Energy aspects of arene domain presence in the coal structure under the sorption process

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Abstract − This work presenst two way dissertation on energy aspects of arene domain presence in the coal substance and its interactions with sorbate molecules under the sorption process. Newly elaborated approach aimed at adsorption mechanism identification is discussed and the estimation procedure of energy profile of possible molecule location in the pores of graphite-like substance is presented. Wider view on the sorption process is included in the Multiple Sorption Model with regard to the absorption-adsorption character of the phenomena taking place under the location of sorbate molecules in the sorption system. Both approaches give us information on effect of arene domains and overall view on sorption process and coal structure.

Key words − coal structure, porosity, modeling, adsorption, absorption.

I. Introduction

The complexity of the coal structure (i.e. combination of multiple components) causes continuous need in the development of the material description and sorbate molecules interactions.

The statistical approach to the introduction of the coal structure components to the model is already used in Multiple Sorption Model (MSM). In MSM all compounds present in the coal mass are divided to the main groups of components and modeled together as a class of the physical objects with common properties of the segments of each object.

The novel attempt is to model the molecule behavior in the porous system of the component class – arene domain – qualified as quasi-graphite compositions. This attempt is developed in newly elaborated adsorption mechanism identification approach [1]. It enables to examine the effects of the adsorbent structure diversity on adsorbate molecule properties with special regard to the surface geometrical heterogeneity. More specifically, it draws information on the adsorbate volume, and hence applying *PVT* relationship for liquid bulk phase enables for estimation of energy profile [2].

In further considerations arene domains are the component of a total sorption system. Coal substance is composed by main components:

- Arene domains – quasi-crystalline formations of condensed benzene rings plates connected each-other by the relatively strong bonds;
- Linked chains (aliphatic, alicyclic and heterocyclic) connected each-other and with arene domains in nodes;
- Unlinked chains (aliphatic, alicyclic and heterocyclic) without connection in nodes;
- Pores present in coal surface and bulk (especially submicropores with diameter comparable to molecule size), understand as the constituent with connection to a vacuum if it is empty;
- Mineral admixtures with negligible sorption properties in comparison to coal matter porous system.

Two first components constitutes the limitedly rigid structure and is called macromolecular phase. Third component forms the elastic part of the coal substance and is called molecular phase [3], [4]. Special attention is taken on the arene domains and its behavior under the sorption process in this work.

Modeling of such complex system is burdened with uncertainty because of many parameters setting up in the starting point of simulation on the base of theoretical deliberations and earlier investigations (e.g. Hombach curve of cohesion energy density δ_c [5], [6] or results of optimization models of dual sorption). More detailed information on the excess energy of the molecules in the contact with arene domains porous system let to more precise modeling of the sorption phenomena in the hard coals.

II. Effects of adsorbate properties in graphite-like pores

Rigorous examination of surface diversity effects on adsorption phenomena may be performed for the discreetly represented graphite-like pores. Thus, it is required for the nanostructure of predefined shape (i.e. niche, cavity) to be formed by the carbon atoms at fixed positions. Such a representation enables to approximate the structure of the single coal arene domain as a graphite-like cavity (see Fig. 1), and hence to consider the individual adsorptive particle movement near the surface. More specifically, the individual particle mass center moving within free space is considered (the volume of space available for the particle). In a free space of volume V_{fi}, the molecule movement is limited by an equipotential surface $U_{bdry}(V_{fi})$. Moreover, at the boundary translation is limited to the surface and hence the movement accounts for two degrees of freedom. Therefore, kinetic energy represented by the temperature $k_B\tau_i$ is compensated by the decrease of, the corresponding to the volume V_{fi}, average potential $U_{avge}(V_{fi})$. Having in mind that the considerations are performed for the individual particle, $U_{bdry}(V_{fi})$ is the only component of the potential generated at the boundary, coming from solid-fluid adhesive forces. Hence, the kinematic equilibrium may be expressed in the following form:

$$\tau_i = \frac{U_m(V_{m_{pi}}) - U_{m_{adh}}(V_{m_{pi}})}{R} \qquad (1)$$

where R is gas constant and $U_m(V_{m_{pi}})$, $U_{m_{adh}}(V_{m_{pi}})$ are $U_{bdry}(V_{fi})$ and $U_{avge}(V_{fi})$ related to the one mole of particles, respectively. The volume V_{fi} corresponding to the volume occupied by the molecule mass center is subsequently recalculated as a volume of the moving particle – more detailed see [1].

