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Adsorption of volatile hydrocarbons on natural zeolite-clay material

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Abstract This study investigated the vapor-phase sorption of hydrocarbons (HC) of various chemical nature (n-hexane, iso-octane, benzene, toluene and p-xylene) on zeolite-clay material (ZCM) of Tatarsky-Shatrashansky deposit (Tatarstan, Russia). For comparison, we also studied HC sorption on natural high-grade zeolite (Z) of St. Cloud Mine (New Mexico, USA), two local bentonite clays and synthetic zeolite-molecular sieve Ms5A. As a result, sorption capacity of ZCM towards aliphatic and aromatic HC was significantly higher than the sorption capacity of Z but lower than that of clays. In addition, the data showed that HC sorption on ZCM occurs as surface adsorption. The comparison with Ms5A and erionite ZAPS, a natural Mexican zeolite, revealed that both ZCM and Z do not interact as microporous selective sorbents with linear alkanes. The main differences in HC sorption on ZCM and Z were ZCM higher sorption capacity towards both aliphatic and aromatic HC, as well as its lower sorption sensitivity to the type of HC. We found that the reason for these differences is the presence of large amount of clay minerals in ZCM. To summarize, ZCM can be considered as a suitable adsorbent for protection and remediation of HC-contaminated soils.

Keywords Hydrocarbons · Vapor-phase sorption · Zeolite-containing materials

Nomenclature

HC	hydrocarbons
ZCM	natural zeolite-clay material
Z	natural zeolite of St. Cloud Mine
Ms5A	zeolite-molecule sieve 5A
MGAB	modified Guggenheim-Anderson-De Boer equation
BET	Brunauer-Emmett-Teller equation
DSC	Differential Scanning Calorimetry
TG	Thermogravimetry
P/P_0	relative vapor pressure (dimensionless)
Vs	sorption value, mg/g
Vm	sorption monolayer value, mg/g
RH	relative humidity (dimensionless)
σ	kinetic diameter of a molecule, Å
B. p.	boiling point, °C
K_{OW}	octanol-water partition coefficient (dimensionless)

1 Introduction

In comparison to other adsorbents, natural zeolites have not yet found a prominent role in commercial separation and purification of gaseous mixtures containing volatile hydrocarbons (HC). The abundance and low cost of natural zeolitic raw materials rarely offset such disadvantages as variable composition, low purity and often poorer separation performance as opposed to more favored synthetic zeolites (Ackley et al. 2003; Sircar 2006). Few data exist on the application of zeolites in their natural form. For instance, chabazite was proposed to be utilized in refinery separating of gas mixtures of n-paraffins and iso-paraffins (Barrer 1978). Another example is Mexican natural adsorbent (ZAPS) with the crystalline phase corresponding to erionite that was investigated for separation of n-paraffins from cyclic and aromatic HC (Aguilar-Armenta and Díaz-Jiménez 2001). To improve the gas separation potential of natural zeolites towards the sorption of organic compounds, various induced

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structural chemical changes were proposed. Armenian dealuminated zeolite-clinoptilolite demonstrated good adsorption of benzene vapors (Gevorkyan et al. 2002). For separation of toluene/p-xylene/n-pentane mixtures, dealuminated faujasite and mordenite were shown to be more suitable than synthetic zeolite ZSM-5 (Carsten and Meininghaus 2000). Nevertheless, chemical and petrochemical industries currently favor utilization of synthetic zeolites, even though they are more expensive (US EPA 1998, 1999).

On the other hand, application of natural zeolites as sorbents can be economically justified in remediation technologies such as HC retention in contaminated soils. Soils are subjects to intensive HC contamination due to large amounts of vapor and liquid HC entering the soil surface during industrial accidents, leakages and spills. It is known that the sorption binding of volatile HC is one of the main means of their immobilization and retention in contaminated soil (Minnich 1993; Breus and Mishchenko 2006). Natural soils generally exhibit only modest capacities for sorption of most organic contaminants, and hence the spread of these substances into the atmosphere and ground waters can be reduced through the addition of an appropriate sorbent. A variety of materials have been suggested as potential sorbent additives to soils, including activated carbon, fly ash and natural geosorbent materials (Gullick and Weber 2001).

In such cases, the absence of HC sorption selectivity by natural zeolites does not prevent their usage and thus can be cost-effective to utilize low-grade natural zeolite-containing materials. In fact, materials that are poor in zeolite content (as low as 10–30%) and contain many clay minerals as well as other natural sorbents, are widespread in different countries. In the European part of Russia, where many soils are subjected to intense oil HC contamination due to highly developed oil recovery and refinery, such zeolite-clay materials (ZCM) can be found in almost every region. Here, one of the main ZCM deposits is Tatarsky-Shatrashansky volcanic sedimentary rock of the clinoptilolite type (zeolite content ca. 10–20%, clay minerals ca. 20–30%, with montmorillonite being most abundant). However, its sorption properties towards HC have not yet been studied. In Tatarstan republic its current sole usage is as ameliorant in agriculture.

The objective of this study was to evaluate the vapor sorption activity of Tatarsky-Shatrashansky ZCM with regard to aliphatic and aromatic HC. The following aims were established:

(i) to determine ZCM sorption capacity towards HC at different relative vapor pressures, under both oven-dried and moist conditions;
(ii) to compare HC sorption values on ZCM and high-grade natural zeolites, local clays and also synthetic zeolite-molecular sieve;
(iii) to estimate ZCM sorption selectivity as related to HC of various chemical nature.

2 Materials and methods

2.1 Sorbents

The resources of Tatarsky-Shatrashansky ZCM deposit form 50–75 million ton. It contains about 10–20% of zeolite minerals that are mainly clinoptilolite and more seldom heulandite (Yakimov 2001). These minerals have pore openings of about 4–5 Å that indicate that they can act as molecular sieves (Barrer 1978). The levels of toxic and radioactive elements in ZCM are in accordance with sanitary regulation (Yakimov 2001). Tables 1–3 show mineralogical content and physical and chemical specifications of ZCM. Prior to sorption measurements, ZCM samples were homogenized and put through a sieve of 0.5 mm (35 mesh).

For comparison with ZCM, we studied HC vapor sorption on the natural high-grade zeolite (Z) kindly provided by Prof. Robert S. Bowman from New Mexico Tech University, USA. Z sample was a representative of natural clinoptilolite-rich zeolitic tuff from the St. Cloud Mine in south central New Mexico, near Winston. St. Cloud zeolite is a calcium-sodium-potassium aluminosilicate $(Ca, Na_2, K_2)(Al_6\ SiO) \cdot 24H_2O$, similar to the synthetic zeolite of the A type (Barker et al. 2004; St. Cloud Mining Company 2006). Based on internal standard X-ray diffraction analysis, it consists of about 74% clinoptilolite and has a surface area of about

Table 1 Mineralogical composition of zeolite-clay material (ZCM) and St. Cloud zeolite (Z), wt.%

	Clinoptilolite	Smectite	Quartz	Opal-CT/Cristobalite	K-Feldspar	Illite	Calcite	Mica	Total
ZCM[*]	12[**]	20	18	26	2		18	4	100
Z[***]	74	5	10[****]		10	1			100

[*] Analysis was performed by using FULLPAT QXRD method

[**] Clinoptilolite/Heulandite

[***] According to Chipera and Bish (1995)

[****] Quartz/Cristobalite

Table 2 Chemical analysis of zeolite-clay material (ZCM) and St. Cloud zeolite (Z), wt.%

	CaO	K_2O	MgO	Al_2O_3	Fe_2O_3	SiO_2	P_2O_5	Na_2O	TiO_2	SiO_2/Al_2O_3
ZCM*	14.9	1.2	1.3	5.4	2.3	56.8	0.11	0.14	0.3	10.5
Z**	3.6	3.2	1.4	11.9	1.6	64.9	<0.05	0.3		5.4

*According to Yakimov (2001)

**According to St. Cloud Mining Company (2006)

Table 3 Physical and chemical specifications of zeolite-clay material (ZCM) and St. Cloud zeolite (Z)

	Bulk density, g/cm^3	Specific gravity (relative density), g/cm^3	Total porosity, %	Pore size (diameter), Å	BET (N2) surface area, m^2/g (degassing temperature 200 °C)
ZCM	1.13*	2.29*	51		42
Z	0.99–1.06**	2.2–2.4**	52–59	4–7**	40***

*35 mesh (according to Yakimov 2001)

**14 by 40 mesh (according to St. Cloud Mining Company 2006)

***According to Barker et al. (2004)

40 m^2/g (Barker et al. 2004). The main mineralogical, physical and chemical specifications of Z are given in Tables 1–3. The sample of Z used in sorption experiments was homogenized and put through a 0.4–1.4 mm sieve (40-14 mesh).

