Identification of hard coal surface structure using polar and apolar small molecule substances

Grzegorz S. Jodłowski¹ · Marta Wójcik¹ · Agnieszka Orzechowska-Zięba¹

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Abstract The paper presents a numerical approach to the analysis of the statistical effect of functional groups on the sorption of methanol and water on hard coal samples. The material used for the analysis was obtained from numerous samples of hard subbituminous and bituminous coals up to anthracite from different Polish coal mines and includes sorption isotherms of water and methanol vapors, as well as carbon dioxide and methane on these samples. Measurements were made of the sorption isotherms of water and methanol vapors and the data set has been supplemented with the sorption isotherms of water, methane and carbon dioxide taken from the literature for the precise estimation of the model parameters. More precise estimation is reached by using a strong setting of the coal structure parameters for a bigger number of sorption system, and in each case the same parameters of coal geometry are constant with an exact fitting of sorption isotherm. The adsorption-absorption model of the sorption in coal (Multiple Sorption Model-MSM) is used in the numerical experiments and the parameters of hard coal structure and the sorption systems are estimated. It has been stated that water as a polar substance together with methanol, as well as carbon dioxide and methane give good estimates of coal structure and let us quantify the polar effect of surface groups present in hard coal. The polar effect is introduced

in the model in the range of adsorption and expansion sub-processes. The presence of oxygen groups in the bulk of coal matter has no significant effect and can be neglected. A weak decreasing tendency of polar factors ratio for water and methanol is discovered.

Keywords Hard coal · Polar groups · Adsorption · Sorption · Modeling

1 Introduction

Hard coal is a very complex substance containing copolymer matter which is partially rigid and partially elastic. This problem is further complicated by functional groups present on the surface (Hao et al. 2013). Such a structural composition creates difficulties in modeling sorption phenomena and the identification of coal structure. Functional groups existing on the coal surface (as well as in the bulk) play an important role in numerous observed phenomena and technological processes. In the combustion process, the hydroxyl groups (–OH) and segments of coal matter (–CH₃, –CH₂–) play a substantial role (Cao et al. 2015). Surface groups of coal have a small effect on the liquefaction, gasification, pyrolysis (Feng et al. 2013; Lin et al. 2014; Yu et al. 2013) and wettability (Zhou et al. 2015b) of coals. They play a particularly important role in the competitive adsorption of H₂O, CH₄ and CO₂ molecules in coals (Gensterblum et al. 2014). Support for the adsorption of the CO₂ molecules in the surface groups is observed but finally carbon dioxide aggregates built up in the neighborhood of the surface group create adsorption sites which are unstable and the adsorption of carbon dioxide is not increased by the polar effects of these groups (Huang et al. 2014). The polar interactions of water with

✉ Marta Wójcik
mwojcik@agh.edu.pl

Grzegorz S. Jodłowski
jodlowsk@agh.edu.pl

Agnieszka Orzechowska-Zięba
azieba@agh.edu.pl

¹ AGH University of Science and Technology, al.
A.Mickiewicza 30, 30-059 Krakow, Poland

surface groups result in a great sorption capacity despite the hydrophobic character of the coal surface (Liu et al. 2015). The consequences and modeling of the polar effects of the functional groups present on the coal surface are the subject of this paper.

The idea of presenting the interactions of polar substances by the factor describing the excess forces compared to apolar ones led to the analysis of the statistical influence of functional groups on the adsorption of small molecule polar substances. Using a simultaneous analysis of the sorption isotherms of different polar and apolar sorbates while maintaining coal structure factors allows a successful identification of the structure and texture of hard coals (Nishino 2001; Švábová et al. 2011; Charrière and Behra 2010). The only drawback to this kind of analysis is the statistical (general) approach to the effects of these functional groups.

