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APPLICATION OF GAS CHROMATOGRAPHY TO THE CHARACTERIZATION OF POROUS STRUCTURES

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SUMMARY

The adsorption and transport properties of a set of twenty rock samples were tested. The characterization was performed on the basis of thermal desorption (determination of the specific surface area) and by gas adsorption chromatography (determination of the rôles of specific adsorption and of transport phenomena).

INTRODUCTION

The ability of some rocks to retain molecules of gases is from a physical point of view due to their porous structure. The interaction taking place at the phase boundary between the gas and the solid phase, *i.e.*, the rock, may be considered, as follows from the results described below, as a specific physical adsorption. From the point of view of the magnitude of the surface area, which represents a criterion of the adsorption capacity, interest will be concentrated on rocks having a pronounced internal porosity due to a system of mutually interconnected microscopic cracks and channels (pores). In these cases the specific surface area, which is related to a unit mass of the material, will be at least one order of magnitude greater than the external geometric surface area.

The solid phase generally comprises a system of compounds of various chemical compositions, and of crystalline or amorphous character. This results in heterogeneity of the surface which in turn affects the adsorption properties.

Besides these equilibrium characteristics of the adsorbent, transport phenomena and the possible presence of another (*i.e.*, liquid) phase also play an important rôle in the adsorption process. When the equilibrium between the adsorbed gas and the gas phase is disturbed gas is evolved from the pores. The rate of this gas evolution is dependent on the pressure within the cavities of the rock and on the character of the pores through which the gas passes.

EXPERIMENTAL

Thermal desorption

This method is commonly used for the determination of the specific surface areas of porous materials. The measurements performed were based on principles published previously[1]. Nitrogen adsorbed at 78°K was detected in a thermal conductivity detector after its desorption at room temperature. The amount adsorbed is proportional to the surface area of the adsorbent. A detailed description of the apparatus and its operation was given previously[2,3]. Vanadium pentoxide (V_2O_5) was applied as a standard, its specific surface area was 0.75 m^2 g^{-1}, determined by the BET method. The rock samples were not subjected to any thermal pretreatment before the measurements.

Gravimetric determination of sorption capacities

The measurements were performed on a sorption balance with a quartz spiral. The samples were degassed to a pressure of $1.3 \cdot 10^{-2}$ Pa and then argon at a pressure of 1.3 Pa was introduced. The weight increase due to the argon adsorption was determined.

Gas adsorption chromatography

A simple laboratory chromatograph CHROM-4 (Laboratorní přístroje, Czechoslovakia) with katharometer was applied. The experiments were performed at room temperature, with helium as carrier gas; flow-rate 30 cm^3 min^{-1}. The dimensions of the chromatographic glass column were 3 m × 3 mm I.D. Ethane, ethylene, propane, propene, *n*-butane, butene-1, butene-2 and butadiene-1,3 were used as adsorbates. The retention volumes determined were corrected for the free volume of the column and expressed per gram of the adsorbent.

Samples

A set of twenty rock samples (1–20) representing the so-called collector rocks from various localities in Czechoslovakia was investigated. The materials were ground and fractionated; this pretreatment was necessary because of the investigation techniques applied. For the measurements a grain fraction of 0.1–0.2 mm was used. In the case of homogeneous porous materials, the sorption and transport properties are not disturbed by grinding; the interparticle spaces cannot simulate the transport pores, as is shown by a comparison of the grain size and the pore diameter (grain, $1 \cdot 10^{-4}$–$2 \cdot 10^{-4}$ m; transport pores, 10^{-7} m; micropores, $2 \cdot 10^{-9}$ m). The increase in geometric surface area of the materials upon grinding can be neglected when compared with the total surface area in the case of porous rocks. In the case of heterogeneous rocks —sandstones— the powder fraction containing clay binders was not discarded. Rocks with a specific surface area less than 0.1 m^2 g^{-1} were considered as compact and non-porous.

