


Article

Vapour Sorption on Coal: Influence of Polarity and Rank

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Abstract: The surface properties of coal, interactions with gaseous and vapour media, and knowledge of the pore structure are important in terms of preparation, use, and utilisation of coal. This publication combines new unpublished data with analyses included in earlier publications by the research team to expand and systematise information on the sorption of water vapour, methanol vapour, and the saturated and unsaturated hydrocarbons hexane, 1-hexene, heptane, 1-heptene, octane on coals of different ranks. The study showed that the affinity of coal for water and methanol is related to the content of oxygen in the coal rather than the rank of the coal. Water sorption is a multilayer phenomenon, while methanol sorption is a monolayer phenomenon. The water monolayer is greater than that of methanol for low-rank coal, but for the higher-rank coals it is the opposite. The sorption capacity of the applied hydrocarbons depends on the presence or absence of a double bond and the size of the molecule. It increases in the order: n-octane < n-heptane/n-hexane < 1-heptene < 1-hexene. The effect of a double bond is dominant over the influence of the length and shape of the molecule.

Keywords: coal; adsorption; water vapour; methanol vapour; saturated hydrocarbons; unsaturated hydrocarbons



Citation: Czerw, K.; Krzyżanowski, A.; Baran, P.; Zarebska, K. Vapour Sorption on Coal: Influence of Polarity and Rank. *Energies* **2022**, *15*, 3065. <https://doi.org/10.3390/en15093065>

Academic Editor: Rajender Gupta

Received: 14 March 2022

Accepted: 19 April 2022

Published: 22 April 2022

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1. Introduction

Coal surface properties, pore structure, and closely correlated sorption properties, are important issues to address in coal preparation, application, and use processes, in particular coal bed methane (CBM) recovery and CO₂ geosequestration. Coal is a porous material characterised by the presence of voids (pores) in the bulk of the material, which vary in size and shape and are interconnected in a complex irregular network. In this space, diffusion processes and sorption processes of liquid and gaseous media take place. The study of interfacial phenomena in systems based on heterogeneous sorbents is often directed toward the understanding of the mechanism of retention of molecules of a given medium in the porous structure of the sorbent. The reasons lie in the theoretical and practical aspects from the point of view of the natural environment of the sorbent, the original conditions of its occurrence, and the conditions under which the sorbent is used. The coal substance has the ability to sorb low molecular weight substances such as water vapour [1–7], methanol vapour [8–11], and hydrocarbons [12–17]. The process can occur on its surface by physical bonding (physical adsorption) or by formation of covalent chemical bonds (chemical adsorption, chemisorption) or by volumetric absorption that affects its structure (absorption). In the case of physical adsorption, different mechanisms may be involved. There can be intermolecular interactions of van der Waals forces, nonspecific dispersion forces, or forces of a specific nature, including dipole interactions or hydrogen bonds.

Adsorption magnitude and course depend on the nature of the adsorbate, the nature of the adsorbent, and the conditions under which adsorption takes place. Factors that are related to the structure of the adsorbent are (1) the amount and type of surface area potentially accessible to the sorbate and (2) the texture and structure of the pores. The nature and accessibility of the surface area is of particular importance in sorbent-sorbate systems based on specific interactions related to the presence of specific sorption sites.

This factor is also particularly significant in the case of multilayer sorption and in the mechanism of volumetric filling of micropores. The interpretation of isotherms of sorption of small molecule size substances allows one to obtain information about the size and properties of the internal surface of sorbents. Texture and structure parameters such as specific surface area and pore volume with a range of diameters and their distribution, as well as information on which atomic groups are present on the surface of the pores, are of key importance for the practical application of commercial sorbents, and to understand, interpret, and predict the behaviour of natural sorbents in situ. The mechanism of sorption in the case of polar substances vapours involves the binding of sorbate molecules to the polar sorption sites of the sorbent. In the case of bituminous coals, these are oxygen reactive groups, mostly hydroxyl OH, including hydroxyl and phenol groups, carbonyl groups C=O, less often carboxyl groups COOH [18]. The approximate proportion of oxygen contained in reactive groups compared to total oxygen varies between 30–50% on the entire coalification scale up to a C^{daf} content of approximately 89% [19]. Therefore, coal can be considered a system with a double feature: hydrophilic and hydrophobic [20].

In planning the study presented in this paper, the authors were motivated by the recognition of a literature gap regarding studies on the sorption of small-molecule sorbates on coal, including polar compounds, but especially apolar hydrocarbon molecules. This paper aims to gather suitable analytical data and provide an analysis of the relationship between sorption capacity and the physicochemical structure of coal.

1.1. Sorption of Water and Methane

By analysing the relevant literature, it can be concluded that coals as adsorbents show good sorption properties with respect to polar compounds, methanol, and water. Differences in the interaction of these compounds with the porous structure of coal have already been observed in measurements of the real density of coals [21]. In relation to helium density, the results obtained with water are higher for low-rank and medium-rank coals (71–89% C) and lower for high-rank coals. This is due to the progressive loss of oxygen content in the coal and the associated gradual change in the character of the coal surface from hydrophilic to hydrophobic. As noted by Liu et al. [22], water vapour has been used to characterize the pore structure of porous material due to its lower kinetic diameter (0.28 nm) when compared to N_2 (0.38 nm) and CO_2 (0.33 nm). However, surface functional groups may provide extra sorption sites for water molecules that act as secondary sites for further adsorption, forming clusters. The density values obtained with methanol are generally higher than the helium density, irrespective of the coal rank. This regularity is explained by the compression of methanol in small pores as a result of significant specific interactions with the coal surface. Czuchajowski and colleagues [19] studied the sorption of methanol and water vapours on vitrinites of 18 bituminous coals in the range of C^{daf} 69.31–94.30%. The authors postulated chelate bond formation as the sorption mechanism, and proposed that for coals up to 81% C^{daf} , some of the reactive groups are inaccessible to polar sorbates because of the presence of internal hydrogen bonds between them. Korta et al. [23] analysed the effect of the petrographic composition of coal lithotypes of different rank on the sorption properties towards methanol and water vapour at 20 °C. The sorption capacity of vitrains was found to be slightly higher than that of their durain counterparts, but this effect decreases with an increase in the degree of coalification. Allardice and Evans [18] carried out desorption and resorption of water vapour from lignite (66.6% C) at several temperatures (30–60 °C). Type II sigmoidal curves were obtained (according to the IUPAC classification). The authors correlated this fact with three effects: capillary condensation, responsible for the upper part of the isotherm; multilayer sorption, which determines the linear middle part of the curve; and monolayer sorption, which is reflected in a shape of sorption isotherm at low sorbate pressures. The studies conducted by Bhattacharyya [1] aimed to measure the rate of heat release from eight coals (80.7–94.2% C^{dmmf}) during the sorption of water vapour under isothermal (30 °C) conditions with different relative humidity. It was observed that the rate of heat release increases with a deficiency in the equilibrium moisture content of