A demonstration of capabilities describes the relationship between the polarity of the coal surface and the excess adsorption of polar substances using a factor introduced to the formula for the energy of sorption, expressing the phenomenon in a statistical manner. A number of simulations of sorption isotherms using the developed MSW model were carried out for polar and nonpolar sorbates. An analysis of the entered parameters for the energy formula obtained through the simulation of isotherms using a model based on the measurement data is presented in this paper.

2 Experimental Data

Water and methanol vapors were used as polar sorbates to characterize the surface chemistry of the coals based on the adsorption–absorption model. The additional isotherms of CO₂ and CH₄ (Ceglarska-Stefanska et al. 1990) were added to the experimental set for the precise estimation of adsorption–absorption model parameters for nonpolar gaseous sorbates. So that makes it possible to compare the results of structural studies of a heterogeneous coal copolymer obtained by the sorption of gases with those for water vapor in relation to the same coal samples.

Coal samples with various carbon contents C^{daf} were investigated to determine the changes in the model parameters for the coal copolymer over the entire range of hard coal rank (Tables 1, 2).

Samples of coal with a grain size of about 0.2 mm were degassed in a vacuum 0.001 Pa to remove adsorbed molecules. Sorption isotherms of water and methanol vapors were measured in a liquid microburette apparatus at room temperature (298 K). Sorption isotherms of carbon dioxide and methane were measured in the sorption manostate apparatus at the same temperature. The portion of sorbate was added to the sample, and after reaching

Table 1 Proximate and ultimate analyses of the investigated coal samples

Sample	Content (%)						
	A ^a	W ^a	V ^{daf}	C ^{daf}	H ^{daf}	(O + N) ^{daf}	S _t ^a
W-31	2.60	8.75	39.20	75.16	5.56	19.28	0.62
B/82*	2.48	3.76	40.80	80.88	5.26	13.14	0.62
W-32	7.70	3.98	33.90	82.51	5.00	12.49	0.62
W-33	2.00	2.03	30.30	83.31	5.10	8.60	0.30
W-34	8.50	1.63	39.20	84.90	5.88	12.20	0.75
K/87*	16.64	1.32	32.68	86.55	5.22	7.37	0.90
W-35	4.80	0.72	24.40	86.85	4.65	6.51	1.53
W-37	13.80	1.63	25.80	88.95	3.92	9.23	3.36
W-41	9.40	1.13	11.50	91.49	3.93	4.68	1.48
W-42	3.70	0.81	6.09	92.40	3.02	8.18	0.46
M/85*	3.70	0.81	6.09	92.41	3.02	4.09	0.46

* Taken from the dissertation of Ceglarska-Stefanska (1990)

thermodynamic equilibrium (after three or four days) the amount of adsorbed gas was determined and then the next point of isotherm at higher pressure was measured. Measurements of the isotherms in a full range of relative pressures for vapor sorbates were made and for gaseous ones in a range up to 3.5 MPa, which was the limit of the apparatus.

The obtained sorption isotherms were used for the evaluation of simulations made by applying the Multiple Sorption Model.

2.1 Modeling

The Multiple Sorption Model (MSM) was applied for the numerical analysis of the sorption isotherms of water and methanol to investigate surface polarity effects during sorption and the possibility of a statistical description of the functional groups effect on this process. The model depicts the sorption process as a set of simultaneous phenomena occurring on the surface-adsorption and in the bulk of the coal-expansion and absorption (Jodlowski et al. 2007). The effects of the arene domain on the entropy and energy of sorbate molecules in the sorption system were included in the studies, taking into account the complex structure of the coal bulk. The texture of coal surface is included by a model called LBET describing the adsorption in a sub-microporous system and in bigger pores (Duda et al. 2002; Milewska-Duda et al. 2002). The LBET model takes into account the composition of the adsorbate molecule stacks in the porous system, even those incompatible with the BET assumption. A set of LBET models has been developed by the team to enable a better description of the surface heterogeneity (Kwiatkowski and Broniek 2012).