In addition, for comparison with natural zeolites we examined HC vapor sorption on the synthetic zeolite-molecular sieve 5A (Ms5A, pore openings 5 Å, composition $0.8CaO: 0.2Na_2O: 1Al_2O_3: 2.0 \pm 0.1\ SiO_2: n\ H_2O$), Cat. No. 2-0300, Supelco, size 0.4–0.6 mm (40-30 mesh).

Moreover, benzene sorption on two bentonite clays from Biclyansky and Koshakovsky deposits in Tatarstan was also assessed. These clays are represented by the alkaline-earth montmorillonite with calcium exchange complex $(Ca,Na)(Mg,Al,Fe)_2(OH)_2\ [(Si,Al)_4O_{10}]\cdot nH_2O$. Biclyansky clay contains 62–65% of montmorillonite; 15–20% of chlorite/kaolinite; 11–14% of mica; 11–12% of quartz; 3–4% of feldspar; 1–1.5% of calcite, while Koshakovsky clay is poorer, with only 65% of clay minerals (Yakimov 2001). Both clays are common throughout Tatarstan territory and are used in building and well-boring industry. Prior to measurements, clay samples were homogenized and put through a 0.5 mm sieve (35 mesh).

2.2 Sorbates

As sorbates, aliphatic (n-hexane and iso-octane-2.2.4-trimethylpentane) and monoaromatic (benzene, toluene and p-xylene) HC were used. Prior to application, sorbates were purified by standard techniques; their purity was controlled chromatographically and was above 99%. Table 4 shows physical and chemical parameters of these sorbates.

2.3 Mineralogical analysis and BET surface area measurement of ZCM

Both types of ZCM analyses were performed by Los Alamos National Laboratory, USA. To determine the content of main minerals, a full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns (FULLPAT QXRD method) was performed by Mr. Steven J. Chipera (Chipera and Bish 2002). The results are presented in Table 1. Determination of ZCM surface area was done by High Speed Gas Sorption Analyzer (Quantachrome Instruments Nova 1200, high purity N_2) using standard BET adsorption method (N_2, 77 K). Prior to analysis, ZCM samples were grinded and homogenized, and BET surface area values were then obtained using the six-point method for both sieved (<1 mm, 18 mesh, without fractionation) and not sieved samples. All measurements were run on samples previously dried at various degassing temperatures (50 °C–350 °C) for 2.5 h in vacuum. Table 3 shows BET surface area values for ZCM oven-dried at 200 °C.

2.4 Thermogravimetric analysis of sorbents

Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analyses were done using STA 449 C Jupiter (NETZSCH Instruments Inc., Burlington, MA) as follows. Approximately 10–20 mg of native sorbents in aluminum lid was placed on micro-balance pan. The oven was then purged with Ar gas, and the sorbent weight loss and thermal effects were measured at 30 °C–400 °C, with the temperature ramp rate of 4.0 °C/min. Figure 1 shows the obtained TG and DSC curves for ZCM, Z, Biclyansky clay and Ms5A.

Table 4 Physical and chemical specifications of studied hydrocarbons (HC)

HC	Molecular weight, g/mol	Density (25 °C), g/cm^3	Molar volume, cm^3/mol	Molar refraction, cm^3/mol	Kinetic diameter σ, Å	Cross-sectional molecule area, Å^2	Dipole moment, (20 °C), *D*	B. p., °C	Vapor pressure (25 °C), Pa	Water solubility (25 °C), mg/L	Octanol-water partition coefficient, log K_{OW}	Diffusion coefficient in air, m^2/s 10^{-6}
Benzene C_6H_6	78.1	0.874	89.4	34.28	5.9	30.59	0.0	80.1	12700	1760	2.1	9.3
Toluene C_7H_8	92.1	0.862	106.9	40.74	5.9	34.45	0.31	110.6	3800	550	2.7	8.5
p-Xylene C_8H_{10}	106.2	0.857	123.9	47.19	6.5	38.03	0.10	138.4	1170	200	3.2	6.7
n-Hexane C_6H_{14}	86.2	0.655	131.6	40.31	4.3	39.59	0.08 (25 °C)	68.7	20170	12.8	4.11	7.3
iso-Octane C_8H_{18}	114.2	0.688	166.1	52.69	6.2	46.23	0.0	99.2	6570	2.44	4.09	6.5

2.5 Determination of sorption equilibrium isotherms

Sorption isotherms of HC vapors were measured on oven-dried (at 105 °C and 300 °C), moistened (up to 7 wt.%) and water-saturated (relative humidity, RH of 100%) sorbents. For the preparation of dried sorbents, samples (0.4 g of ZCM, 0.4 g of Z, 0.2 g of clay and 0.1 g of Ms5A) were placed in the open 15 mL glass vials and oven-dried at 105 °C and 300 °C for 6 hours. Next, vials containing samples were placed into cartridges with perfluoroethylene (0.2 mm) and silicone (5 mm) liners, hermetically capped and cooled to room temperature. Completely hydrated sorbents were prepared by equilibrating the samples (0.2–0.4 g) with water vapors at RH of 100% in 15 mL vials at 25 °C for 2 weeks. To moisten the sorbent to 7% wt.%, necessary amount of distilled water was added to the oven-dried sorbent prior to the addition of sorbate into the ampoule. This was followed by the equilibration of the system as described above.

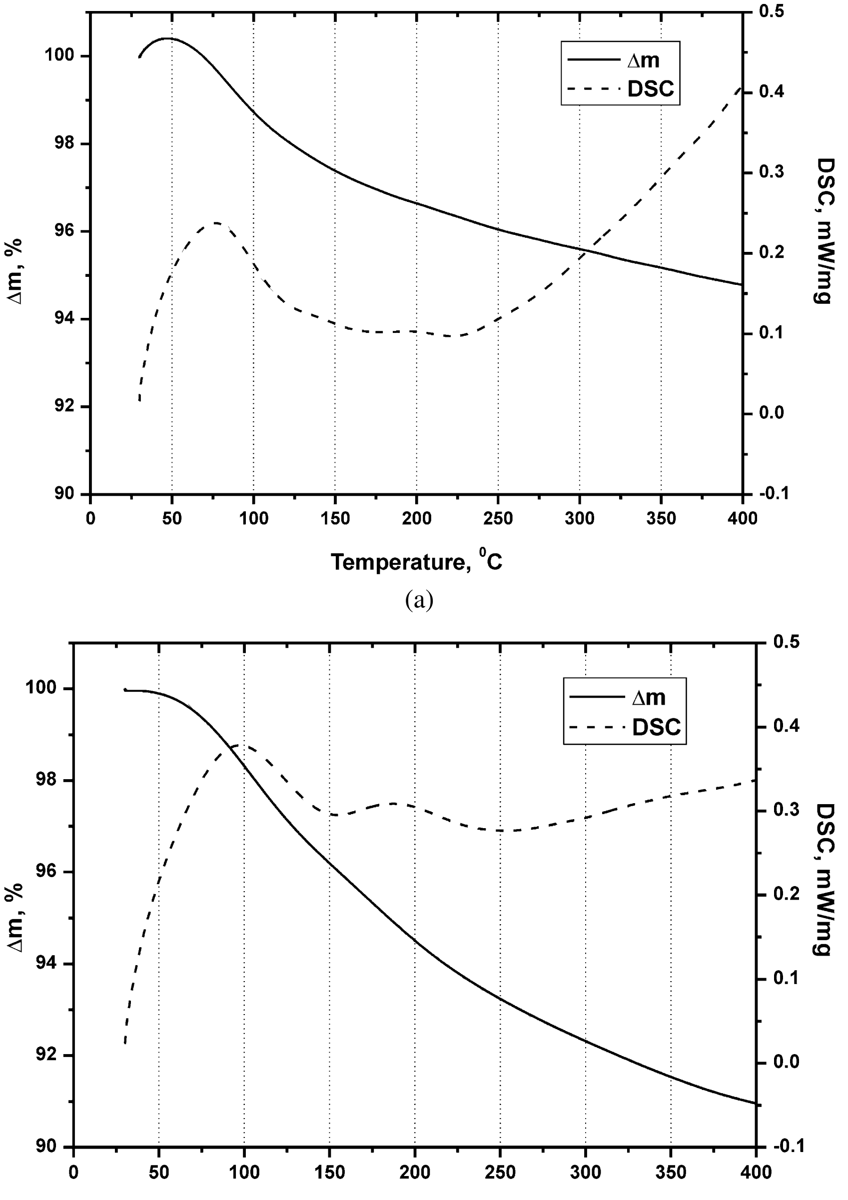
We first determined sorption kinetics for dried and hydrated sorbent-sorbate systems. As a result, two to three days were chosen in order to achieve the sorption equilibrium for systems examined in this study. To determine vapor sorption isotherms, liquid sorbates were dozed to 0.4 mL open glass vials that were placed inside the vials with equal quantity of dried/hydrated samples of a sorbent, prepared as described above. Hence, during equilibration, the organic sorbate was sorbed by a sorbent only through a vapor phase. The amount of added liquid sorbates was in the range of 0.5–80 µL for dried ZCM, 0.5–25 µL for dried Z, 0.3–35 µL for dried clays, 0.5–60 µL for dried Ms5A and 0.5–10 µL for hydrated sorbents. Immediately after dosing, vials were placed in cartridges, hermetically capped and equilibrated for 48–72 h at 25 °C.