the coal and depends on its hygroscopicity and not directly on its degree of coalification. Lasoń and Żyła [20] carried out measurements of multiple sorption of water and methanol vapours on five Polish bituminous coals of varying ranks (C^{daf} 73.52–94.30%) to observe the phenomenon of swelling of the coal accompanying adsorption. The obtained water vapour isotherms were assigned to type II for the lower-rank coals, and type III for the higher-rank coals. The work of Spitzer's team [10] presents the results of a study of the sorption of methanol vapour on 20 coals differing in their rank (64–91% C^{daf}) at 20, 40 and 70 °C. The obtained data were described using the Dubinin-Kagener-Radushkewich (DKR) equation and the BET equation in the range of relative pressure from 0.05 to 0.35. Comparable values of the parameters corresponding to the monolayer capacity were obtained in terms of both models. Ceglarska-Stefańska et al. [2] have studied the course of the sorption of water vapour under low pressure isothermal-isobaric conditions, at 25 °C, on two bituminous coals and concentrates of liptinite and vitrinite macerals. It was confirmed that because of the low degree of ordering of the liptinite structure, the low aromaticity, and the significant content of aliphatic compounds these macerals have a higher water vapour sorption capacity than base coals and vitrinite. Takanohashi et al. [11] reported the results of studies of the effect of coal extraction on the sorption of methanol vapour in coal at 30 °C. Coals with low extraction efficiency sorbed similar amounts of methanol as their post-extraction residues, but the sorption on the residue from the high extraction-efficiency coal increased significantly compared to that of the base coal, suggesting that the extraction resulted in a more microporous system. Krzyżanowski and Żyła [9] presented the results of studies on sorption of water vapour, methanol, and benzene on three coals of different rank. The authors found that the sorption of water vapour on bituminous coals depends not only on the polar character of the coal surface but also on its capillary structure. On the other hand, the sorption of vapours of organic compounds occurs in both polar and in apolar sites as a result of dispersion forces. Charrière and Behra [3] carried out isothermal studies of water vapour adsorption and desorption on bituminous coal and lignite 298 K. Water sorption isotherms corresponding to type II were obtained and were described with a modified BET model to estimate water adsorption on primary and secondary adsorption sites. The authors assumed that the sorption of water vapour in coals with increasing relative pressure can be divided into four stages: (I) adsorption on primary sites, i.e., on oxygen-containing functional groups; (II) adsorption on secondary sites, via hydrogen bonding between water molecules; (III) formation of water clusters; and (IV) filling of micropores by water clusters and capillary condensation in narrow pores. The amount of water adsorbed at the primary sites was estimated to be 50% and 35% of the total sorption for bituminous coal and lignite, respectively. Švábová and co-workers [7] conducted a study of water vapour adsorption on three coals at temperatures: 25, 35, and 45 °C to observe the role of primary and secondary adsorption sites on the adsorption process. It was observed that at low relative pressures, adsorption at primary adsorption sites dominates, while adsorption at secondary sites becomes more important with increasing pressure. The percentage of adsorption at secondary sites depends on the concentration of the oxygen-containing functional groups. Baran et al. [8] presented the results of methanol sorption on three coals of different rank and elemental and petrographic composition. A positive relationship was found between the amount of adsorbed methanol and the oxygen content of the coal. The authors assumed that methyl alcohol molecules can be adsorbed at both the polar and a polar adsorption sites because of the dual nature of the molecule: the –OH group is polar and the methyl group –CH₃ is apolar. Orzechowska-Zięba et al. [24] investigated the sorption of water vapour on five coals of varying rank. The sorption and desorption isotherms obtained at 303 K were classified as type II characteristic for sorbents containing micro- and mesopores. As part of their study, Chen and co-workers [4] measured the water vapor adsorption/desorption isotherms and the corresponding kinetics at preset relative humidity (P/P_0) steps on five coals of different rank (R_0 0.65–3.18%). Samples of low-rank coal and high-rank anthracite exhibit higher sorption capacity, pronounced hysteresis features, and a sharp step-down of the desorption isotherms at a P/P_0 of approximately 0.5. On the contrary, the desorption

curves of the other three samples follow a path approximately parallel to the adsorption curves. In their review, Liu and co-workers [5] focused on the relationship between the occurrence of H₂O and the metamorphism of the coal, the presence of functional groups containing oxygen, the influence of mineral matter and other internal factors. The authors postulate that the H₂O adsorption process can be well described by the modified Brunauer–Emmet–Teller (BET) model with the assumption of double adsorption sites.

1.2. Sorption of Hydrocarbons

Coal is an adsorbent with a dual-surface nature, which is also of particular importance for the sorption of apolar sorbates. This area of research is based primarily on practical aspects, since apolar compounds are the main constituents of a mine gas. In addition to methane, nitrogen, and carbon dioxide, the lower hydrocarbons (C1–C5) and medium hydrocarbons (C6–C9) present in the gas mixture are also of great importance as their content in some sections of coal-bearing formations may exceed even 10% [25] and are sorbed on coals to varying degrees [26,27]. However, the literature on this subject is not extensive. Dudzińska [26] investigated the sorption capacities of bituminous coals toward gases present in the mine atmosphere. It was found that the volume of gas sorption on bituminous coal decreases in the following order: CO₂~C₂H₂ > C₂H₄ > C₃H₆ > C₂H₆ > C₃H₈ > CO > H₂. Relatively high sorption of unsaturated hydrocarbons was attributed to the interaction of double- and triple-bond electrons with the energy centres of the coal surface. It has been found that lower-rank coals with higher porosity are characterised by the highest sorption capacity. According to Dudzińska [26], it can be assumed that when in contact with the surface of the coal, a pair of binding electrons in the molecules of unsaturated hydrocarbons is shifted and a dipole structure is formed and they can electrostatically interact with polar adsorption sites with donor or acceptor properties. Dudzińska et al. [13] conduct research in the field of assessing the self-heating rate of coal by studying sorption/desorption of gases released into the mine atmosphere as a result of coal oxidation including unsaturated hydrocarbons: ethylene, propylene, acetylene. The volume of sorbed gases is closely related to the rank of coal and its porous structure and the volume of adsorbed acetylene is approximately 2–3 times larger than the volume of adsorbed ethylene or propylene [15]. Acetylene molecules are smaller than those of ethylene and propylene and due to the triple bond between the carbon atoms, have a higher electron availability of weak π bonds than ethylene and propylene. Wojtacha–Rychter and Smoliński [16,17] studied the effects of transporting a multicomponent gas mixture through a sorption column filled with granular coal and inert material and the sorption of multicomponent gas mixtures of ethane, ethylene, propane, and propylene during flow through coal masses of different degrees of coalification. The gases migrated through the coal bed at different rates. The presence of a double bond was found to be responsible for the strongest selectivity of propylene on coal. However, the selectivity of ethylene on coal was the lowest, which was contrary to expectations. The authors emphasised that the complex mechanisms of adsorption on coal for multicomponent gas mixtures have not been fully elucidated, leaving this issue open for further research. Zhao and co-workers [28] conducted adsorption and desorption measurements of carbon dioxide, methane, ethane, propane, n-butane, and iso-butane on two different shales and kerogen at temperatures of 35, 50, and 65 °C, in a wide pressure range. At 2 bar, the highest adsorption was observed for n-butane, followed by isobutane, propane, carbon dioxide, ethane, and methane. Longer molecules were found to provide a stronger interaction with the sorbent surface and higher adsorption. Krzyżanowski and Zarębska [29] carried out measurements of n-heptane and 1-heptene vapour sorption in bituminous coals and concluded that the sorption of vapours of apolar substances is mainly surface-bound and significantly depends on the porosity of coals and that the presence of a double bond influences the sorbent-sorbate type interactions and the sorption capacity. These results were confirmed by Baran and co-workers [12] who performed sorption studies of hexane, 1-hexene, heptane, 1-heptene, octane, and benzene vapours on low-rank bituminous coal.

The study of the course of sorption of vapours and gases with different physico-chemical properties is a source of information on the porous structure of coals and the mechanism of adsorption of sorbates. The paper is a continuation of research carried out in the Adsorption and Environmental Engineering Group, Faculty of Energy and Fuels, AGH University of Science and Technology. The publication combines information presented in previous works of the team [8,9,12,29] with new, unpublished data to summarize, expand and systemise information on the sorption of water vapour, methanol vapour, and saturated and unsaturated hydrocarbons: hexane, 1-hexene, heptane, 1-heptene, and octane, on bituminous coal.

2. Materials and Methods

The research was carried out on three selected Polish coals, provided by three operating coal mines of the Upper Silesian Coal Basin, that differ in the degree of coalification. The samples weighing several kilograms were acquired in accordance with the Polish standard PN-G-04502:2014-1, crushed in a jaw crusher, ground, sieved on Fritsch sieves to the fractions 0.500–0.700 mm, 0.125–0.250 mm, and 0.063–0.075 mm, and stored in nitrogen atmosphere.