The analysis of the temperature τ_i and volume $V_{m_{pi}}$ relationship makes possible to gain information on the adsorption mechanisms, when compared to the liquid phase properties (i.e. following classical localized adsorption mechanism assumption - vaporous adsorbate is approximated by the liquid state properties).
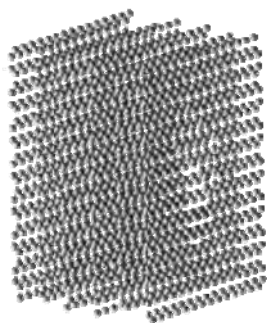
Fig. 1. Arene domain structure approximated by the graphite-like cavity model. The model is formed by the carbon atoms at fixed positions, and hence chemical heterogeneity is neglected. The cavity parameters are 0.7 nm depth and diameter: at the top layer 1.1-1.6 nm and at the second layer 0.8-1.9 nm [7]

The adsorption mechanism identification is a significant step in analysis, with special regard to the comparability of the dissertation on energy aspects of arene domain presence in the coal substance. As discussed in Sect. III MSM arbitrary assume localized adsorption mechanism, and hence it is necessary to define at first, the temperature range at which localized mechanism occurs. Subsequently, having in mind the volume additivity at the localized mechanism range and assuming that the excess energy evolved due to particle interaction with surface carbon atoms may be assumed to be withdrawn, in order to hold the constant temperature in isothermal adsorption, the system parameters may be averaged according to the Maxwell-Boltzmann distribution.

The Maxwell-Boltzmann averaging enables for evaluation of the system parameters, i.e. particular mechanism fractions and its ratio leading to the qualitative identification of the predominating mechanism or kinematic and thermodynamic temperatures. Finally, performed averaging leads to the key parameter in estimation of the energy effects of adsorbate molecules under the adsorption process – averaged molar adsorbate volume $\overline{V_{m_p}}$ at the temperature T (the temperature range may be freely selected). This volume may be seen as a realistic adsorbate molar volume in adsorption system of predominating localized mechanism. Originally it was exploited for calculations of surface texture parameter ζ, employed as a validation parameter when compared to the earlier studies performed in our team [8]. ζ describes possible contact of the adsorbate molecule with the adsorbent surface molecules, and hence may be seen as an effective contact ratio. Thus, it may be calculated taking the values for molar adhesion energy $\overline{E_{adh}}(\overline{V_{m_p}})$ and effective adhesion energy $\overline{U_{m_{adh}}}(\overline{V_{m_p}})$:

$$\zeta = \frac{\overline{U}_{m_{adh}}(\overline{V}_{m_p})}{\overline{E}_{adh}(\overline{V}_{m_p})} \qquad (2)$$

In this paper, the application of ζ to the arene domain energy profile analysis is considered. In particular, the molar adhesion energy $\overline{E_{adh}}(\overline{V_{m_p}})$ may be of practical significance, and hence is evaluated applying Berthelot rule by combining adsorbate and adsorbent cohesion energies:

$$\overline{E}_{adh} = 2\delta_c \sqrt{E_{vap}\overline{V}_{m_p}} \qquad (3)$$

where δ_c is the solubility parameter of adsorbent matter, E_{vap} is the adsorbate cohesion (evaporation) energy, both referring to the adsorbate reference state (for vaporous substances it is the liquid state).

The van Krevelen method [6] may be applied to calculate the solubility parameter δ_c. Nevertheless, it has to be taken into account that despite the modeled graphite-like cavity model is geometrically heterogeneous, it cannot be treated equivalently with the diverse coal structure. Hence, the value for δ_c was taken to be constant and $\delta_c = 30$ (i.e. it was assumed that graphite-like surface results in decrease of the carbon content). Subsequently, the adsorbate cohesion energy is evaluated with PVT relationship for liquid bulk phase [9].

Hence, newly elaborated approach aimed at adsorption mechanism identification provides interesting information on adsorbate properties, enabling to get an insight also in energy aspects for the model approximating arene domains.