The sorption isotherms were determined using the static method of gas chromatographic headspace analysis described in details elsewhere (Gorbatchuk and Solomonov 1996). The relative vapor pressure (P/P_0) of the organic sorbate in the system was determined directly by the ratio of sorbate chromatographic peaks for vapor samples of the studied system to pure liquid sorbate. The sorbate uptake (sorption value, *Vs*, mg/g) was determined as a difference between the amount of sorbate added and sorbate remained in the vapor phase after equilibration. The vapor phase of each sample was analyzed in five replications. The standard deviations of P/P_0 values were within 5% in the range of $P/P_0 > 0.5$ and 10% with $P/P_0 < 0.5$. In a mock experiment (without a sorbent) sorbate losses were estimated. The obtained data were represented graphically as experimental sorption isotherms, *Vs* versus P/P_0. Static gas chromatographic headspace analysis method was used for the measurement of HC sorption kinetics.

3 Results and discussion

3.1 Characteristics of sorbents

The comparison of two zeolite-containing sorbents revealed that their zeolite type was similar (clinoptilolite type to Z and clinoptilolite/heulandite type to ZCM), however, ZCM appeared to contain significantly less zeolites (12%, compared to 74% in Z), Table 1. On the other hand, ZCM contained more smectite (20%, compared to 5% in Z), as well as



(a)

(b)

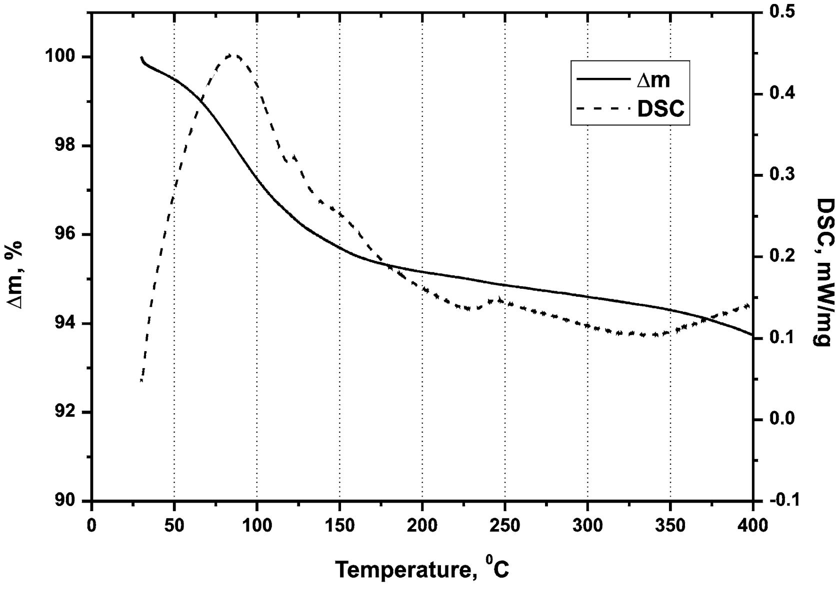
Fig. 1 TG and DSC curves of sorbents (<1 mm, 18 mesh, without fractioning). Sorbents: (**a**) Zeolite-clay material (ZCM), (**b**) St. Cloud zeolite (Z)

more cristobalite and calcite. Both sorbents showed similar total porosity values.

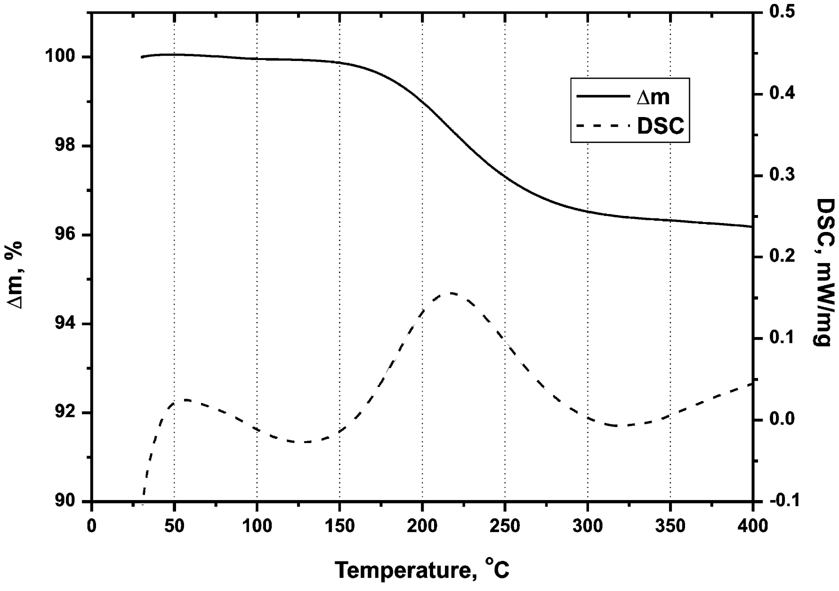
Table 3 shows the values of BET (N_2) surface area for both sorbents oven-dried at 200 °C. It is notable that moisture significantly influenced the BET surface area of microporous sorbents. For example, for air-dried (22 °C) Mexican natural zeolite (erionite) ZAPS, the total BET surface area was 39 m^2/g but for oven-dried (350 °C) ZAPS it increased to 400–500 m^2/g (Aguilar-Armenta and Díaz-Jiménez 2001). In this regard, ZCM BET surface area was explored as a function of degassing temperature (drying for 2.5 hours at 50–300 °C). Its values for sieved (<1 mm, 18 mesh) and not sieved ZCM samples did not differ statistically, and were therefore averaged (Fig. 2a). Here, the ZCM surface area increased up to ca. 45–47 m^2/g at 280–300 °C and then did not change significantly, suggesting the low content of micropores in the ZCM sample.