Coal analysis was carried out at the Department of Solid Fuel Quality Assessment of the Central Mining Institute in Katowice (Poland) and at the Faculty of Energy and Fuels of the AGH University of Science and Technology in Kraków (Poland), using the requirements and procedures specified in Polish standards (Table 1). Micropore surface area and volume determined on the basis of carbon dioxide sorption at 298 K using Dubinin–Raduszkiewicz model (D-R) were presented in Table 1. The tests were performed using the Micromeritics ASAP 2010 apparatus.

Table 1. Specification of coal samples C1, C2, C3: proximate and ultimate analysis, petrographic analysis, vitrinite reflectance, densities, and porosity.

Coal	C1	C2	C3
Proximate analysis			
W ^a [%]	1.75	1.85	11.11
A ^a [%]	3.01	14.18	14.45
V ^{daf} [%]	27.12	29.88	35.63
Ultimate analysis			
C ^{daf} [%]	84.24	70.82	57.83
H ^{daf} [%]	4.58	3.35	3.37
N ^{daf} [%]	1.52	1.28	0.87
S ^{daf} [%]	0.39	3.50	1.10
O ^{daf} [%]	4.58	6.29	11.30
Petrographic analysis and vitrinite reflectance			
vitrinite [%]	73	60	67
liptinite [%]	7	9	5
inertinite [%]	20	31	28
mineral matter [%]	1	14	11
R ₀ [%]	0.92	0.78	0.51
Structural properties			
d _{real} [g/cm ³]	1.26	1.27	1.37
d _{bulk} [g/cm ³]	1.22	1.23	1.16
porosity [%]	3.20	3.40	15.90
V _{micro} [cm ³ /kg]	0.070	0.063	0.229
S _{micro} [m ² /g]	115.8	103.2	419.6

W: moisture content, A: ash content, V: volatile matter content, C, H, N, O, S: content of element C, H, N, O, S, respectively, a: analytical basis, daf: dry-ash-free basis, R₀: vitrinite reflectance, d_{real}: real density (helium density), d_{bulk}: apparent/bulk density (mercury density), V_{micro}: D-R micropore volume, S_{micro}: D-R micropore surface area.

FTIR spectra of the samples C1, C2, and C3 are presented in Figure 1. The FTIR results provided information on the structure of our 3 coals in terms of carbon and hydrogen

groups and oxygen groups, enabling the assessment of differences in the structure and character of sample surfaces. Spectra are characterized by:

- a broad hydroxyl stretching region, with peak at 3425 cm^{-1} for C1 and C2 and shifted peak at 3390 for C3,
- a clearly visible aliphatic stretching region, with two peaks for asymmetric bonds at 2920 cm^{-1} and symmetric bonds at 2855 cm^{-1} ; the latter is most pronounced for C1 and least pronounced for C2,
- a prominently displayed aromatic carbon region with a peak at 1600 cm^{-1} , most pronounced for C1,
- an aliphatic bending region with peak at 1435 cm^{-1} for C1 and C2 and peak at 1430 cm^{-1} for C3,
- peaks at 1032 cm^{-1} assigned to the stretching vibration of minerals, such as Si-O-Si or Si-O-C, most pronounced for C3 and almost indistinct for C1,
- noticeable three aromatic out-of-plane peaks within $900\text{--}650\text{ cm}^{-1}$ region,
- peaks at 535 and 460 cm^{-1} region assigned to the Si-O bending vibration of feldspar and quartz minerals, most pronounced for C3 and indistinct for C1.

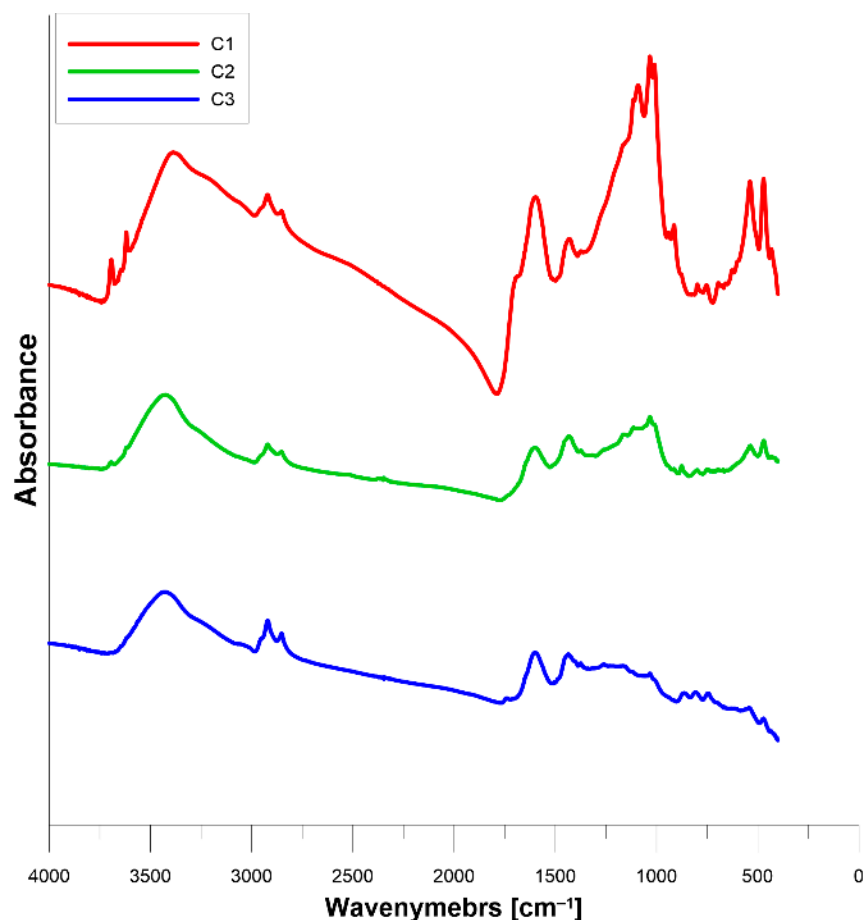


Figure 1. FTIR spectra of coals C1, C2 and C3.

Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM/EDS) analysis was carried out with the aid of JEOL JSM-7500F, coupled with an AZtecLiveLite Xplore 30 (Oxford Instruments) system. The secondary electron detector provided SEI images, and the back-scattered electron detector provided BSE (COMPO) micrographs. SEM images were recorded for the samples coated with 30 nm Cr. SEM (Scanning Electron Microscopy) makes use of secondary electron signal imaging to observe the surface morphology of the sample, to infer material components and to reveal the microstructure on the micro- and

nanometre scale. The SEM photographs in Figure 2 present the topography of the coal's surface and its phase diversity for fraction below 0.075 mm.

