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Characteristics of water, methanol and benzene vapours sorption properties of selected metamorphic types of hard coal

Key words

Hard coal, sorption properties, sorption of water, methanol and benzene

Abstract

The paper presents the results of investigations of sorption of water, methanol, and benzene vapours on samples of coal that significantly differ in the degree of metamorphism and the resulting content of polar groups as well as in their texture. The consideration of the structure of applied sorbates and possible types of sorbate – coal interactions, makes possible the explanation of the course of sorption isotherms and the relations between them.

Introduction

Hard coal is commonly considered to be an organic polymer (Ceglarska-Stefańska 1974); Milewska-Duda1988) composed of benzene rings, binding to form the systems of several condensed rings. These aromatic systems form tri-dimensional complexes, bound with –CH_2–, –C_2H_4– bridges, and often with ether systems (Marzec 1986). In the tri-dimensional structure of hard coals there are free spaces of a closed or open structure, of variable size and shape, creating a very heterogeneous capillary structure. These free spaces are responsible for the general porosity of coals, consisting of various systems: submicro-, micro-, meso-, and macro-pores, up to fissures and crackings of micron dimensions. The content of

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submicro and micro-pores determines the value of specific surface area, while their volume depends upon the quantitative contribution of the largest macropores in the capillary structure of coal. Usually the contribution of mesopores is small, both in specific surface area and in total volume of pores (Walker et al.1988). Nevertheless, meso- and macropores are the sites of mono- and poly-molecular adsorption and therefore the adsorption capacity of coal is determined by surface area of these pores.

Molecular hydrocarbons, forming aliphatic and alicyclic systems (Marzec 1986) may also be found in coal structure. They may block the access of various molecules of applied sorbates to the pore structures. At the edges of aromatic and aliphatic complexes there are located reactive groups that contain oxygen and more rarely nitrogen. To these reactive oxygen groups belong the hydroxylic, carboxylic, carbonyl and methoxyl groups (Chemistry... 1985) that impose a definite polar character to the basic, apolar hard coal matter. In this way the system of a double hydrophilic- hydrophobic character is formed. This structural feature of hard coal determines many of its properties, such as swelling, spontaneous ignition, and first of all – the sorption properties in relation to vapours of polar and apolar substances (Kreiner 1991; Żyła et al. 1991). The degree of polarity of hard coals is also significantly determined by the donor-acceptor centres that may impose a basic or acidic character to the surface of coal additionally increasing coal sorption properties, particularly towards vapours of polar compounds. The presence of polar groups in the structure of hard coals reduces sorption of vapours of apolar substances. It is ascribed to screening the apolar coal surface by oxygen groups (Lasoń et al. 1960).

Earlier sorption studies (Stachurski, Żyła 1995) show that the hydrophylic character of hard coals decreases with their metamorphism. Sorption of water and methanol vapours on coals of low carbon content is considerably privileged and it is several times higher than sorption of hexane, cyclohexane and even benzene (Żyła et al. 1997). It should be stressed that the investigations of the sorption of hydrocarbon vapours on hard coals are limited, despite the variable interaction of hydrocarbons with the coal matter (Grzybek et al. 1997). Sorption and desorption phenomena are accompanied by the processes of volume deformations and reduction of surface energy (both factors may affect the state of the stresses of a rock mass and consequently they may cause several undesirable and dangerous phenomena accompanying exploitation of hard coal). For this reason the studies of sorption of simple compounds (water, short chain alkanols, carbon dioxide, short chain alkanes and alkenes) are well justified.

The aim of the work was to show the relation between structure sorbate molecules and active centre on the coal sample surface.

1. Equipment and methods of measurements

The results of the measurements of sorption and desorption of the vapours of water, methanol and benzene on the samples of hard coals from the following coal mines: Jaworzno Coal Mine, bed 209 (coal Jaworzno), Sośnica Coal Mine, bed 413 (coal Sośnica) and Pniówek Coal

Mine, bed 360/1 (coal Pniówek) are presented. The samples were prepared in the Department of Mining Aerology of the Central Institute of Mining (Katowice, Poland), following the PN-90/G-04502 polish standard. Sorption experiments were carried out at 303 K, on the grain fraction 0.125–0.250 mm, using fluid micro-burettes equipment (Lasoń, Żyła 1963).