In a similar temperature range, thermogravimetric analysis of the same ZCM sample was carried out (Fig. 1a). In addition, we determined the thermograms for samples of Z (Fig. 1b), Biclyansky clay (Fig. 1c) and molecular sieve Ms5A (Fig. 1d). Total weight losses of air-dried samples were 5.24% for ZCM, 9.06% for Z, 6.29% for Biclyansky clay and 3.78% for dry sample of Ms5A (as provided by Supelco). The comparison of weight loss curves and the accompanying DSC curves showed that in ZCM and Biclyan-

Fig. 1 (*Continued*) TG and DSC curves of sorbents (<1 mm, 18 mesh, without fractioning). Sorbents: (**c**) Bentonite Biclyansky clay, (**d**) Zeolite-molecular sieve 5A (Ms5A)



(c)



(d)

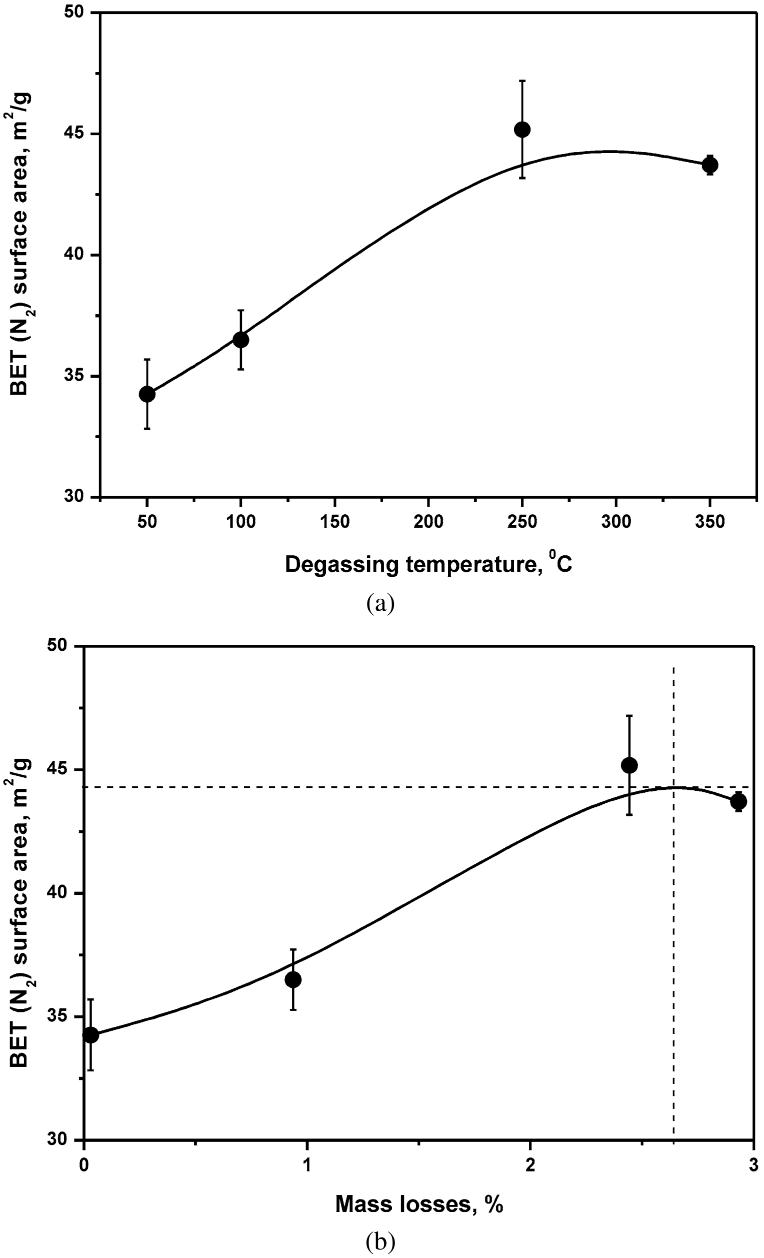
sky clay the hygroscopic water is mainly bound on the sorbent surface and within the interlayered space of clay minerals. We further found that in Z it is bound on the surface and to a lesser degree in micropores, whereas in Ms5A it is almost entirely held in micropores.

Next, we compared the results of thermogravimetric analysis of ZCM (Fig. 1a) and its BET (N_2) surface area values (Fig. 2a). As a result, the correlation between ZCM surface area and mass losses during heating was obtained (Fig. 2b). It is known that for a zeolite-containing material these losses are mainly caused by its gradual dehydration. Therefore, Fig. 2b demonstrates the connection between the increase in ZCM surface area and the removal of water during heating (Noyan et al. 2006), while Fig. 2c shows the influence of water content in ZCM on the decrease in surface area. Here, its slight decrease after heating at temperature higher than 280–300 °C can be explained by some structural changes in ZCM. It has been shown that upon drying under high temperature conditions, pore openings of hydrated zeolites can decrease to 7–8% (Tsitsishvili 1985). Thus, it is probable that samples oven-dried at 300 °C ZCM can be considered practically dehydrated.

3.2 Sorption isotherms

The well-known reason for good adsorptive properties of zeolites is their high porosity. For crystalline zeolites as micro-

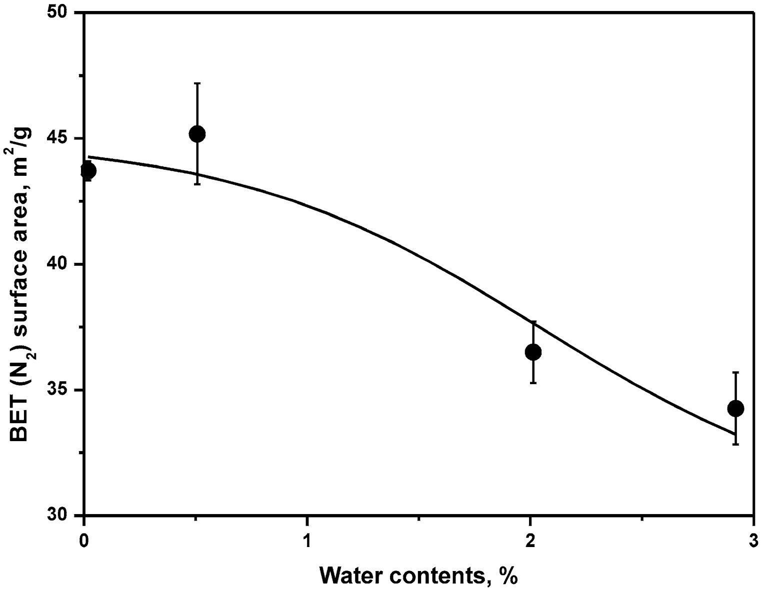
Fig. 2 The relationship between ZCM BET surface area values and thermogravimetric data. (**a**) ZCM surface area versus degassing temperature (data for sieved (<1 mm, 18 mesh) and not sieved samples are within experimental error), (**b**) ZCM surface area versus mass losses during heating



porous sorbents, sorption isotherms of type I are typically expected (Barrer 1978; Kornatowski 2005). Such isotherms are characterized under very low P/P_0 by very high Vs, corresponding to sorbate molecule binding in micropores, and further by Vs “saturation” (plateau area of an isotherm) (Gregg and Sing 1982; Aranovich and Donohue 1998). Due to the proximity of the surrounding pore walls to sorbate molecules, the sorption mechanism of volume pore filling is realized in the microporous space of zeolites. Because the diameter of zeolite micropores (less than 15–20 Å) is comparable to HC molecular volumes, after entering the micropore HC molecule will interact with pore walls almost throughout the entire volume of the micropore. Hence, micropore filling is the reason for high sorption selectivity for molecules of different volume and shape. The latter effect has a great practical value since it allows to effectively separate gas and vapor mixtures of organic compounds.

The vapor sorption capacity of ZCM was studied in comparison with Z and synthetic molecular sieve Ms5A, as all of these sorbents contain zeolites with similar pore size. For the approximation of all isotherms, with the exception of n-hexane sorption on Ms5A, the four-parametric empirical MGAB equation (1), which is a modification of Guggenheim-Anderson-De Boer equation, was used. We previously proposed this equation for the description of

Fig. 2 (*Continued*) The relationship between ZCM BET surface area values and thermogravimetric data. (**c**) ZCM surface area versus moisture content



(c)

vapor-phase multilayer sorption on geosorbents (Breus et al. 2006):

$$Vs = \frac{x^d}{(k_1 + k_2 x^d)(1 - k_3 x)} \qquad (1)$$

Here, Vs is a sorption value, $x = P/P_0$ relative partial pressure of sorbate vapors ($0 \le P/P_0 \le 1$) and k_1, k_2, k_3 and d are empirical parameters. The study of more than 100 of experimental vapor-phase sorption isotherms of 27 different organic sorbates on soil and mineral sorbents demonstrated that MGAB equation is best suited for the approximation of experimental sorption data in the full isotherm range (Breus et al. 2006; Mishchenko et al. 2007).