RESULTS AND DISCUSSION

The application of gas–solid chromatography (GSC) to the characterization of solid phases is well known. This simple method enables one quickly to obtain

TABLE I

CHARACTERISTICS OF THE SAMPLES

Sample No.	Specific surface area $(m^2\ g^{-1})$	Adsorption capacity $(mmol\ Ar\ g^{-1})$
1	0.86	0.26
2	0.26	0.28
3	0.56	0.22
4	1.20	0.41
5	0.07	0.00
6	0.27	0.27
7	0.28	0.07
8	0.54	0.23
9	0.21	0.25
10	0.03	0.00
11	0.33	0.24
12	0.19	0.17
13	0.08	0.00
14	0.07	0.00
15	0.37	0.21
16	0.81	0.22
17	0.36	0.20
18	0.95	0.25
19	0.44	0.25
20	0.08	0.00

TABLE II

RESULTS OF GC MEASUREMENTS

Sample No.	Corrected retention volume $(cm^3\ g^{-1})$							
	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8-1	C_4H_8-2	C_4H_6-1,3
1	4.0	6.7	21.4	31.1	–	78.1	109.8	148.4
2	1.2	3.9	7.3	11.9	–	25.6	41.1	–
3	5.5	9.4	15.6	29.1	–	68.1	106.4	175.3
4	12.2	13.2	28.5	56.5	105.4	123.7	195.0	286.4
5	–	–	–	–	–	–	–	–
6	1.9	5.6	17.3	37.9		91*		
7	2.2	8.8	16.0	27.9	53.9	78.0	97.6	140.4
8	7.3	7.9	21.9	48.1	–	83.2	114.1	189.0
9	1.4	–	4.5	9.4	–	23.7	32.2	–
10	1.3	0.2	2.0	5.7		16*		
11	1.8	4.2	8.8	10.3	12.3	22.5	33.1	36.8
12	1.5	–	2.9	15.2	–	16.5	26.1	–
13	–	–	–	–	–	–	–	–
14	–	0.2	1.9	3.2		11*		
15	4.6	6.7	14.8	25.7	42.4	56.4	78.9	133.0
16	46.2	53.1	205.8	346.1	599.8		700.3**	
17	2.4	5.0	14.2	23.7	28.9	52.3	81.9	113.7
18	14.4	16.1	41.1	75.9	88.0		217.6**	
19	11.2	17.4	32.5	57.9	71.2	117.6	164.0	253.6
20	0.3	0.5	3.0	4.4		11.0*		

* Corrected retention volume for unresolved C_4 hydrocarbons.
** Corrected retention volume for unresolved C_4 unsaturated hydrocarbons.

information about the type of interaction in the system[4,5], to test the homogeneity of microporous structures[6] or to characterize a new adsorbent[7].

The aim of the present measurements was to determine the adsorption properties of the investigated materials in the form in which they exist in nature, *i.e.,* without previous vacuum or thermal dehydration. For this reason the thermal desorption (TD) and gas chromatographic (GC) measurements were performed on the original untreated samples. However, such conditions could not be maintained with the gravimetric method. In this case, full dehydration and evacuation to $1.3 \cdot 10^{-2}$ Pa are necessary before gravimetric adsorption measurement. As is seen from Table I, the results obtained by the two methods used cannot be correlated. The surface areas of the samples were characterized only by the TD data.
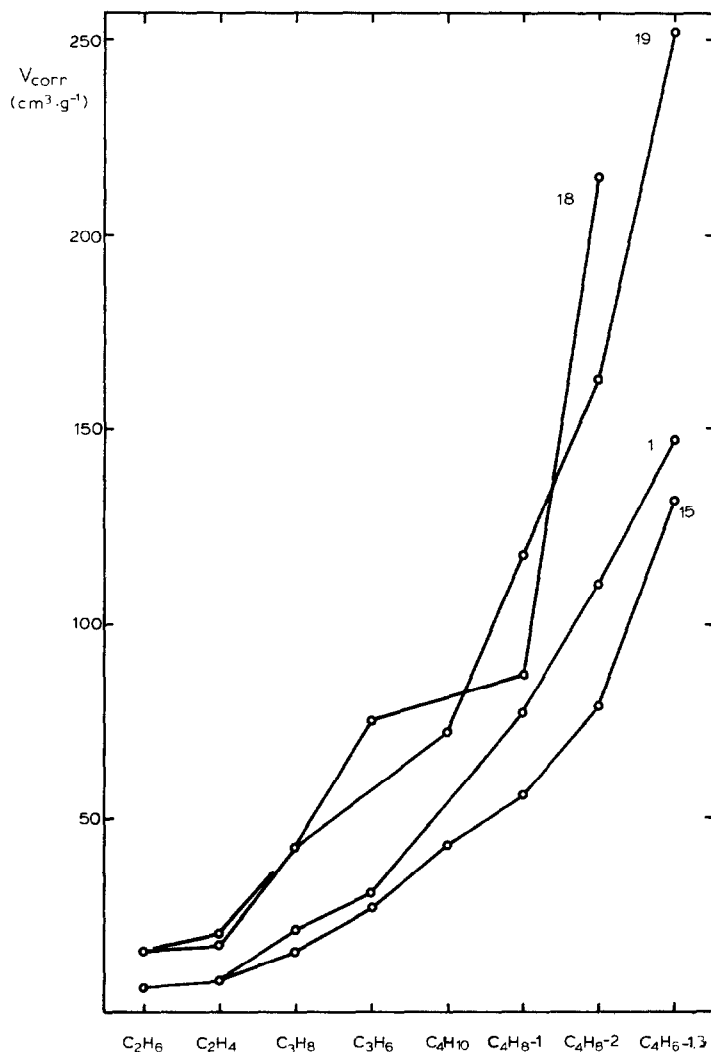