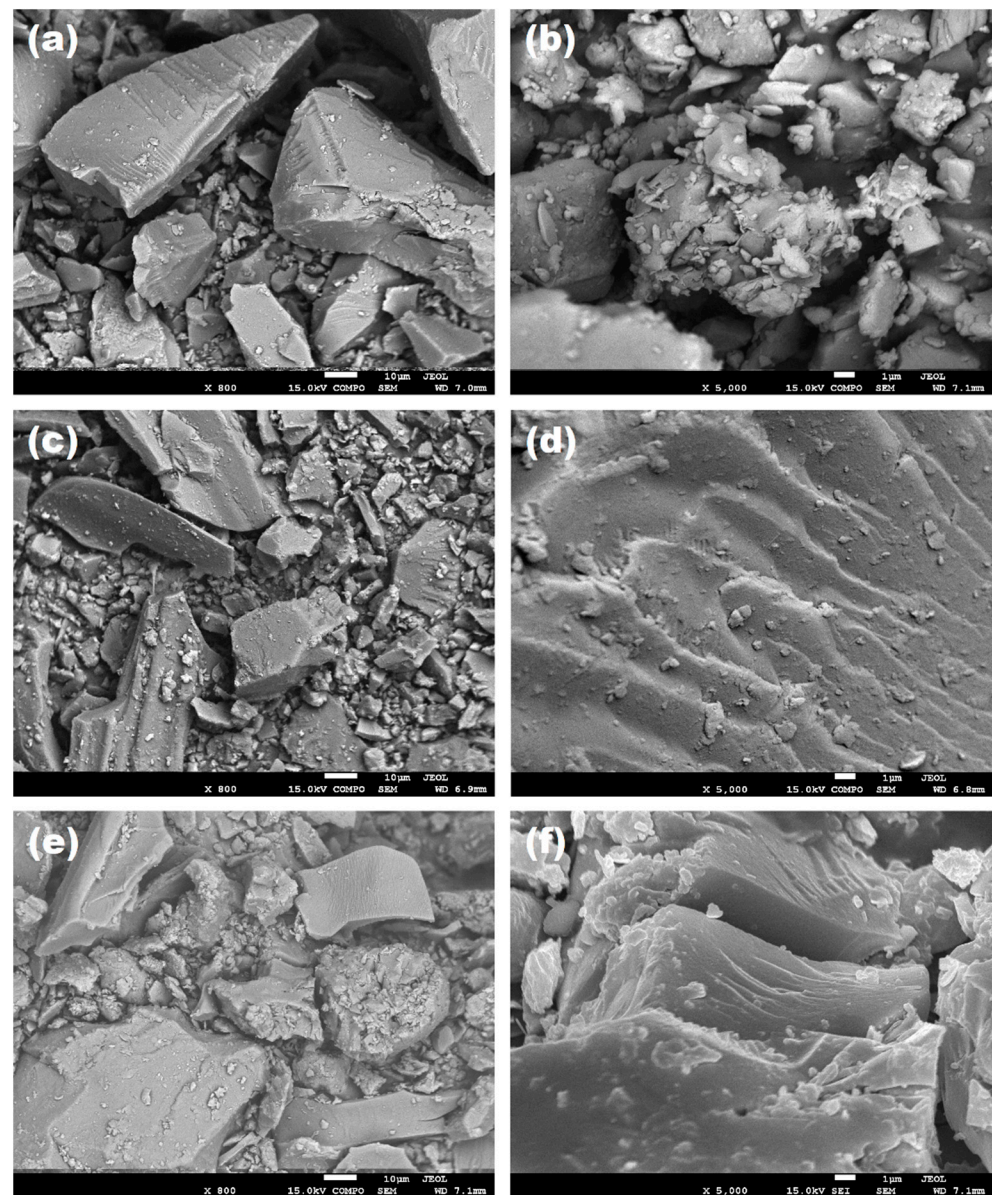


Figure 2. The surface morphological characteristics of the SEM pore-fracture system in (a,b) coal C1, (c,d) coal C2, (e,f) coal C3. Magnification = 800 (left), magnification = 5000 (right).

The choice of sorbates was dictated by both cognitive and practical aspects. Water vapour and liquid water occur naturally in coal seams. The amount of water vapour and its form of bonding with the coal is determined by hydrogeological conditions and the depth of deposit. The sorption of water vapour on coal depends on the polar character of the coal surface and its capillary structure, which enables the formation of multilayer clusters. The sorption of methanol has a more universal character because of the specific structure of the molecule, containing a polar and an apolar section. Medium hydrocarbons (C6–C9), saturated and unsaturated, can be present in the mine atmosphere; thus, the results of the studies can be used to determine the predisposition of selected coals for their storage. The selected sorbates differ in structure (saturated and unsaturated hydrocarbons), size and shape of the molecules (molar mass; angular, spatial, linear structure of the molecule) and

physical properties (equilibrium vapour pressure), they are also present as components of gas mixtures, including coal seam gas (Table 2).

Table 2. Characteristic of sorbates.

Sorbate	T_C [°C]	p_C [MPa]	M [g/mol]	d_{kin} [nm]	p_0 [Pa]	μ [D]
water	373.99	22.06	18.02	0.265	4240	1.85
methanol	240.00	78.50	32.04	0.380	21,065	1.70
n-hexane	234.64	3.04	86.18	0.430	24,598	0.00
1-hexene	230.83	3.21	84.16	0.430	30,507	0.44
n-heptane	266.87	2.74	100.20	0.430	7786	0.00
1-heptene	264.08	2.92	98.19	0.430	9533	0.44
n-octane	295.75	2.49	114.23	0.430	2240	0.00

T_C : critical temperature, p_C : critical pressure, M : molecular weight, d_{kin} : kinetic diameter, p_0 : vapour pressure at 303 K, μ : dipole moment.

The sorption isotherms were determined using a volumetric technique with so-called liquid microburettes, at a temperature of 303 K. This technique allows the determination of isotherms of adsorption and desorption of vapours of polar substances, such as water or alcohols, and nonpolar compounds, for example, benzene, carbon tetrachloride, hydrocarbons, ether, and amines, in the entire range of relative pressures, i.e., from absolute vacuum to equilibrium vapour pressure. The measuring instrument is made almost entirely of glass and is placed inside an air thermostat to maintain a constant temperature with an accuracy of 0.1 °C. The apparatus consists of several independent basic units. A schematic of a single measuring unit is shown in Figure 3.

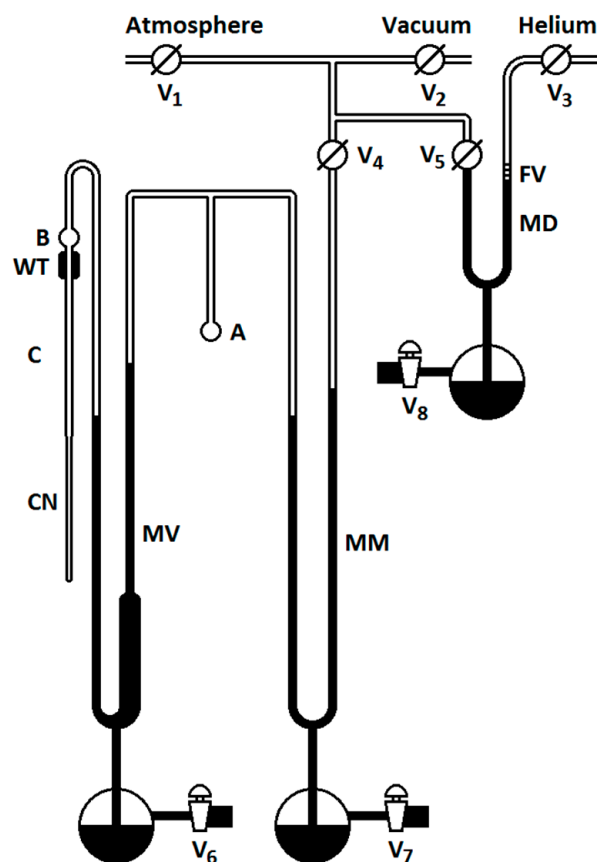


Figure 3. Schematic of sorption apparatus (C: measuring capillary, CN: narrower part of capillary tube, B: glass bubble, WT: cotton tampon damp in water, A: sample ampoule, MM: mercury manometer and valve, MV: mercury valve, MD: helium dosing unit with mercury valve, FV: float valve, V_1 – V_8 : valves and glass taps).