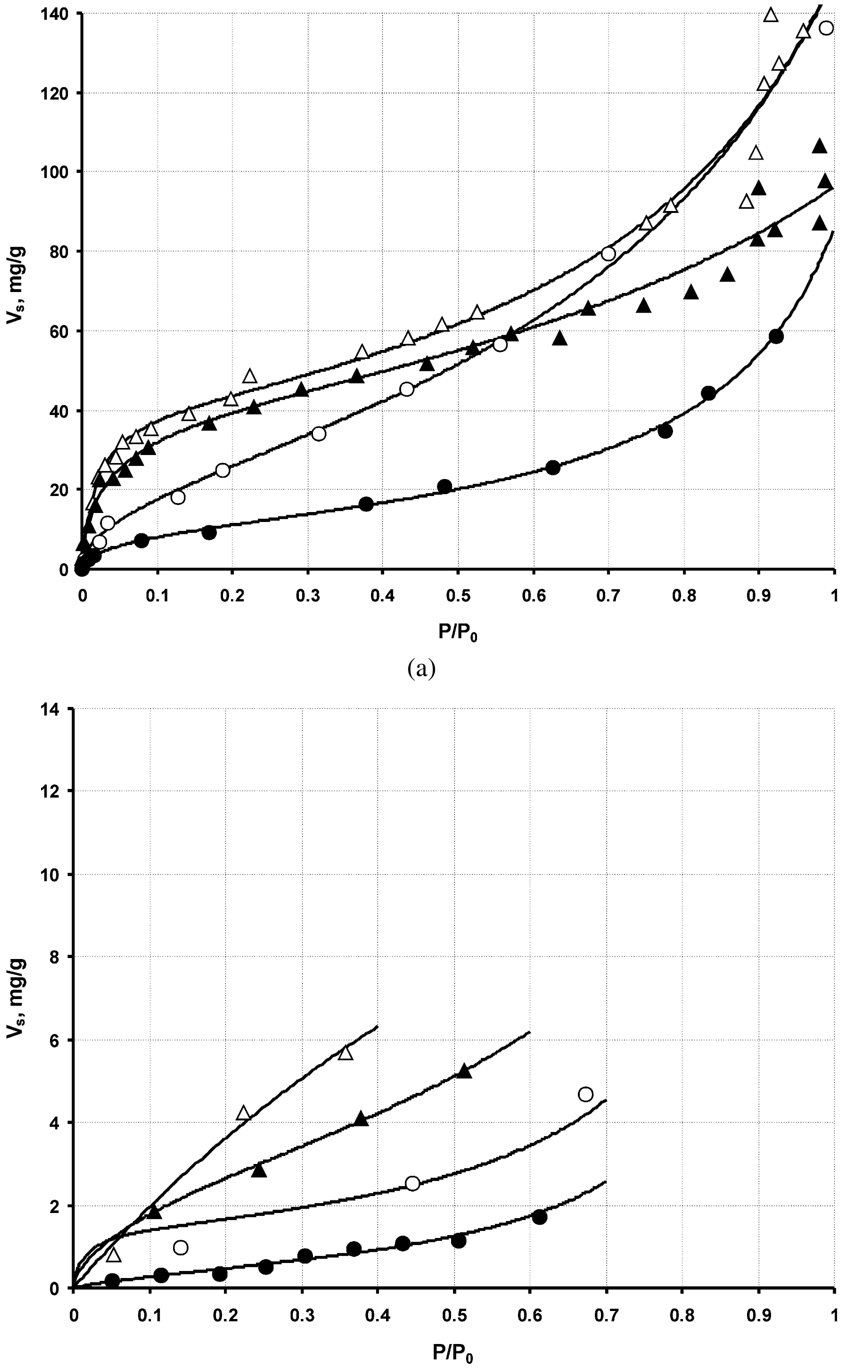
3.2.1 *The comparison of sorption capacity of ZCM with that of other mineral sorbents*

Figure 3a shows sorption isotherms of benzene vapors on oven-dried ZCM and Z (with residual moisture content of 3.3% and 4.6%, respectively). In both cases, we found isotherms to be of type 2 and not of type 1 that is characteristic for microporous sorbents. According to this classification, benzene sorption on both ZCM and Z occurred as sorption on the surface (adsorption). Here, benzene was sorbed 2-fold more actively on ZCM than on Z that contains 6 times more clinoptilolite due to its microporous structure. The reason for such differences is evident from the comparison of benzene sorption on ZCM with its sorption on two oven-dried bentonite clays (Fig. 3a). Here, the sorption activity of adsorbents was in accordance with their clay mineral contents (6% for Z, 24% for ZCM, 65% for Koshakovsky clay and 90% for Biclyansky clay). Thus, the advantage of ZCM over Z in benzene sorption was mainly due to the presence of great amount of clay minerals, predominantly smectites, Table 1.

Figure 3b represents the comparison of sorption isotherms of benzene on the same four sorbents that were moistened up to RH of 100%. Here, upon the significant decrease of Vs values, the range of sorbent activities remained the same: Biclyansky clay > Koshakovsky clay > ZCM > Z. However, the decrease of sorption due to moistening differed for various sorbents, despite the similar values of residual moisture content (17.6% for ZCM; 14.9% for Z; 15.6% for Biclyansky clay; 10.2% for Koshakovsky clay). Vs values themselves, as well as their sensitivity to moistening, changed according to the clay content in a sorbent. For instance, at $P/P_0 = 0.4$, Vs of benzene decreased on Z 18-fold, on ZCM 15-fold and on Biclyansky and Koshakovsky clays 12-fold and 9-fold, respectively (Fig. 4). It is possible that such a decrease was a result of intercalation, i.e. the penetration of water into the interlayer space of clay minerals not accessible to HC. Because of the amount of water used in intercalation, the percentage of water molecules that blocked sorption sites accessible to HC sorption was decreased.

3.2.2 *Estimation of ZCM sorption selectivity as related to aliphatic and aromatic HC*

We first investigated the vapor sorption of HC of various chemical nature (aliphatic n-hexane and branched isooctane, and monoaromatic toluene) on dry zeolite-molecular sieve Ms5A with the pore openings of 5 Å that are similar to clinoptilolite contained by ZCM and Z (Fig. 5). Our



(a)

(b)

Fig. 3 Sorption isotherms of benzene at 25 °C on natural, (**a**) oven-dried (105 °C) and (**b**) water-saturated sorbents (RH = 100%). MGAB approximations are presented as *solid lines*. Sorbents:
○ Zeolite-clay material (ZCM),
● St. Cloud zeolite (Z),
△ Biclyansky clay,
▲ Koshakovsky clay

aim was to determine whether (and to what degree) the sieve effect occurs for HC examined in this study and by doing so to evaluate HC sorption selectivity on ZCM. Despite the fact that toluene, being an aromatic compound, is capable of stronger intermolecular interactions, n-hexane sorption exceeded the sorption of toluene as well as iso-octane 5–6 times within the range of $0 < P/P_0 < 0.8$. Sorption isotherm of n-hexane corresponded to type 1 and was best described by the three-parametric Aranovich-Donohue equation (Aranovich and Donohue 1995) that is well suited for describing sorption isotherms on microporous sorbents such as Ms5A.

In contrast, isotherms of toluene and iso-octane were of type 2 that is characteristic for surface adsorption, and were well described by the MGAB equation (1). This is likely due to the fact that n-hexane has a kinetic diameter ($\sigma = 4.3$ Å, Table 4) smaller than the pore openings of Ms5A. It provides high Ms5A selectivity towards the sorption of linear

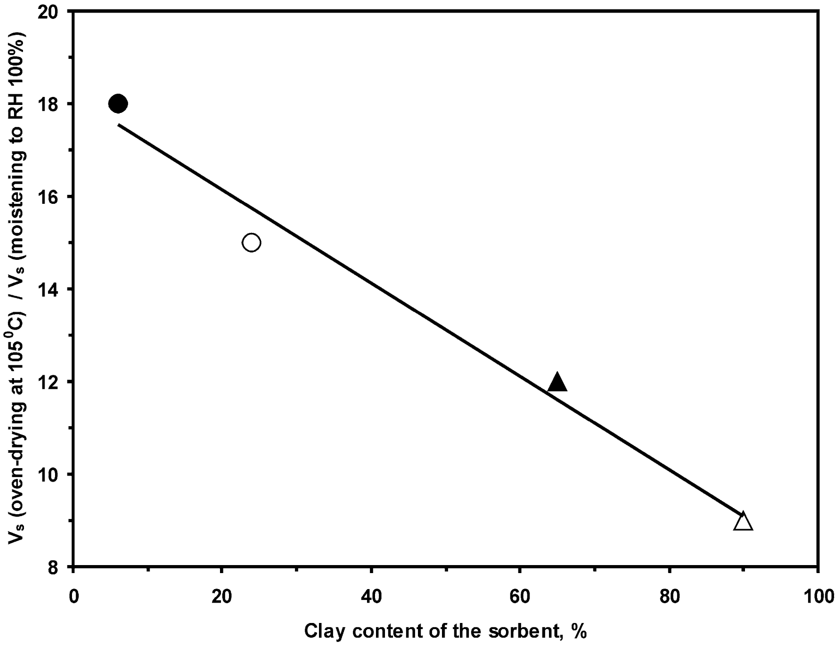


Fig. 4 The decrease of benzene sorption ($P/P_0 = 0.4$) due to sorbent moistening as related to the clay content in a sorbent. Sorbents: ○ Zeolite-clay material (ZCM), ● St. Cloud zeolite (Z), △ Biclyansky clay, ▲ Koshakovsky clay