Prior to measurements the samples were degassed to 10^{-3} Pa, with additional He washing during degassing. Chemical, technological and petrographic parameters of the studied coals are shown in Table 1a and Table 1b.

TABLE 1a

Elemental and technological analysis of the studied hard coals

TABELA 1a

Analiza chemiczna i technologiczna badanych węgli

Content	$[\text{wt.\%}]^{daf}$	Coal Jaworzno	Coal Sośnica	Coal Pniówek
Carbon		57.83	70.82	84.24
Sulphur		1.10	3.50	0.39
Pyritic sulphur		0.71	3.20	0.01
Hydrogen		3.37	3.35	4.58
Nitrogen		0.87	1.28	1.52
Sulphur in ash		0.03	1.27	0.07
Combustible sulphur		1.07	2.23	0.32
Oxygen[a]		11.30	6.29	4.58
Moisture		11.11	1.85	1.75
Ash		14.45	14.18	3.01
Volatile matter		28.39	29.88	27.12

[a] – by difference.

^{daf} – dry and ashless state.

Elemental analysis of the studied hard coals was carried out in the Department of Solid Fuels Quality Assessment of the Central Institute of Mining in Katowice (Poland).

TABLE 1b

Petrographic analysis of the studied hard coals

TABELA 1b

Analiza petrograficzna badanych węgli

Maceral	[vol.%]	Coal Jaworzno	Coal Sośnica	Coal Pniówek
Vitrinite		67	60	73
Liptinite (egzinite)		5	9	7
Inertinite		28	31	20
Mineral substance		11	14	1
Reflectivity of vitrinite	[%]	0.51	0.78	0.92

2. Results and discussion

The obtained results for water vapour sorption studies are shown in Figure 1. The isotherms show the highest sorption capacity for this sorbate on coal from the Jaworzno Coal Mine. This coal, of a very low metamorphism degree has the lowest content of carbon (57.8%) and the highest content of oxygen (11.3%). Samples of considerably higher content of carbon (Sośnica – 70.82% C and 6.29% O, and Pniówek of 84.24% C and 4.58% O) are much worse sorbents of water vapour.

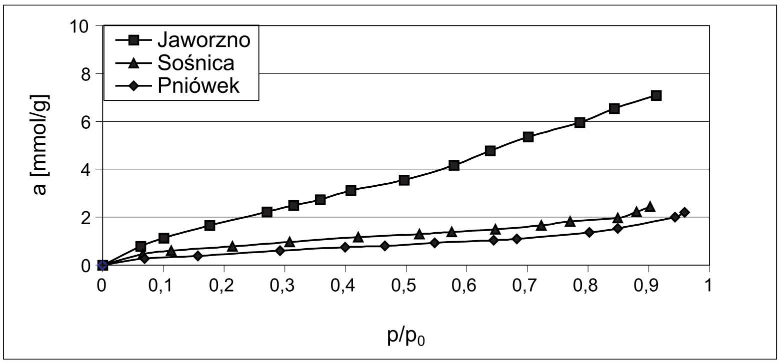

Fig. 1. Sorption isotherms of water vapour for the studied coal samples (T = 303 K)

Rys. 1. Izotermy sorpcji par wody dla badanych próbek węgla (T = 303 K)

The mutual interaction of water vapour and coal matter may be considered in three aspects: adsorption in micro-pores, interfacial sorption and variable sorption capacity, dependent on coal metamorphism (Hard coal 1994). It is generally accepted that water vapour sorption on coal has the character of polar sorption (Lasoń et al. 1960; Ceglarska--Stefańska 1990). The coal samples of low degree of metamorphism contain considerable amounts of oxygen strongly bound in the form of functional groups (–OH, =CO, –COOH) on the surface of coal matter. These groups are strong adsorption centres, capable of bounding water molecules (Ceglarska-Stefańska, Brzóska 1993).