Measuring capillary C is filled with liquid by immersing the open narrower part of measuring capillary CN in adsorbate, creating negative pressure by MV valve, and sucking the liquid into bubble B (half of the volume). After closing the MV valve, the end of the CN capillary is sealed. Then, with the MV and MM valves open and valve V₄ open, the liquid is degassed to remove its vapours and dissolved gases and to obtain a uniform column of liquid in capillaries C and CN. When this stage is complete, the MM and V₄ valves are closed. Below the meniscus of the liquid, on the measuring capillary C, a cotton swab pre-soaked in water WT is placed in order to locally lower the temperature in order to counteract the predistillation and condensation of the adsorbate outside the measuring capillary C. The next step is to plot the curve of the dependence of the lowering of the meniscus level of the liquid in the measuring capillary C on the vapour pressure of the sorbate in the adsorption space, to determine the correction for the dead space of the system. The glass sample ampoule A containing the adsorbent is connected to the system with a gas burner. The sorption space and sample are then degassed to remove the free gas and previously sorbed compounds from the pore system and the surface of the coal. In the case of coal, the heating of samples is not practiced to remove the vapours and gases contained in the pores of the sorbent. Instead, the so-called helium bath is used. After the initial degassing of the sample, a portion of helium (pressure of several kPa) is introduced into the system for 1–2 h, after which the degassing is continued (10⁻³ Pa). Helium atoms, which are not adsorbed themselves, provide the necessary kinetic energy to the molecules of sorbed gases and vapours, forcing them off the sorbent surface [30].

Sorption experiments were carried out for 0.125–0.25 mm grain samples of coal weighing approximately 1 g. Prior to the main test, the samples were outgassed (10⁻⁷ Pa) and flushed under helium atmosphere at least 3 times in total, and next kept under vacuum at the room temperature to a stable residual pressure. The actual measurement begins by reading the baseline liquid level in capillary C using a cathetometer with an accuracy of 0.02 mm. Opening the MV valve results in the distillation of a certain amount of liquid into the adsorption space. The amount of adsorbed vapour is calculated from the difference in the level of the meniscus of the liquid in the measuring capillary C, taking into account the dead volume of the apparatus and the volume of the sample. The equilibrium pressure of sorption is checked on the MM manometer using a cathetometer, with the MV valve closed. The MM gauge acts as a pressure gauge and a valve between the sorption part of the system and the section for degassing and aeration of the system. During the measurements, the optimum equilibrium waiting time of 24 h was selected, after which no change in equilibrium pressure was detected.

The multilayer adsorption model of the Brunauer, Emmett, and Teller equation (BET) [31] was used to describe the experimental data. It assumes that if a sorbate molecule encounters an occupied adsorption site on the surface of an adsorbent, it does not leave it immediately, but it forms an adsorption complex. With increasing vapour pressure, the number of available unoccupied adsorption sites decreases, as well as the number of sites occupied by one molecule, because complexes are formed which are dual-molecular and with more molecules. The interpretation of the obtained curves is based on the linear form of the BET equation:

$$\frac{\frac{p}{p_0}}{a \cdot \left(1 - \frac{p}{p_0}\right)} = \frac{1}{a_m \cdot C} + \frac{C - 1}{a_m \cdot C} \cdot \frac{p}{p_0}, \quad (1)$$

where: p —equilibrium vapour pressure of the sorbate [Pa], p_0 —saturated vapour pressure of the sorbate at the measurement temperature [Pa], a —sorption capacity of the adsorbed vapour at equilibrium pressure p [mmol/g], a_m —adsorption capacity of the monolayer [mmol/g], C —equation constant, depending on the heat of adsorption and measurement temperature.

3. Results

3.1. Sorption Isotherms

The course of sorption isotherms is presented as a dependence of the sorption capacity of the sorbate (mmol/g) and the relative pressure of the sorbate (p/p_0). The sorption isotherms of water and methanol for the studied systems are presented in Figure 4. The isotherms of hydrocarbon sorption on samples C1, C2, and C3 are illustrated in Figure 5.

3.2. BET Parameters

The BET adsorption model was used to describe the experimental adsorption data. Classically, the BET method is used to describe the low temperature (77 K) sorption of nitrogen and to determine the specific surface area of the adsorbents from the a_m values. Korta et al. [23] postulated that the monolayer capacity (a_m) determined for the coal-water sorption system corresponds to the number of polar active groups that make up the water sorption sites and not to the compact sorbate monolayer capacity. In our present study, the characteristic parameters of the BET equation, the monolayer capacity (a_m), were calculated. However, we followed the view presented by Allardice and Evans [18] that the determined parameters represent the capacity of a single first adsorbent layer. For the purposes of this theoretical analysis, the data were not differentiated in terms of similarity to type II isotherms and calculations were carried out for each isotherm obtained. It was assumed that the agreement of the experimental data with the linear equation of BET is in the range of relative pressures from 0.05 to 0.4.

The monolayer capacity values (a_{BET}) were presented graphically in relation to the maximum sorption capacity values (a_{max}) in Figure 6. The values of the maximum sorption capacities (a_{max}) of the sorbents with respect to each sorbate were correlated with the molar mass of the sorbates and the kinetic diameter of the sorbate molecules (Figure 7) in order to evaluate the presence or absence of dependence of these parameters on the determined quantities.

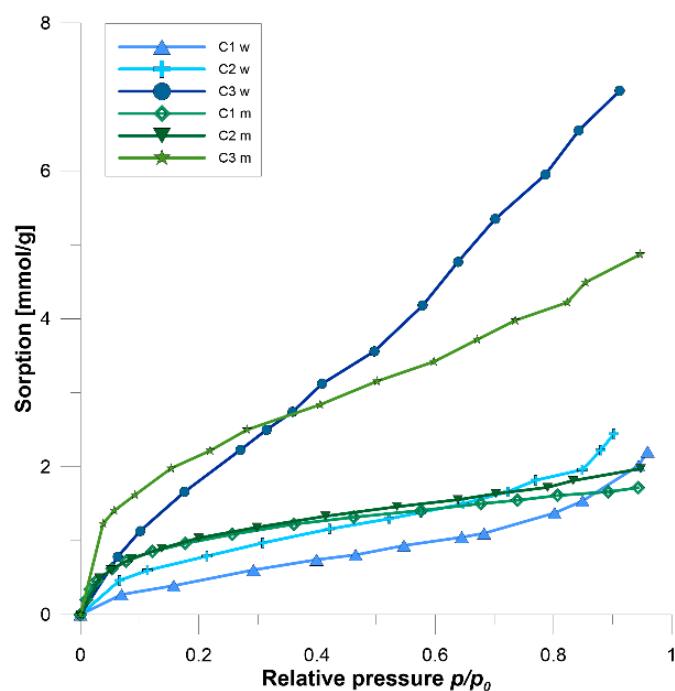


Figure 4. Sorption isotherms of water vapour (Ci w) and methanol vapour (Ci m) on coals C1, C2, C3.