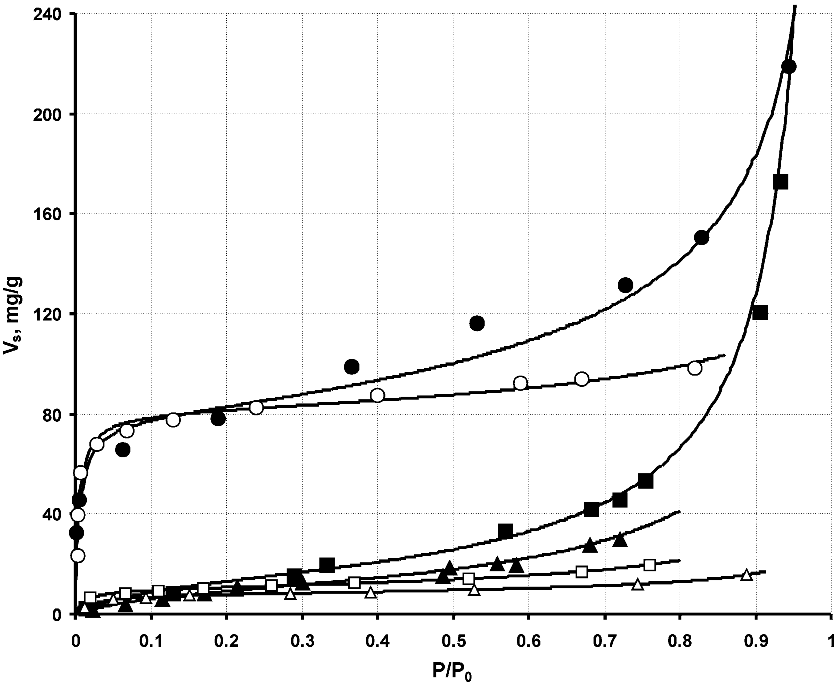


Fig. 5 Sorption isotherms of hydrocarbons at 25 °C on dry zeolite-molecular sieve 5A (Ms5A) and Mexican natural adsorbent (ZAPS, according to Aguilar-Armenta and Díaz-Jiménez 2001). As *solid lines*, MGAB approximations for all hydrocarbons except n-hexane (Aranovich and Donohue 1995 approximation) are presented. Sorbents: Ms5A *black dots*, ZAPS *white dots*. Hydrocarbons: □ Benzene, ■ Toluene, ▲ iso-Octane, ○● n-Hexane, △ Cyclohexane

HC. Toluene and iso-octane that do not interact with the microporous system only slightly differed in sorption values: in the range of $0 < P/P_0 < 0.8$ aromatic toluene was 15–20% more active than aliphatic iso-octane.

It is well known that some natural zeolites demonstrate a sieve effect. We correlated our experimental results with the reported data on the porous structure and sorption capacity of the natural Mexican adsorbent ZAPS (Aguilar-Armenta and Díaz-Jiménez 2001). ZAPS contains erionite (85%), clinoptilolite, as well as traces of cristobalite, quartz, feldspar, and has channels of approximately 5 Å. Figure 5 shows vapor sorption isotherms of n-hexane, benzene and cyclohexane on oven-dried ZAPS as compared with isotherms of n-hexane, toluene and isooctane on oven-dried Ms5A. Not only we were able to demonstrate the anticipated effect of sorption selectivity, but we also found that sorption isotherms of both ZAPS and Ms5A nearly overlapped for n-hexane (which filled micropores of both sorbents), aromatic HC (toluene and benzene) and saturated HC (iso-octane and cyclohexane).

Next, we studied sorption of five HC (aliphatic n-hexane and iso-octane, and aromatic benzene, toluene and p-xylene) on two oven-dried zeolite-containing sorbents—ZCM and Z. These HC differ in molar volumes, molecule shapes and consequently in kinetic diameters, Table 4. In addition, aliphatic and monoaromatic HC have different electron systems: the first are only capable of Van-der-Waals interactions with adsorbent surface, while the second, due to the π-electronic system, are also able to interact with sorption sites of zeolites and clay minerals by using additional donor-acceptor mechanism. In Fig. 6 sorption isotherms of these HC on ZCM and Z are presented. Similarly to benzene, all of these isotherms were of type 2 that is typical for surface adsorption. For all HC, *Vs* values on ZCM (Fig. 6a) were significantly (2–2.5 times) higher than on Z (Fig. 6b). The absence of correlation between *Vs* and kinetic diameters of HC molecules, σ (Table 4) indicated that the sorption of studied HC was not governed by their diffusion into the microporous space of both ZCM and Z. Therefore, σ value of benzene molecule (5.9 Å) is significantly higher than that of n-hexane (4.3 Å), while *Vs* values for n-hexane sorption on ZCM and Z were lower 1.5 and 2.5 fold, respectively, as compared with benzene. On ZCM at $P/P_0 < 0.6$–0.7, sorption values of all studied HC were relatively similar (Fig. 6a). At the same time, considering somewhat increased sorption of aromatic benzene, toluene and p-xylene, we can propose an additional contribution of specific (donor-acceptor) interactions.

On Z, which has a significantly higher clinoptilolite content, HC sorption isotherms were more clearly divided into two groups (as compared to ZCM) of aromatic and aliphatic HC (Fig. 6b). Here, the first group was 2–2.5 times more active. The higher *Vs* values of aromatic HC on Z can be caused first by a more compact molecule packaging in a sorbate monolayer (in such case the values of monolayer volume, *Vm*, should be overstated) and second by a higher number of sorption layers on sorbent surface. For further analysis, *Vm* values for both aliphatic and aromatic HC sorption on Z were calculated using the most common two-parametric BET model of multilayer sorption (Brunauer et al. 1938). The analysis of obtained *Vm* values as well as Vs/Vm relationship showed that aromatic HC (*Vm* for benzene, 12.0 mg/g, toluene, 9.5 mg/g, p-xylene, 9.5 mg/g; Vs/Vm at $P/P_0 = 0.4$ for benzene, 1.9, toluene, 1,8, p-xylene, 1,8) formed a monolayer of a greater volume and higher number of sorption layers as compared with aliphatic HC (*Vm* for n-hexane, 4.8 mg/g, iso-octane, 4.9 mg/g; Vs/Vm for n-hexane, 1,2, iso-octane, 1,4). These differences are however not great enough to provide any sorption selectivity of aromatic HC by Z.

There are two possible explanations of the absence of a sieve effect towards the linear n-hexane on ZCM and Z (Fig. 6a, b). The first explanation is the inequality of kinetic diameter of n-hexane molecule ($\sigma = 4.3$ Å) and the real size of clinoptilolite (heulandite) channels in ZCM and Z. This may be due to effects of the type(s) of cation(s) present in the zeolite structure, and/or to the influence of zeolite hydration grade on the effective pore openings of a zeolite. Channel diameters have been reported for hydrated zeolites (Panin and Chamuha 1992). However, during high-temperature drying their possible constriction can reach 5–7% and thus completely block the microporous space of zeolites to the entry of n-hexane molecules. The second possible explanation is the presence of impurities in zeolite channels. Here, complete blocking would be unlikely, while the partial participation of micropores in the binding of linear alkanes molecules is plausible.