Table 2 Densimetric properties of hard coal samples

Sample	Apparent density d_{Hg} (g/cm ³)	Helium density d_{He} (g/cm ³)	Pore volume V_{He} (cm ³ /g)	Porosity (%)
W-31	1.343	1.617	0.126	7.40
B/82*	1.255	1.356	0.060	7.53
W-32	1.328	1.473	0.074	9.84
W-33	1.336	1.403	0.036	4.78
W-34	1.359	1.413	0.028	3.80
K/87*	1.306	1.355	0.028	3.66
W-35	1.305	1.399	0.051	6.67
W-37	1.357	1.452	0.048	6.54
W-41	1.355	1.444	0.045	6.16
W-42	1.357	1.434	0.040	5.43
M/85*	1.357	1.434	0.040	5.43

* Taken from the dissertation of Ceglarska-Stefańska (1990)

MSM is a complex numerical tool for the analysis of sorption phenomena in a coal structure. Some parameters are introduced to describe the composition of non-BET stacks and the polarity of the surface. The others are connected with specific interactions of surface groups with polar molecules of sorbates. It is common opinion that water and methanol are polar substances but even in the case of methane, which is regarded as an apolar substance, the effect of surface groups presence is considered (Zhou et al. 2015a, b). In our opinion, surface groups are present inside the pores and they are the source of the pores that appear after the desorption of water, carbon dioxide and methane molecules present there before opening of the coal bed. In the samples investigated, functional groups are

The correction factor describing the geometric and energetic properties of the sorbent bulk and surface is represented by the function (2) in which four regions in the submicropores distribution are distinguished:

1. Absorption with pore size $R_{ha} = 0$;
2. Expansion with large cohesion energy of coal matter in small submicropores of a radius smaller than that characteristic for pore distribution R_B (size of pores in which cohesion energy is the same as for the elastic copolymer);
3. Expansion with small cohesion energy of coal matter in larger submicropores of a radius larger than R_B ;
4. Adsorption with the pore size $R_{ha} \geq R_p$.

$$\zeta_a = \zeta(R_{ha}/R_p) = \begin{cases} 1 & \text{for } R_{ha} = 0 \text{ adsorption} \\ Z_B \cdot C_{pa} \cdot R_{ha}/R_p & \text{for } 0 < R_p < R_B \\ \left[Z_B + (Z_A - Z_B) \frac{R_{ha} - R_B}{R_p - R_B} \right] \cdot C_{pa} & \text{for } R_B < R_{ha} < R_p \\ Z_A \cdot C_{pA} = \zeta_A & \text{for } R_{ha} \geq R_p \text{ adsorption} \end{cases} \quad (2)$$

accessible for sorbate molecules. The energy of adsorption is described by the unit-less term:

$$\chi_{ac} \stackrel{def}{=} \varphi_c^0 \cdot (w_a^* \cdot \chi_{ch} - \zeta_a \cdot 2\sqrt{\chi_{ph} \cdot \chi_{ch}}) + \chi_{ph} \quad (1)$$

where φ_c^* is related to surface porosity (the ratio of surface of coal molecules to the sum of surface of coal molecules and surface of pores which create voids in the coal matter); w_a^* coefficient of surface expansion during the sorption process; χ_{ch} energy factor of coal matter—vacuum contact; χ_{ph} —energy factor of sorbate molecule—vacuum contact; ζ_a —factor describing heterogeneity of the coal matter.

where R_B is the characteristic size of the coal sorbent pore; R_{ha} is the actual size of the pore in the pore distribution function; R_p is the size of the sorbate molecule in the system; Z_A is the geometrical correction factor for energy in smaller pores ($R_{ha} < R_B$); Z_B is the geometrical correction factor for energy in bigger pores ($R_{ha} > R_B$); C_{pA} is the correction factor for polar interactions

Previous investigations by the team showed that the polar interactions of functional groups in absorption could be completely neglected (the first term in Eq. 2). Factors Z_A and Z_B are related to imperfect contact of a molecule with coal matter, calculated as the ratio of the actual number of

contacts to the maximum number of contacts in the space of spheres network. When the number of contacts is smaller than their maximum, the parameters Z have values from the range 0–1. The coefficient C_{pA} denotes specific interactions of the functional groups with sorbate molecules. The above description (Eqs. 1 and 2) of the energy gives a continuous picture of the sorbate molecule interactions in all subsystems of the sorption process. The correction factor complex functions can be described with the schematic diagram (Fig. 1).