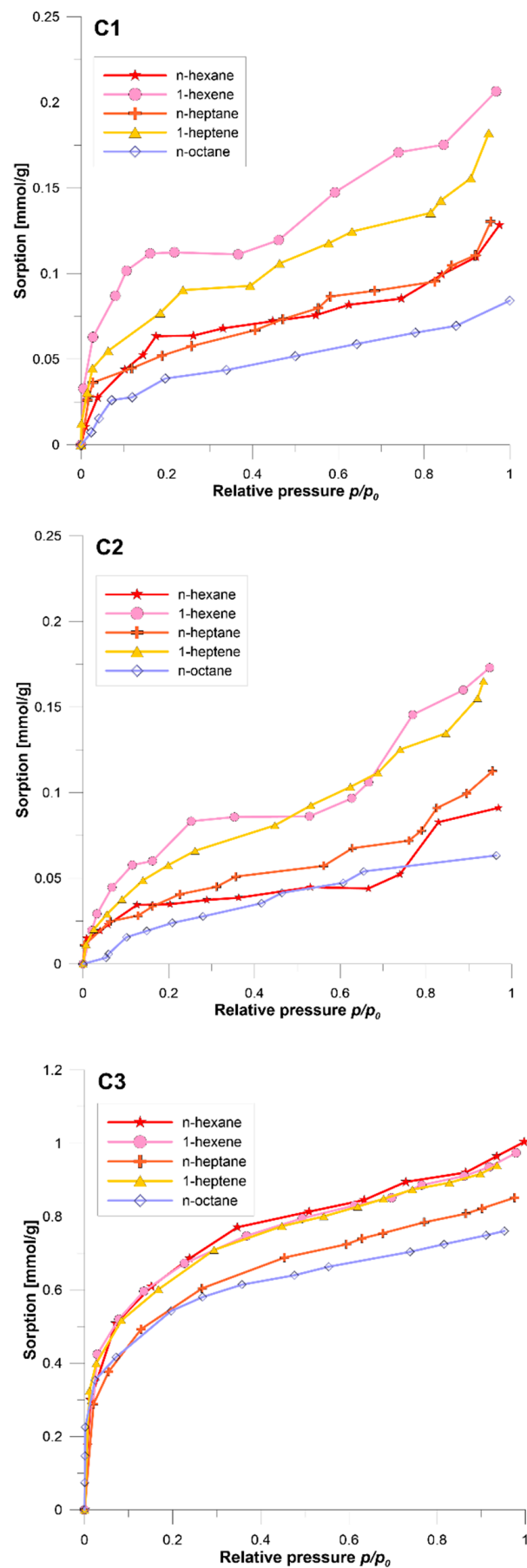


Figure 5. Sorption isotherms of n-hexane, 1-hexene, n-heptane, 1-heptene, and n-octane on coals: C1, C2 and C3.

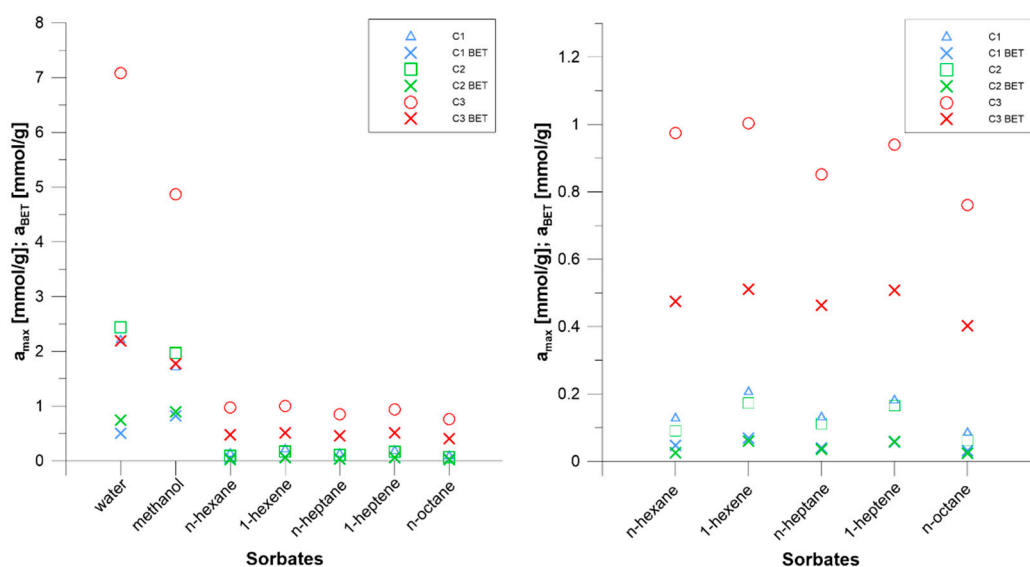


Figure 6. Maximum values of sorption (C_i max) and BET monolayer adsorbed quantities (C_i BET) of water vapour, methanol vapour, n-hexane, 1-hexene, n-heptane, 1-heptene, and n-octane on coals C1, C2, C3.

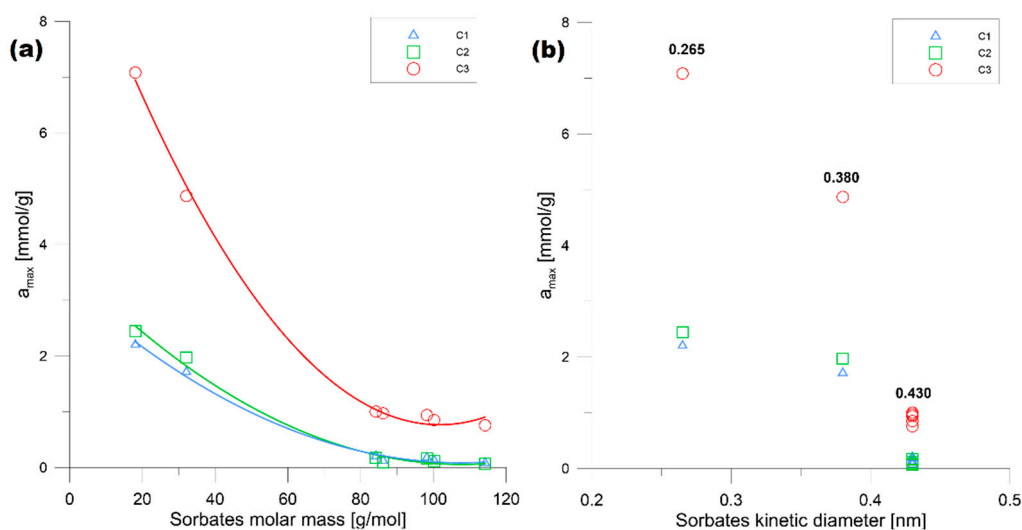


Figure 7. Maximum values of sorption a_{max} of water vapour, methanol vapour, n-hexane, 1-hexene, n-heptane, 1-heptene, and n-octane on coals C1, C2, C3: (a) in relation to molar mass of sorbates and (b) in relation to kinetic diameter of sorbates.

4. Discussion

The shape of the water sorption isotherms is sigmoidal and corresponds to type II according to the IUPAC classification (Figure 4), characteristic for sorbents containing micro- and mesopores. It indicates the initial monolayer adsorption followed by multilayer filling. The formation of a sorption monolayer corresponds to the initial part of the isotherm. The slope of the isotherm is steeper along this section, the greater the accumulation of polar sorption sites, which are identified with oxygen groups. The phase of filling subsequent adsorption layers corresponds to the transition of isotherms into a linear line. Previously adsorbed water molecules become sorption sites for the next sorbate molecules. This is a cluster-type phenomenon. At higher relative pressures, the isotherms tend to shift in the vertical direction. The cause may be the appearance of sorption in the network of the coal matrix, followed by swelling of the coal or condensation of sorbate vapours on the surface

of the pores [9]. For higher-rank coals, the filling of the monolayer takes place at a lower relative pressure than for lower-rank coals and the part of the isotherm that is close to the linear line is sloped at a smaller angle to the relative pressure axis. The Type II isotherm corresponds to processes with higher adsorption energy of the first layer compared to the subsequent layers, in contrast to type III, which corresponds to a process with opposite characteristics [20].

The shape of methanol sorption isotherms corresponds to type I according to the IUPAC classification, characteristic for microporous adsorbents (Figure 4). In the initial part of the isotherm, corresponding to the monolayer filling process, adsorption is limited by the number of adsorption sites. In the case of methanol, this number is potentially higher than in the case of water. Methanol molecules can be adsorbed not only by polar sites but also by non-specific apolar sites. Methanol sorption is less dependent on the nature of the coal surface than water sorption. The possibility of the formation of another layer after the formation of the first layer is limited by both the capillary structure of the sample and the interactions strength between the sorbate molecules.