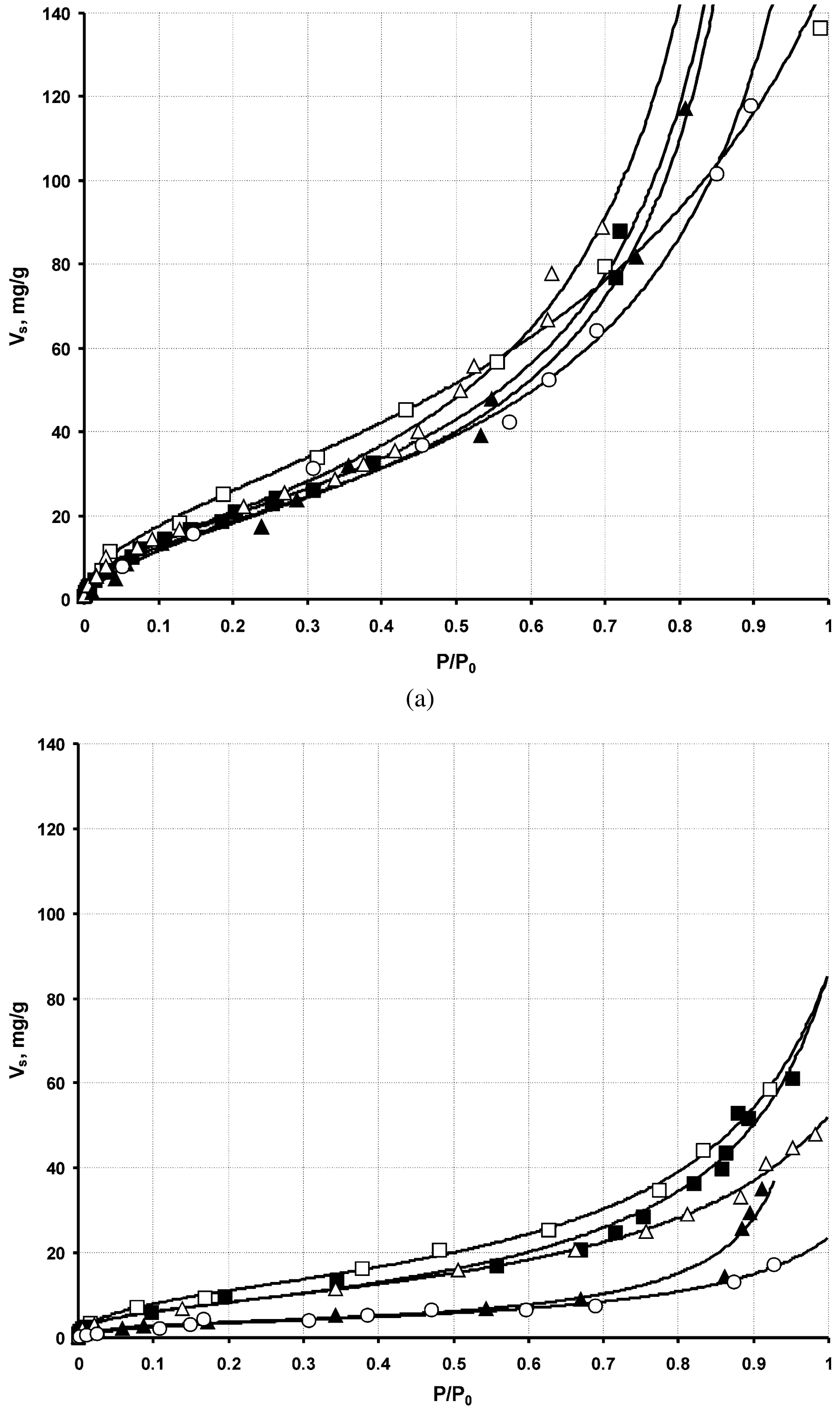
We then investigated ZCM samples that were either oven-dried (at 300 °C, 0% of water; at 105 °C, 3.3% of water) or partially (7.0% of water) and completely (RH of 100%, 17.6% of water) hydrated (Fig. 7a, c). Similarly, Z samples of 0%, 4.6%, 7.0% and 14.9% moisture content were also studied (Fig. 7b, d). Figure 7a, b show that hydration of both ZCM and Z decreased benzene sorption, especially at 17.6% and 14.9% of moisture. Here, in both cases *Vs* values at $P/P_0 = 0.4$ were approximately 1–2 mg/g. On the contrary, moistening ZCM to 3.3% and Z to 4.6% did not affect benzene sorption. It is possible that water-filled zeolite sorption sites are not accessible to benzene molecules. Considering the kinetic diameter of benzene molecules ($\sigma = 5.9$ Å), such sites may be microporous channels (≤ 5 Å) in zeolite-containing sorbents.

At the same time, in case of n-hexane sorption at $P/P_0 = 0.4$, ZCM moistening to 3.3% led to the decrease in *Vs* values to 15%, while Z moistening to 4.6% led to a 30–40% decrease (Fig. 7c, d). These data demonstrate that both oven-dried sorbents have a small volume of micropores accessible to filling by linear alkanes molecules with kinetic diameters less than 5 Å. Such results are not unexpected assuming that some impurities were present in zeolite channels of ZCM and Z, which is especially typical for natural zeolites (Panin and Chamuha 1992). Hence, the small micropore volume accessible for HC provided the basis for low selectivity of ZCM and Z towards the HC vapor sorption.

4 Conclusions

(a) Studied ZCM demonstrated high sorption capacity with regard to aliphatic and aromatic HC vapors. For both aliphatic and aromatic HC, ZCM sorption activity was significantly higher than that of Z enriched with zeolites, but it was lower when compared to local bentonite clays.

(b) Similarly to Z, ZCM does not appear to have any selectivity to sorption of aliphatic and aromatic HC. The comparison with zeolite-molecular sieve 5A and natural



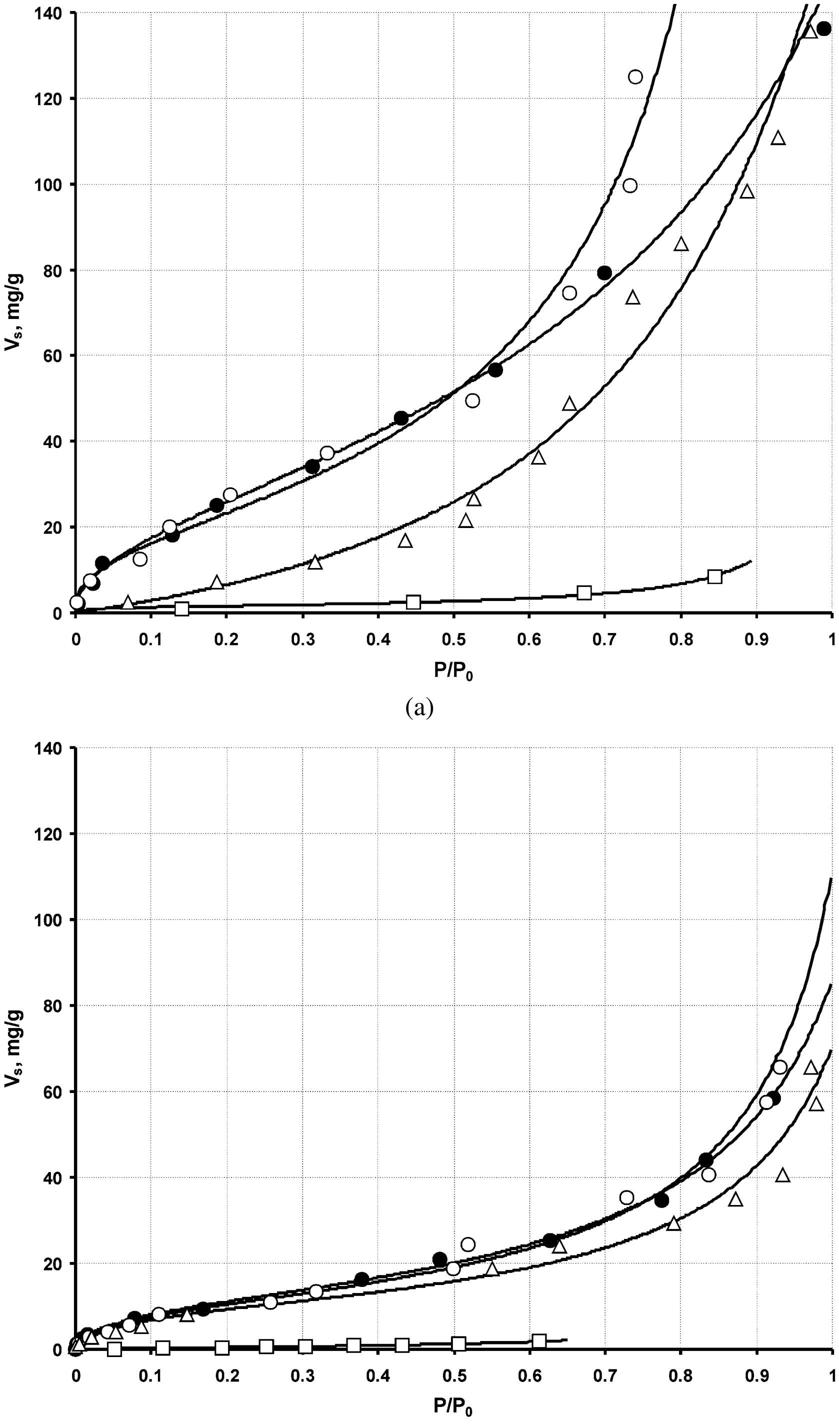
(a)