Thus, one can observe that the polar interactions factor plays a leading role in pores comparable in size to the sorbate molecule and bigger. Certainly, the aggregates of molecules are formed in micro- and meso-pores. This is presented in the model by an equation which takes into account the possibility of building non-BET aggregates of the molecules. The additional parameter describing the ratio of BET to non-BET aggregates is introduced in the so-called LBET model (Milewska-Duda et al. 2000). When aggregates are not formed the parameter is set to 0 and the model becomes the expanded Langmuir adsorption one. On the other hand, when BET aggregates are created the parameter is set to 1, and it becomes the expanded BET model with the possibility of forming layers of limited capacity (non-BET aggregates). Thus, the model describes both monolayer and poly-layer adsorption.

Another problem is establishing the actual volume and cohesion energy of a molecule for gaseous sorbates. A suitable equation of state is included in the model computation packet (Milewska-Duda and Duda 2002).

Simulations of sorption isotherms for the set of structural and energetic parameters related to the type of coal are made and applied to the measured (empirical) isotherms. Numerical experiments provide the characteristics

of the structure of hard coal matter, energetic factors (e.g. cohesion, adhesion, absorption and adsorption) as well as polarity coefficient C_{pA} .

3 Results

The parameter C_{pA} which describes polar effects shows no regular tendency versus the carbon content in the set of coal-sorbate systems studied. Generally, the polarity of the coal surface decreases a little with increasing carbon content because of the decreasing tendency of the polarity factor C_{pA} (Fig. 2). This is in accordance with the decreasing content of the surface groups in coals with increasing carbon content.

Computations show a slowly decreasing tendency of the polar interaction coefficient for water. Its molecule interacts very strongly with functional groups. The ratio of complex factor $C_{pA} \cdot Z_A$ (polarity and geometry coefficient) of water to methanol shows more clearly the differences between adsorption of polar and apolar substances (Fig. 3).

The ratio of complex polar and apolar interactions is irregular and a tendency towards a decrease of polarity effects can be observed. One should note that parameter $(C_{pA} \cdot Z_A)$ includes a description of the non-ideality of the coal matter contact with sorbate molecules in the pores. Thus this complex parameter describes the complex behavior of the sorbate on the coal surface. The results of $C_{pA} \cdot Z_A$ for all sorption systems studied are presented in Fig. 4.

Fig. 1 Schematic presentation of the complex function of sorption energy correction factors

Fig. 2 Polarity coefficient C_{pA} versus carbon content for water vapor adsorption

Fig. 3 Complex factor of polarity and geometry ratio for water and methanol

Fig. 4 Tendencies of the complex geometrical and polar factors for different sorbates

The complex geometric-polar parameter (C_{pA}) for water is greater than 1, which indicates specific, polar interactions, and its changes versus carbon content are irregular. This comes from the changes in the geometry of the pores and the content of the surface groups which are not concurrent. When the C_{pA} parameter shows a decreasing tendency, the Z_A coefficient increases in coals up to orthocoking ones (85 % C_{daf}) and decreases in the direction of anthracites. In the first zone, development of porous structure contributes to the increase of Z_A , whereas in the second zone the rigidity of structure limits the number of effective contacts. In the case of methanol, C_{pA} values are lower than 1, which indicates weak polar interactions with a simultaneous worse fit of the sorbate molecules to submicropores shape (lower Z_A values and in consequence

lower term $Z_A * C_{pA}$ —see Fig. 4). Methane and carbon dioxide show smaller values of the complex parameter because of a lack of polar interactions and the value of $C_{pA} = 1$. In such a way the complex parameter for these gases presents only the geometrical properties of the coal texture. Values of C_{pA} for methane, carbon dioxide and methanol are nearly the same and they are related rather to the geometry of the pores. Thus the ratio of complex parameters for water and methanol gives full insight into the nature of polar interactions with surface groups (see Fig. 3).