With the increase of the vapour pressure of water above the coal sample the number of water molecules bound to a particular hydrophilic group increases and cluster-like systems are formed. This leads further (with the increase of p/p_0) to the condensation of water vapour in the pores present in coal matter. The formation of larger associates of the adsorbed water molecules causes also the phenomenon of deformation of the lattice of a carbon copolymer. The formation of the system of the cluster or associate type is more favoured by the open texture of a coal matrix. The coal sample of low carbon content (the sample from the Jaworzno Coal Mine) has a significant amount of low-molecular unions, and the molecules of macro-polymer have a low degree of ordering (Żyła et al. 2005). Therefore the matrix of such coal is considerably looser which enables water molecules to relatively penetrate the capillary structure rapidly and freely. The forming aggregates of water molecules may occupy free spaces of pores. On the other hand, the coal samples of higher degree of metamorphism (the samples from the Sośnica and Pniówek Coal Mines) have a considerably lower number of low-molecular bonds and a significant number of macromolecules of a higher degree of ordering. The structure of these coals is stiffer and less susceptible to the penetration by sorbate molecules. However, it should be noted that water sorption capacity of the coal sample from the Sośnica Coal Mine may also be affected by a high content of mineral substance (14%), represented by carbonate minerals of variable microscopic features (Cygankiewicz et. al. 2006). The results of the methanol vapour sorption on the analyzed samples of coal are presented in Figure 2. The highest sorption capacity is again shown by the coal sample from the Jaworzno Coal Mine, young coal of the highest content of hydrophilic functional groups at its surface. As the degree of metamorphism increases (with increasing content of carbon and decreasing content of oxygen) the sorption of methanol decreases (the coal sample from the Sośnica Coal Mine). Methanol is a specific sorbate, because in addition to a polar hydroxylic group it contains an apolar methyl group $-CH_3$. Therefore methanol molecule may be bound to coal surface by specific interactions (–OH group to the polar centres at coal surface) and by non-specific (dispersive) interactions ($-CH_3$ group to apolar surface of a coal matrix). This specific interaction of methanol with coal substance is well illustrated in Figure 3, where the sorption isotherms of water and methanol vapours are compared. For the Jaworzno coal, methanol sorption is higher within the region of low relative pressure values, afterwards both isotherms cross each other and finally water sorption is higher than methanol sorption. In the initial range of the isotherm, corresponding to the process of filling of the first monolayer, adsorption is determined by the number of adsorption centres. This number is larger for methanol that can be bound not only by polar centres but also by non-specific apolar centres. The possibility of the formation of a further layer after completing the first monolayer is determined both by the capillary structure of a sample and by the strength of interactions between the sorbate molecules. A more opened structure of pores of young coal from Jaworzno facilitates the formation of clusters and associates of strongly mutually interacting molecules of water (with the strongest dipol –

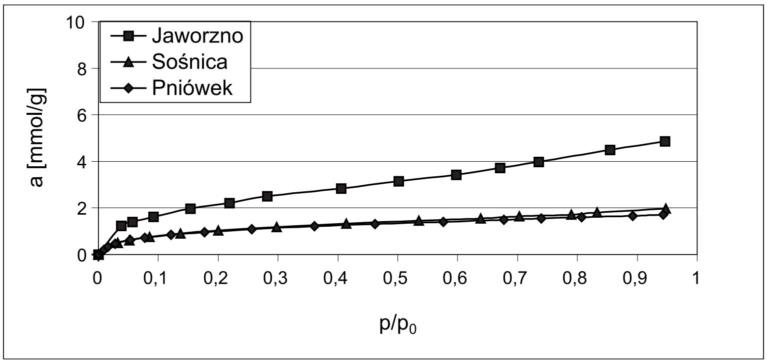

Fig. 2. Sorption isotherms of methanol vapour for the studied coal samples (T = 303 K)

Rys. 2. Izotermy sorpcji par metanolu dla badanych próbek węgla (T = 303 K)