(b)

Fig. 6 Sorption isotherms of hydrocarbons at 25 °C on oven-dried (105 °C) zeolite-containing sorbents. (**a**) Zeolite-clay material (ZCM), (**b**) St. Cloud zeolite (Z). MGAB approximations are presented as *solid lines*. Hydrocarbons: □ Benzene, ■ Toluene, △ p-Xylene, ▲ iso-Octane, ○ n-Hexane

Mexican natural zeolite—erionite ZAPS, both of which have micropore openings close to ZCM and Z (5 Å), proved that both ZCM and Z do not interact as microporous selective sorbents towards the linear alkanes. The small micropore volume accessible to HC provides the basis for their low sorption selectivity. At the same time, sorption of aromatic HC on Z was slightly more favorable in comparison with aliphatic HC.

(c) The study of thermograms of water desorption from ZCM and Z samples demonstrated that even for water molecules which are smaller ($\sigma = 2.6$ Å) than n-hexane molecules ($\sigma = 4.3$ Å), the filling of micropores of both ZCM and Z is not considered the main contribution to



(a)

(b)

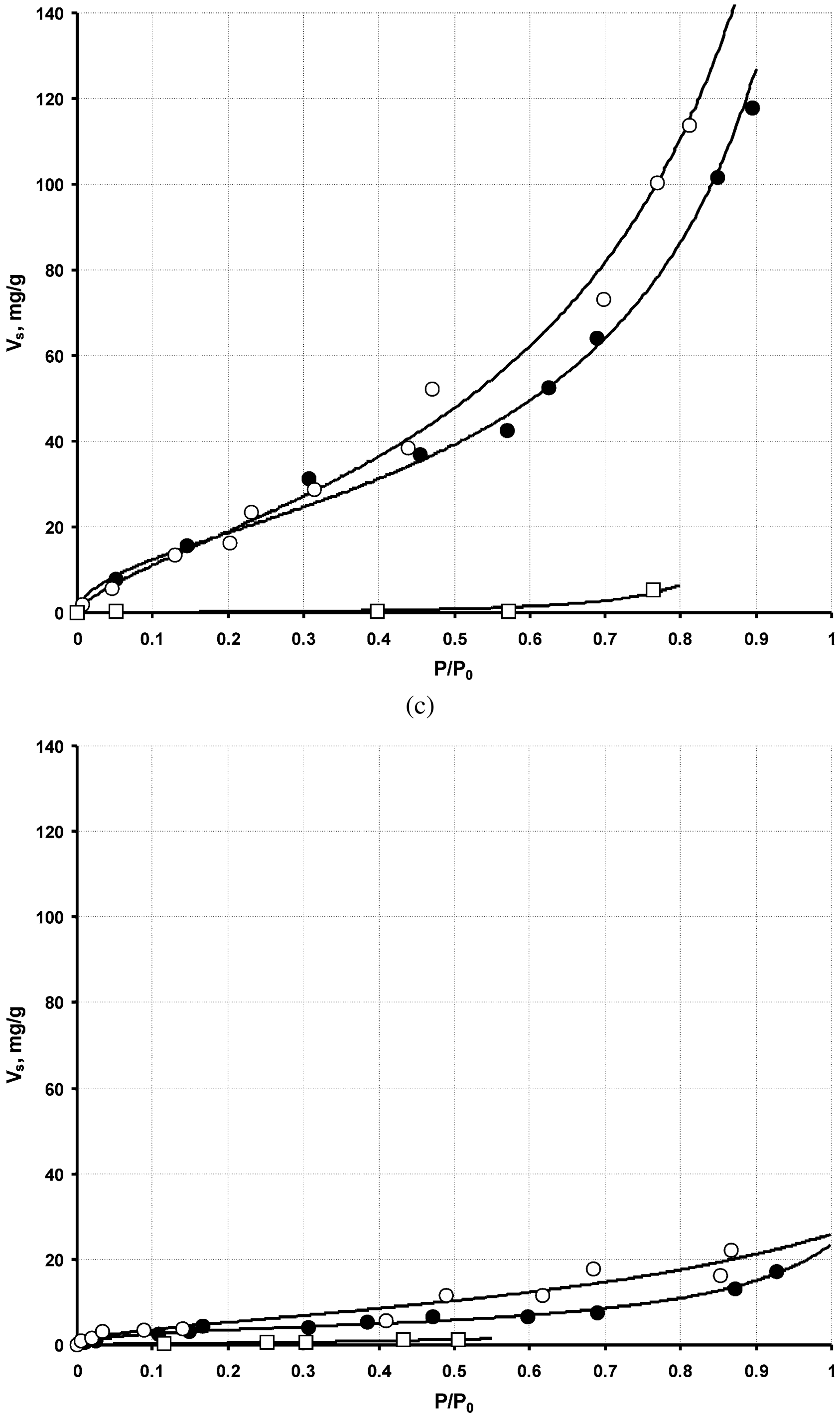
Fig. 7 Sorption isotherms of hydrocarbons at 25 °C on zeolite-containing sorbents with different moisture. MGAB approximations are presented as *solid lines*. Hydrocarbons: (**a**), (**b**) Benzene. Sorbents: (**a**) Zeolite-clay material (ZCM), (**b**) St. Cloud zeolite (Z). Moisture conditions: ○ Oven-dried sorbents (300 °C), ● Oven-dried sorbents (105 °C), △ Water content, 7 wt.%, □ Water-saturated sorbents (RH = 100%)

the total sorption. The study of the effect of moistening in benzene and n-hexane sorption on ZCM and Z allowed us to propose that the small volume of accessible micropores of examined natural sorbents is caused by the presence of impurities in zeolite channels.

(d) The obtained data (shape of isotherms and type of approximation equations, values of specific surface area and their temperature dependency, correlation between the decrease of HC sorption upon moistening and clay mineral content in a sorbent, as well as the absence of sorption selectivity) demonstrate that HC sorption on the ZCM occurs as surface adsorption.

(e) To summarize, the basic differences in HC sorption on ZCM of Tatarsky-Shatrashansky rock and on Z of

Fig. 7 (*Continued*) Sorption isotherms of hydrocarbons at 25 °C on zeolite-containing sorbents with different moisture. MGAB approximations are presented as *solid lines*. Hydrocarbons: (**c**), (**d**) n-Hexane. Sorbents: (**c**) Zeolite-clay material (ZCM), (**d**) St. Cloud zeolite (Z). Moisture conditions: ○ Oven-dried sorbents (300 °C), ● Oven-dried sorbents (105 °C), △ Water content, 7 wt.%, ☐ Water-saturated sorbents (RH = 100%)



(c)

(d)

St. Cloud deposit were ZCM higher sorption capacity towards both aliphatic and aromatic HC, and its rather lower sorption sensitivity to the HC type. The main reason for these differences is the presence of large amounts of clay minerals (ca. 24 wt.%) in ZCM. Thus, studied ZCM possesses effective sorption retention ability towards HC vapors and can be considered as a suitable adsorbent for the protection and remediation of HC-contaminated soils. The obtained sorption isotherms demonstrate high ZCM activity in a wide range of relative HC vapor pressures.

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