Figures from 5, 6, 7, 8, 9 present the results of the simulation experiment—sorption isotherms obtained from the model by using the presented approach.

Curve 6 shows pure absorption increased by the volumetric expansion of the holes occupied by sorbate molecules. The difference between pure absorption (line 4) and the expansion curve (line 6) shows the contribution of adsorption-absorption phenomena in the deposition process of small-molecule substance in the coal material. The isotherm of “pure” LBET adsorption (line 3) shows the properties of coal as a classical adsorbent (excluding the effect of dependence on a “pure” adsorption on the sorption of the other subsystems). The difference between this curve (LBET) and the curve of the capacity of the pores—Line 1, allows the inadequacy of the classical models of adsorption with respect to coal structure to be evaluated.

Fig. 5 Theoretical and experimental isotherms of the sorption of water vapor in coal sample W-35. Chart description: black circles—experimental isotherm of sorption; black line—total theoretical sorption; 1—“classic” total pore capacity as in the dual model (total sorption decreased by absorption); 2—adsorption after taking into account the poly-layered nature of the phenomenon; 3—“Pure” adsorption BET (without taking into account interaction with other subsystems); 4—absorption (taking into account only cohesion forces); 5—hypothetical absorption for classic model adsorption (without taking absorption into account); 6—expansion with absorption

Fig. 6 Theoretical and experimental isotherms of sorption of methanol vapor in coal sample W-35. *Chart description:* black circles—experimental isotherm of sorption; black line—total theoretical sorption; 1—“classic” total pore capacity as in the dual model (total sorption decreased by absorption); 2—adsorption after taking into account the poly-layered nature of the phenomenon; 3—“Pure” adsorption BET (without taking into account interaction with other subsystems); 4—absorption (taking into account only cohesion forces); 5—hypothetical absorption for classic model adsorption (without taking absorption into account); 6—expansion with absorption

Fig. 8 Theoretical and experimental isotherms of sorption of methane in coal sample K/87. *Chart description:* black circles—experimental isotherm of sorption; black line—total theoretical sorption; 1—“classic” total pore capacity as in the dual model (total sorption decreased by absorption); 2—adsorption after taking into account the poly-layered nature of the phenomenon; 3—“Pure” adsorption BET (without taking into account interaction with other subsystems); 4—absorption (taking into account only cohesion forces); 5—hypothetical absorption for classic model adsorption (without taking absorption into account); 6—expansion with absorption

Fig. 7 Theoretical and experimental isotherms of sorption of water vapor in coal sample K/87. *Chart description:* black circles—experimental isotherm of sorption; black line—total theoretical sorption; 1—“classic” total pore capacity as in the dual model (total sorption decreased by absorption); 2—adsorption after taking into account the poly-layered nature of the phenomenon; 3—“Pure” adsorption BET (without taking into account interaction with other subsystems); 4—absorption (taking into account only cohesion forces); 5—hypothetical absorption for classic model adsorption (without taking absorption into account); 6—expansion with absorption

Fig. 9 Theoretical and experimental isotherms of sorption of carbon dioxide in coal sample K/87. *Chart description:* black circles—experimental isotherm of sorption; black line—total theoretical sorption; 1—“classic” total pore capacity as in the dual model (total sorption decreased by absorption); 2—adsorption after taking into account the poly-layered nature of the phenomenon; 3—“Pure” adsorption BET (without taking into account interaction with other subsystems); 4—absorption (taking into account only cohesion forces); 5—hypothetical absorption for classic model adsorption (without taking absorption into account); 6—expansion with absorption

While the difference between the curve (line 2) and the model of LBET (line 3) shows the effects of the adsorption poly-layer. The LBET model used in this study (Milewska-Duda 2000; Milewska-Duda and Duda 2002) can be seen as a coarse description of the effects of the aggregation of molecules in the pores. It is an improvement on the BET model taking into account the additional geometric reduction in the capacity of the pores.