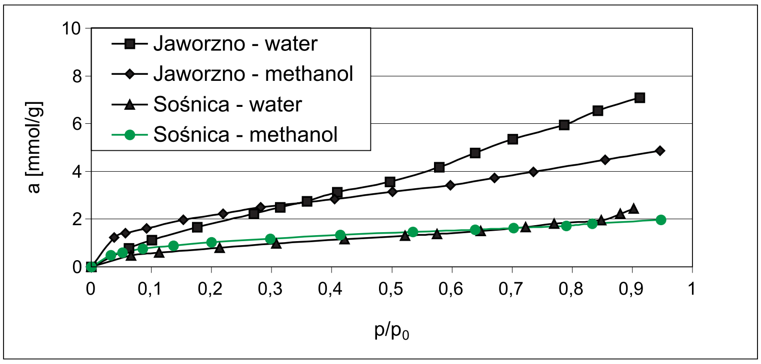

Fig. 3. Sorption isotherms of water and methanol vapours for the coal samples from the Jaworzno and Sośnica Coal Mines (T = 303 K)

Rys. 3. Izotermy sorpcji par wody i metanolu dla próbek węgli z KWK Jaworzno i KWK Sośnica (T = 303 K)

dipol interactions and hydrogen bonding). In the case of methanol these interactions also occur but they are much weaker and despite of the advantageous texture of coal sorption increases mildly (almost linearly) with the increase of p/p_0. The crossing of isotherms occurs at the relative pressure of 0.35. In the case of coal from the Sośnica Coal Mine, of a considerably larger degree of metamorphism, the sorption of methanol vapour (in the presence of non-specific interactions) is larger than that of water vapour. Also in this case the isotherms cross, but it is less visible and occurs at much higher values of the relative pressure. The texture of this coal does not favour the formation of multiple adsorption layers, and some increase of water sorption in the end range of the relative pressure may be related to the condensation of water vapour at the external surface of the sample (occurring also more easily for water than for methanol), or to the lattice sorption accompanied by swelling.

The course of the benzene sorption isotherms shows considerably larger sorption capacities of the Jaworzno coal than those of the Pniówek coal (Fig. 4). A low carbonized coal sorbs more benzene than a high carbon content coal. A similar correlation between the benzene interaction and coal matrix was observed in the studies of the influence of coal metamorphism on the sorption of the vapours of benzene and its alkyl derivatives (Żyła, Krzyżanowski 2000). The advantageous structure of younger coals, containing a larger content of meso- and macro-pores (the Jaworzno coal) favours the sorption of benzene to a greater degree than a microporous texture of coals of a higher degree of metamorphism. Moreover it should be remembered that benzene is not a typical apolar chemical compound. The presence of a delocalized sextet of π electrons, above and below the plane of the molecule, sterically accessible, imposes a nucleophilic character (a Lewis base) to a benzene molecule. This enables interactions of benzene not only with the apolar coal substance but also with polar groups on coal surface that are Lewis acids (much more numerous in the Jaworzno which contains 11.3% O).

The coal sample from the Pniówek Coal Mine, despite a significantly higher degree of aromatic condensation (the present aromatic units should be strong adsorption centres for benzene) shows a reduced porosity, resulting from its condensed structure. This efficiently inhibits the possibility of interactions: coal substance – benzene molecule.

The importance of these interactions for sorption may be confirmed by comparison of the sorption of benzene and cyclohexane vapours on the same coal sample (the coal sample from the Jaworzno Coal Mine) (Fig. 5). Despite some similarity of the structure and close kinetic diameters of both molecules, sorption of benzene is almost twice higher than the cyclohexane sorption. It may be assumed that a global sorption of benzene vapour is determined both by specific and non-specific interactions. Cyclohexane is on the other hand a classical example of an apolar substance not capable of additional interactions: nucleophile – electrophilic centre. This leads to a considerably lower sorption value.

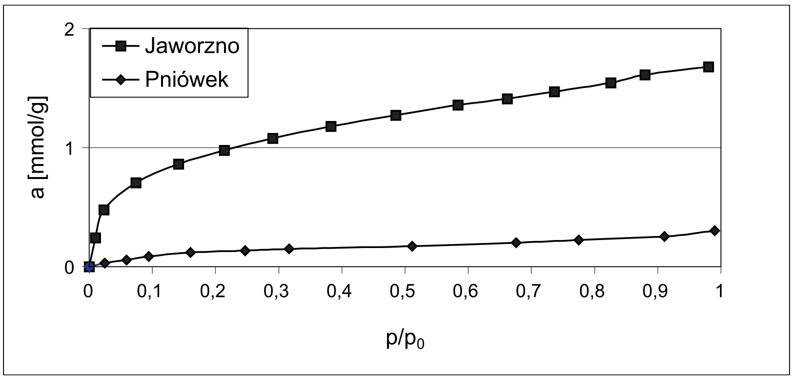

Fig. 4. Sorption isotherms of benzene vapours for the studied coal samples (T = 303 K)

