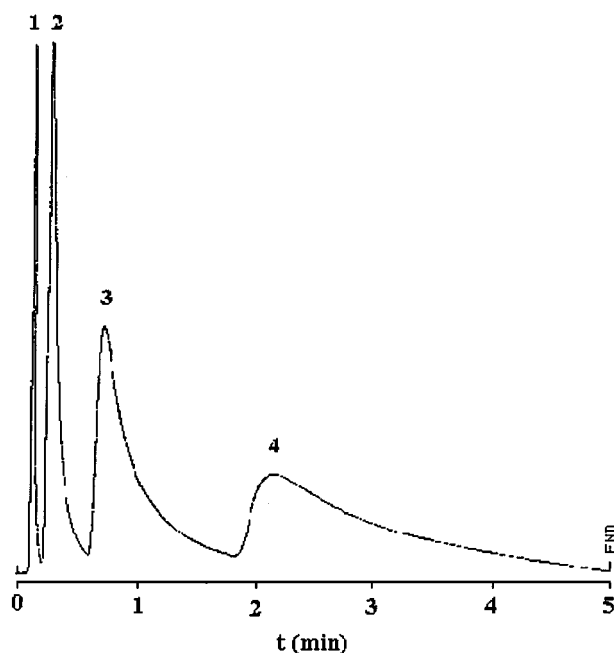


Figure 4 Chromatogram of the vapor mixture of *n*-pentane (1), *n*-hexane (2), *n*-heptane (3) and *n*-octane (4) on hydroxyapatite. Experimental conditions: column 25 cm \times 2.2 mm i.d., column temperature 343 K, nitrogen flow rate 24 cm³/min.

Unfortunately there are no literature data on hydroxyapatite surface free energy for comparison. The γ_s^d value for hydroxyapatite is of the same order of magnitude as that for pure silicas [27].

The gas-solid chromatography proves to be a superior technique in the analysis of low boiling mixtures such as mixtures of permanent gases and aliphatic compounds. It is also likely to be superior both at very low and very high column temperatures [28]. The most used adsorbents in gas-solid chromatography are carbon, alumina, silica and molecular sieves [28].

The results of *n*-alkanes gas mixture separation on hydroxyapatite are given in Fig. 4. All components of the mixture are completely separated under the given experimental conditions. The results can be important for a possible analytical application of hydroxyapatite as well as for understanding of the migration processes of alkanes in the environment, where hydroxyapatite rich sediments act as the stationary phase.

4. Conclusions

The surface characteristics of pure, well-crystallized hydroxyapatite synthesized by wet method were studied by IGC. Saturated alkanes adsorption parameters were used for the thermodynamic functions (ΔH_d^0 , ΔS_a^0 and ΔG_a^0) calculations. The standard adsorption enthalpies for investigated alkanes are 1.7 times higher than the corresponding heats of liquefaction. These data as well as the negative values of the standard free energy changes of adsorption suggest a strong adsorption of saturated alkanes on HAP, through non-specific interactions. The calculated dispersive components of the surface free energy, γ_s^d , are of the same order of magnitude as that for pure silicas, in the investigated temperature range. The γ_s^d values obtained can be used as a measure of the hydroxyapatite surface purity since we analyzed

a stoichiometric, highly pure and crystallized product. IGC appears to be a useful, fast and accurate technique, which can be successfully applied to comparing various samples. As shown, the gas mixtures of *n*-alkanes can be completely separated in a column filled with hydroxyapatite at given experimental conditions.

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