Fig. 1. Dependence of the corrected retention volumes on the type of the adsorbent.

The specific areas of the materials tested differ by orders of magnitude. These results cannot yield sufficient information about the transport properties of the materials.

The GC measurements were performed in order to determine the transport properties of the investigated rocks and to verify the influence of the surface heterogeneity on the adsorption capacity. Gaseous hydrocarbons, both saturated and unsaturated, were used as model adsorbates, permitting the determination of the influence of heterogeneity (double bond) as well as of transport phenomena (chain length). The results of the GC measurements are given in Table II.

With all samples the influence of the surface heterogeneity is manifested by an increase in retention volume of the unsaturated hydrocarbons. Information about the gas diffusion rate in the investigated samples was obtained from the relationships between the retention volumes and the forms of the chromatographic elution curves. Figs. 1 and 2 illustrate the behaviour of materials with different transport properties. Samples with comparable specific surface areas were chosen.
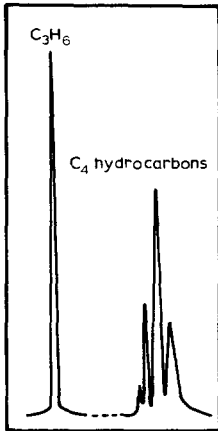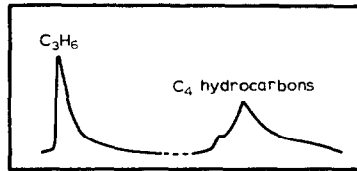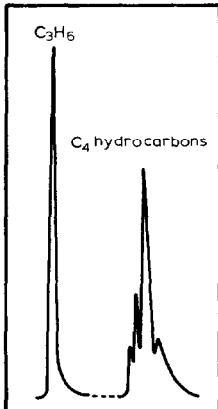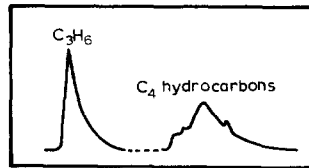

Fig. 2. Influence of transport phenomena on the form of the chromatographic elution curves.

On the basis of the data obtained the individual rock samples were classified in the following way:

(1) Materials with the specific surface areas $0.33 \leqslant \rho \leqslant 1.2 \text{ m}^2 \text{ g}^{-1}$ (a) with well developed transport pores, *e.g.*, samples, 1, 3, 4, 11, 15, 17. Symmetrical elution curves and very good separation capacities were found. These materials can act both as gas reservoirs, because of their high adsorption capacities, and as transport layers, as they exhibit a rapid diffusion. (b) With imperfectly developed transport pores, *e.g.*, samples 8, 16, 18, 19. Asymmetrical, tailing elution curves and incomplete separation were obtained. The rate of gas transport in these materials is very low. The adsorption properties of these samples are comparable with those of the rocks of group 1a. These materials can act as gas reservoirs but not as transport layers.

(2) Materials with specific surface areas $0.1 < \rho \leqslant 0.28 \text{ m}^2 \text{ g}^{-1}$. This is the case for samples 2, 6, 7, 9, 12 which exhibit symmetrical elution curves and good separation. This group of rocks are both gas reservoirs and transport layers.

(3) Materials with specific surface areas $\rho < 0.1 \text{ m}^2 \text{ g}^{-1}$. This group is represented by samples 5, 10, 13, 14, 20. The elution curves are symmetrical, and the separation capacity is negligible. Rocks of this type exhibit negligible adsorption capacities, and are compact non-porous materials. They are able to accumulate gases only in macrocavities.

CONCLUSION

The possibility of application of thermal desorption together with gas chromatography for the characterization of collector rocks and determination of their transport properties has been verified for twenty samples. Our investigations showed that a significant correlation exists between the physical properties of the individual rocks as described and their function as gas collectors.

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