Rys. 4. Izotermy sorpcji par benzenu dla badanych próbek węgla (T = 303 K)

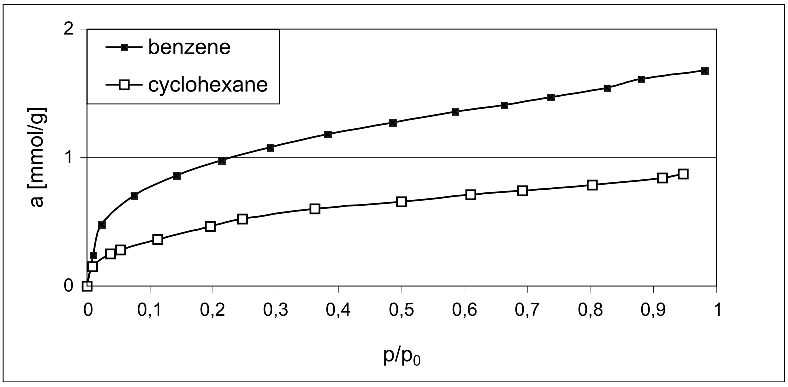

Fig. 5. The comparison of benzene and cyclohexane vapour sorption on the coal from the Jaworzno Coal Mine (T = 303 K)

Rys. 5. Porównanie sorpcji par benzenu i cykloheksanu dla węgla z KWK Jaworzno (T = 303 K)

Conclusions

Sorption measurements of the selected types of sorbates made possible the characterization of the studied coals (Jaworzno Coal Mine, Sośnica Coal Mine, and Pniówek Coal Mine), considerably differing in the degree of metamorphism and the resulting content of polar groups, as well as in their texture. The knowledge of the structure of applied sorbates and the possible types of the interactions between sorbates and coal matter lead to the following conclusions:

1. Sorption of water vapour on hard coals depends not only upon the polar character of coal surface but also on its porosity. The coal samples of the extended capillary structure create the possibility of the formation in free spaces of pores of numerous, significantly extended, aggregates of water (clusters) that may cause deformation of the polymeric structure of coal. The possibility of enhanced desorption of methane from coal due to water sorption cannot be ruled out (Hildenbrand et al. 2006; Tamas et al. 2002).
2. Vapours of organic polar compounds (short chain alcohols, carboxylic acids, alkyl amines, surfactants) may adsorb not only on polar centres but also on typical apolar sites due to the action of the dispersive forces.
3. An important finding is the demonstration of the possibility of the interactions of the delocalized π electrons sextet of benzene, imposing a Lewis base character to its molecule with the apolar part of coal matter surface and with polar groups of the Lewis acid character on the coal surface. Cyclohexane molecules, which do not contain π electrons in their structure are sorbed considerably less effectively.

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ANDRZEJ KRZYŻANOWSKI, MIECZYSŁAW ŻYŁA

CHARAKTERYSTYKA WŁAŚCIWOŚCI SORPCYJNYCH WYBRANYCH, METAMORFICZNYCH ODMIAN WĘGLA KAMIENNEGO W ODNIESIENIU DO PAR WODY, METANOLU I BENZENU

Słowa kluczowe

Węgiel kamienny, właściwości sorpcyjne, sorpcja wody, metanolu, benzenu

Streszczenie

W pracy przedstawiono wyniki badań sorpcji par wody, metanolu i benzenu na próbkach węgla różniących się znacząco stopniem metamorfizmu, a w konsekwencji zawartością polarnych ugrupowań oraz teksturą. Uwzględnienie budowy cząsteczek stosowanych sorbatów i możliwych typów oddziaływań pomiędzy sorbatem a materiałem węglowym pozwoliło na wyjaśnienie przebiegu izoterm sorpcji oraz relacji pomiędzy nimi.