The open pore structure of coal promotes the clustering and association of strongly interacting water molecules with dipole-dipole and hydrogen-bonding interactions. In the case of methanol, these interactions also occur, but are much weaker, and even with favourable coal texture the sorption increases slightly with increasing relative pressure. In general, the texture of higher-rank coals does not favour the formation of multiple layers of adsorbed methanol. This is reflected in the course of the relevant curves (Figure 4). The isotherm of water sorption on the C2 coal lies above that determined for the C1 coal, while the isotherms of methanol sorption on these coals are in their initial part above the mentioned curves and have a very close course. The sorption of methanol vapour is higher than that of water vapour on a significant part of the relative pressure scale. This trend persists longer for the lower-rank coals. The curves cross for C3 coal at a value of p/p_0 of approximately 0.35, for C2 coal at a value of p/p_0 of approximately 0.72, and for C1 coal at a value of p/p_0 of approximately 0.87. When saturation vapour pressure was reached, maximum sorption capacities were obtained, which are higher for coal-water systems than for coal-methanol systems (Figures 4 and 6). The sorption capacity of the investigated coals toward water and methanol depends to some extent on their degree of coalification. As the photographs in Figure 1 show, the organic matter morphology of the samples is similar. The presence of mineral matter in the C2 and C3 coals is responsible for the differences in the images. Hence, it is inferred that the differences in sorption amounts in the systems in question are strongly related to the chemical nature of the coal surface and not directly to its nanostructure. However, this regularity has different magnitude. The differences in sorption capacity between low-rank C3 coal and C2 and C1 coals are greater than between C2 and C1. The parameter that corresponds much better to the sorption properties of coal relative to those of low-molecular-weight polar sorbents is the content of element O in the coal. In the case of water, the dominant factors determining the sorption capacity of coal are (1) the capillary structure of the coal sorbent, enabling diffusion of the medium in the pores and creating conditions for multilayer sorption and condensation of sorbate vapours on the pore walls, and (2) the accessibility of polar adsorption sites, associated with functional groups, mainly oxygen groups. In the case of methanol, the capillary structure of the coal sorbent and the accessibility of the adsorption sites also play a key role. However, two aspects should be kept in mind. First, methanol molecules consist of a polar hydroxyl group and an apolar methyl group, therefore, they can be bonded to the coal surface by specific interactions with polar sites and nonspecific (dispersive) interactions with the apolar surface of the coal matrix. A methanol molecule can screen for more than one sorption site. Second, methanol molecules are larger than water molecules. Their kinetic diameters are 0.38 nm and 0.265 nm, respectively (Figure 7b).

The water sorption results obtained in our study were compared with the sorption capacity values obtained by Švábovet al. [7] and by Chen et al. [4] (Table 3). Coal marked Vitrinite sorbed about 43 mg of water/g of coal [7]. This is just slightly higher than

the 39.7 mg/g obtained for C1 coal. This leads to the conclusion that for coals with a similar degree of coalification expressed by vitrinite reflectance of about 0.9%, the maceral composition does not affect the magnitude of water sorption. The coal marked as Huminite sorbed about 170 mg of water/g of coal [7]. This is considerably higher than the 127.6 mg/g obtained for C3 coal. This is in accordance with the conclusions presented above regarding the relationship of the magnitude of water sorption with the capillary structure of the coal sorbent and the availability of polar adsorption sites, the amount of which decreases with increasing coal rank. The coal marked YZG2 sorbed approximately 82 mg of water/g of coal and the coal marked LH7 sorbed approximately 21 mg of water/g of coal [4]. These values are consistent with the findings from this publication. Analogously, the methanol sorption results presented in this paper were compared with the sorption absorption values obtained by Takanohashi et al. [11] (Table 3). Coal marked as Upper Freeport sorbed approximately 1.2 mmol of methanol/g of coal [11]. This is a little lower than the 1.715 mmol/g obtained for C1 coal. In contrast, the Beulah–Zap marked coal sorbed approximately 6.5 mmol of methanol/g of coal [11]. This is significantly higher than the 1.97 mmol/g obtained for C2 coal. This is in accordance with the deductions presented above concerning the relationship of the magnitude of methanol sorption with the availability of polar adsorption sites. The ratio of sorption capacity of these low-rank coals is 3.3, while the ratio of the amount of elemental O content in these coals is 3.45. This indicates that there may be a near-linear relationship between oxygen content and sorption capacity toward methanol for coals with a similar degree of coalification.

Table 3. Comparison of selected relevant self-reported and literature data.

Coal	R ₀ [%]	C ^{daf} [%]	O ^{daf} [%]	TV [%]	a _w [mg/g]	a _m [mmol/g]	a _{w,prim} [%]
C1	0.92	84.24	4.6	73	39.7	1.715	-
C2	0.78	70.82	6.29	60	44.0	1.97	31
C3	0.51	-	-	67	127.6	-	-
Vitrinite [7]	0.88	-	-	93	43	-	-
Huminite [7]	0.37	-	-	n.a.	170	-	-
YZG2 [4]	0.65	-	n.a.	-	82	-	-
LH7 [4]	1.16	-	n.a.	-	21	-	-
Upper Freeport [11]	n.a.	86.2	4.6	-	-	1.2	-
Beulah–Zap [11]	n.a.	71.6	21.7	-	-	6.5	-
Albert [3]	0.75	-	10.7	-	-	-	50

R₀: vitrinite reflectance, C, O: content of element C, respectively, daf: dry-ash-free basis, T: vitrinite content, a_w: water sorption capacity, a_m: methanol sorption capacity, a_{w,prim}: water sorption share on primary sorption sites calculated as: a_{BET}·100%/a_{max}, n.a.: data not available, -: data not available or irrelevant for purpose of comparison.

The shape of the isotherms of sorption of unsaturated hydrocarbons is close to sigmoidal (Figure 5). When they were assigned type II according to the IUPAC classification, they were supported by the elevation of the curve toward the vertical in the final part of the isotherm. In the case of saturated hydrocarbon sorption, this feature of the curve decreases with increasing length of the aliphatic chain and decreasing degree of coalification, which is well illustrated by isotherms for the sorption of n-octane and n-heptane (Figure 5). The shape of these isotherms is closer to type I according to the IUPAC classification (Figure 5). The sorption of vapours of nonpolar substances mainly involves a surface process and depends primarily on the porosity of the bituminous coal, in particular on the presence and distribution of micro- and mesopores. Coal appears as a molecular sieve in this system. Therefore, the sorption absorptivity of the C3 coal is definitely several times higher than that of the C2 and C1 coals. Therefore, the ratios of the sorption capacities of individual sorbates on the same coal are the smallest for the C3 coal (Figure 5).

The molecular dimensions of unsaturated hydrocarbons and their saturated counterparts are similar (Table 2 and Figure 7). The presence of a double bond in the hydrocarbon molecule affects the sorption mechanism, changes the course of the isotherm with respect

to the saturated counterpart, and leads to higher sorption values. This results from the interaction of the double bond (π electrons) with the polar groups present on the surface of the coals [29]. This effect is more evident in the case of the C1 and C2 coals. The association of unsaturated hydrocarbon molecules on the surface of micropores is likely to occur because adsorbate-adsorbate interactions play a more significant role than adsorbate-adsorbent processes. It should also be noted that in the sorption of unsaturated hydrocarbons, the presence of π -electrons in the aromatic structures of coal is also important. Higher-rank coals have a higher degree of aromatic condensation resulting, on the one hand, in the presence of adsorption sites in the form of a delocalised sextet of π -electrons and, on the other hand, in a lower porosity, which reduces the possibility of interaction of the coal substance with the sorbate molecules. These interactions lead to higher sorption capacities of alkenes relative to alkanes of a chain/molecule length similar to that of these alkanes. Hence, the sorption capacity of the C1 coal toward these sorbates is higher than that of the lower-rank C2 coal (Figures 5 and 6). The sorption capacity of the hydrocarbon sorbates used increases in order: n-octane < n-heptane/n-hexane < 1-heptene < 1-hexene. This pattern is influenced by two factors: the presence or absence of a double bond and the size/length of the molecule. In relation to the maximum sorption values of 1-hexene and 1-heptene obtained for coal C3, 6 and 5 times lower sorption capacities were obtained for coal C2 and C1, respectively (Figure 6). The alkane sorption ratios obtained for coal C3 and coals C2 and C1 are 8 to 12 and 6 to 9, respectively (Figure 6). However, n-hexane and n-heptane sorb on coals C2 and C1 with close capacities and n-octane with lower capacity. For coal C3, the curves for these three homologues differ most clearly (Figure 5). Coal with a lower degree of coalification more clearly differentiates the course of sorption isotherms of alkanes. The higher sorption capacity of alkenes in comparison to that of their saturated counterparts indicates that the effect of double bonding is dominant over the influence of molecule length and shape. The pattern is more evident for higher-rank coals (Figure 5). Moreover, the curves obtained for 1-heptene are above those corresponding to the sorption of n-hexane, which further confirms which feature of the molecule has a greater influence on the sorption capacity.