The total theoretical sorption isotherm (black line) does not fit perfectly to the measured data (black circles) because the formula contained in the model describes the phenomenon in a statistical sense. This isotherm consists of multilayer adsorption with a limited size of aggregates (LBET—line 2), isotherms of absorption (line 4) and expansion (line 6). The other curves shown in this graph, and the next (Figs. 5, 6, 7, 8, 9) have only a supporting role in the assessment of the nature of the phenomena.

The shape of the total sorption isotherm and the poly-layer adsorption corresponds to the forming of aggregates of molecules in the neighborhood of surface functional groups. In this case, the multilayer adsorption phenomena has the greatest influence on the final shape of the isotherms.

In this system (Fig. 6) the absorption of methanol plays a relatively large role (line 4), while the adsorption (line 1) is almost monolayer and in a shape similar to a Langmuir isotherm. Therefore, one does not notice the creation of aggregates as in the case of water. Expansion in this system plays a minor role but is still significant.

Figures 5 and 6 show the basic set of isotherms taken into account when analyzing the impact of the polarity of the surface on the adsorption isotherm. We have analyzed eleven such sets. In order to improve the reliability of the simulation results we also used other sorption systems for which data were available on the sorption of gases like methane and carbon dioxide. In this way one can refine estimates of the carbon structure, as many simulated isotherms have to be based on the same determined carbon structure. Exemplary simulation results for systems which also contain sorption isotherms of CH₄ and CO₂ are shown in Figs. 7, 8, 9.

The dominant phenomenon in the sorption system shown in Fig. 7 is multilayer adsorption. The other phenomena (i.e. absorption and expansion) are almost negligible compared to the adsorption. In this system the surface polarity effect in total sorption is particularly obvious. However, the absorption and expansion are not small enough to be able to neglect them.

One can observe in Fig. 8 that methane is mainly adsorbed on the carbon surface. The molecules of this gas do not form complex aggregates, although adsorption is not a monolayer, but the capacity of the next layers is very limited (non-compliance with the BET theory). The

absorption is almost negligible, and expansion even plays a minor role in the total sorption.

Adsorption of carbon dioxide in the sample of K/87 is practically dual (Fig. 9). In general expansion does not occur here. The dominant part of the phenomenon is monolayer adsorption with a slightly lower share of absorption.

4 Conclusions

The comparison of energetic and geometric parameters of sorption on the same coal sample for water, methanol and the other apolar substances simultaneously gives a better estimation of the structure and energy properties of the surface than the estimation of the individual sorption system (for individual sorbates separately). Some of them, e.g. the parameter describing the copolymeric structure or capacity of the first layer are completely the same for all sorbates on the same coal sample. Such a procedure allows more precise parameters to be calculated describing the geometry of the surface as well as energetic coefficients for both polar and apolar sorbates (Duda et al. 2002). The tendencies in functional group interactions with sorbates of different nature (polar and apolar) obtained from numerical analysis are in accordance with commonly known changes in the general content of surface groups for different hard coals (Chen et al. 2012; Liu et al. 2015). The Multiple Sorption Model is an adequate tool for a statistical explanation of the surface group interactions with sorbate molecules based on sorption experiments. A new approach to the statistical analysis of polar interactions with the coefficient of polarity allows us to model sorption isotherms adequately to the phenomena occurring in the process.

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