When considering the relationship between the obtained values of the monolayer capacity a_{BET} and the maximum sorption capacity a_{max} , the criteria of the type of sorbate should first be taken into account, and then the influence of the type of sorbent should be analysed. This is supported, among other reasons, by the fact that for the higher-rank coals C1 and C2, the a_{BET} values differ only by water sorption, while for the rest of the sorbates, their a_{BET} values are almost the same (Figure 6).

For the sorption of water vapours, a_{BET} represents about 31% of the a_{max} values for C2 and C3 coals and about 23% for the highest rank C1. For methanol, higher values of a_{BET} relative to a_{max} were recorded. A clear dependence on the degree of coalification can also be seen, as the a_{BET} contributions to a_{max} are 36%, 45%, and 48% for the C3, C2, and C1 coals, respectively. Comparison of the a_{BET} for these sorbates reveals that the a_{BET} of methanol for the C1 and C2 coals is higher than that of water and for the C3 coal the ratio is reversed. In other words, the sorption of water on the higher rank C1 and C2 coals is higher than that of methanol but the water monolayer capacity is lower than that of methanol. This is most likely due to the overlapping of two phenomena. First, both sorbates undergo multilayer adsorption, but in the case of water molecules the process is more efficient because of strong dipole-dipole interactions and hydrogen bonds. The second aspect is the affinity of methanol for both polar and nonpolar sorption sites. The effect of decreasing the amount of the former with increasing degree of coalification is reflected in a larger difference between the a_{BET} of water and the a_{BET} of methanol for the C1 coal than for the C2 coal (Figure 6). On the other hand, on low-rank C3 coal, the sorption of water and methanol takes place mainly at numerous polar sorption sites. Because of the shape and larger size of the methanol molecules, they are less efficient at using the available sites effectively, hence the lower a_{BET} value for this sorbate.

The self-reported monolayer capacities obtained a_{BET} and the maximum sorption capacity a_{max} of water were compared with the values obtained by the authors Charrere and Behra [3] (Table 3). For the coal marked Albert in their work, the amount of water adsorbed on the primary sorption sites was 50% [3]. For our C2 coal, the ratio of a_{BET} and a_{max} is 31%. The ratio of the fraction of sorption at the primary sorption sites to the fraction of total multilayer sorption of the compared coals is 1.6, while the ratio of the amount of element O content in these coals is 1.7. These values indicate the possibility of a linear relationship between the oxygen content and the monolayer capacity in water sorption for coals with similar degrees of coalification. This is in agreement with the arguments and conclusions presented earlier in the paper. In the case of hydrocarbon sorption, a_{BET} provides between 28% and 38% of the a_{max} values for C1 and C2 coals. Slightly higher proportions are shown for systems with C2 coal. For the lowest rank C3 coal, the ratios are between 49% and 54%. No clear dependence on hydrocarbon type was observed in this regard. The a_{BET} values for the C1 and C2 coals overlap as in the case of methanol sorption (Figure 6).

5. Conclusions

On the basis of the analysis of the literature on the subject and on the studies carried out and the obtained results, it was concluded that the nature of the adsorbate determines the course and magnitude of adsorption due to the kinetics of the process and in terms of specific interaction with the sorbent surface.

- The shape of water sorption isotherms corresponds to type II according to the IUPAC classification, while the shape of methanol sorption isotherms corresponds to type I according to the IUPAC classification. The sorption in the coal-water system follows a course characteristic for sorbents containing micro- and mesopores with the formation of a monolayer and then a multilayer structure. Sorption in the coal-methanol system follows a course characteristic for microporous adsorbents, including formation of the monomolecular adsorbent layer.
- The difference in the maximum sorption value between low-rank coal C3 coal and higher rank coals C2 and C1 is greater than between C2 coal and C1 coal. The parameter that corresponds better to the sorption properties of coal toward water and methanol is the content of element O in the coal.
- The sorption of methanol vapour is higher than that of water vapour in the initial part of the relative pressure scale. This tendency remains longer for lower-rank coals. The maximum sorption capacity is higher for coal-water systems than for coal-methanol systems. The open-pore structure of coal is responsible for this diversity. It enables the formation of association of water molecules with dipole-dipole and hydrogen bonding interactions. In the case of methanol, these interactions are weaker.
- The factors that determine the sorption capacity of coal toward water are (1) the capillary structure of the sorbent, in terms of diffusion in pores and conditions for the occurrence of multilayer sorption and condensation of sorbate vapours, and (2) the availability of polar adsorption sites, associated with oxygen functional groups. In the case of methanol, the second aspect also includes the availability of an apolar coal surface, since methanol molecules can bond to specific polar sites and nonspecific apolar sites. In addition, one methanol molecule can screen for more than one sorption site.
- The shape of the sorption isotherms of unsaturated hydrocarbons is close to type II according to the IUPAC classification. In the case of saturated hydrocarbons, the shapes of the sorption isotherms change from type II to type I as the length of the aliphatic chain in the molecule increases and the degree of coal coalification decreases. The sorption of vapours of nonpolar substances on coal has a surface character. The pores present in coal act as a molecular sieve in this system.
- The sorption capacity of the applied hydrocarbon sorbates depends on (1) the presence or absence of a double bond and (2) the size of the molecule. The sorption capacity of these sorbates increases in the order: n-octane < n-heptane/n-hexane < 1-heptene < 1-hexene.

- The effect of differentiating the sorption amounts of the studied sorbates increases with the degree of coal coalification. Coal with a higher degree of coalification shows greater differentiation of the course of isotherms of alkane sorption, due to higher microporosity, and greater sorption of alkane and their unsaturated counterparts, due to the presence of π -electrons in aromatic structures of coal. It is significant that the double bond effect is dominant over the influence of the length and shape of the hydrocarbon molecule.
- Based on the analysis of the data description with the BET sorption isotherm equation, it was found that the water monolayer capacity is higher than that of methanol in low-rank C3 coal. The sorption of water and methanol takes place mainly at numerous polar sorption sites. Smaller water molecules are more efficient at using the available adsorption sites.
- Analysis of data using the BET sorption isotherm showed that the water monolayer sorption capacity is lower than that of methanol on the higher-rank coals C1 and C2, although the maximum sorption capacity of water is higher than that of methanol. The affinity of methanol for both polar and nonpolar sorption sites results in a higher monolayer capacity. Multilayer sorption based on strong dipole-dipole interactions and hydrogen bonds between water molecules results in a higher sorption capacity.

Author Contributions: Conceptualization, P.B. and K.Z.; methodology, P.B. and K.Z.; investigation, A.K.; resources, A.K.; data curation, K.C.; writing—original draft preparation, K.C.; writing—review and editing, K.C. and P.B.; visualization, K.C. and P.B.; supervision, K.Z.; funding acquisition, K.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge financial support from the “Initiative of Excellence—Research University—IDUB, Activity no. 4” programme of AGH University of Science and Technology in Krakow, Poland.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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