III. Multiple Sorption Model

Model divides the sorption process into subprocesses: absorption where cohesion energy of the coal substance plays substantial role, expansion subsystems in which pores has size lower than molecule diameter and must be expanded together with location of the molecule, thus both cohesion energy of sorbent and adhesion energy of sorbates are in use and adsorption subsystem collecting molecules located on the surface of pores bigger than molecule diameter and adhesion forces are relevant to this interactions only. In the purpose of the calculations, system is divided to eleven subsystems, starting from absorption with pores relative radius $R = 0$ nine transitional subsystems $0 < R \leq 1$ related to expansion and adsorption with relative radius $R > 1$, see Fig. 2.
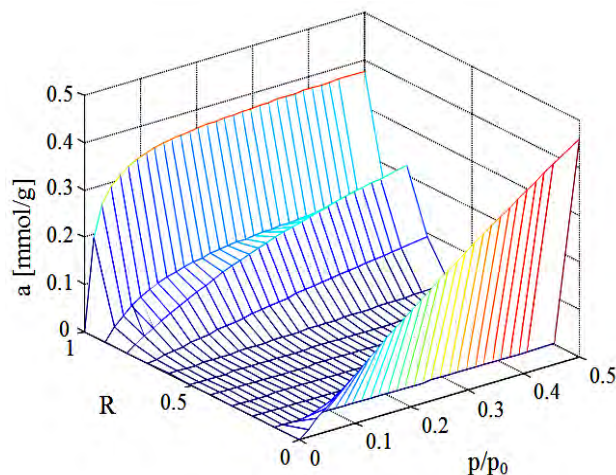

Fig. 2. Exemplary results of multisorption simulation for carbon dioxide and sample of coal

One could observe on the chart (Fig. 2) curves of absorption ($R = 0$) and adsorption ($R \geq 1$) and set of curves describing expansion in the transitional subsystems.

Finally, the adsorption in pores with bigger relative radius (micro-, meso- and macro-pores) is modeled by the formula elaborated for multilayer adsorption with limited

increase of the molecules quantity in the layer called LBET (i.e. clustering based approach aimed at microporous structure characterization) [10]. The model grants to evaluation of multilayer adsorption with aggregates different from BET theory. In such a case model becomes enhanced Langmuir or generalized BET equation dependently on the control parameter.

Polar effects of surface functional groups are taken into account and special coefficient describing possibility of specific interactions for polar sorbates is introduced to the model.
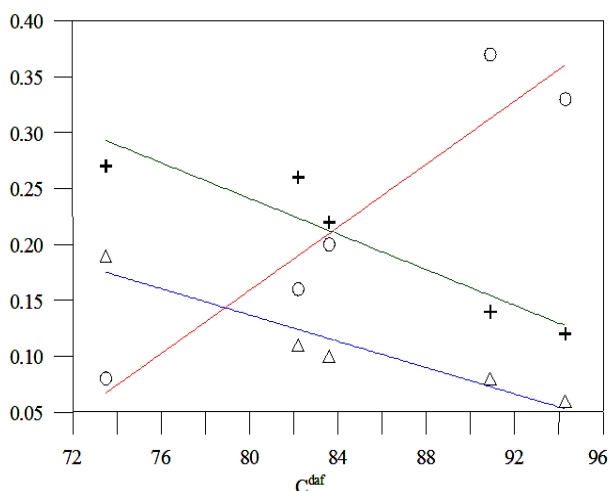

Fig. 3. Tendencies of components content in hard coals vs.
carbon content; line description:
red – arene domains, green – unconnected chains,
blue – pores

In Fig. 3 the tendencies in the changeability of main components of hard coal structure are presented. Content of arene domains strongly increase with carbon content, while unconnected chains and pores decrease. Last one is not strong tendency because some cases of increasing content of pores in coal matter for higher carbon content (above 88% C^{daf}) are stated.
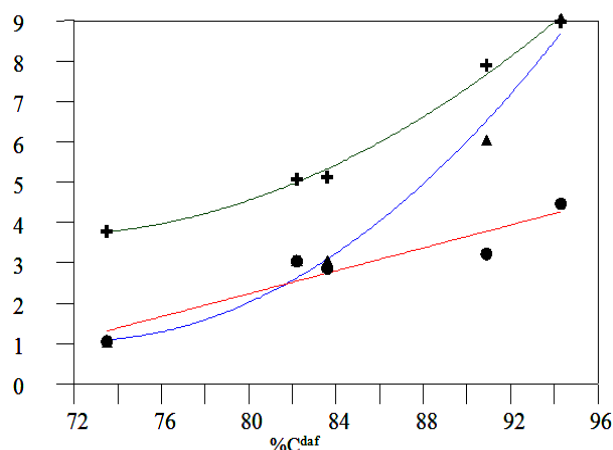

Fig. 4. Composition of arene domains in the coal samples
of different carbon content; lines description:
red – domain compactness, blue – number of plates
in the domain, green – number of plates in the domain

All the parameters of the arene domain structure increase with increasing carbon content in the coal substance what results in growing importance of this component presence in coal structure. Both effects are taken into account in the detailed physicochemical analysis: the entropy of mixing decrease due to the limitation of space available for molecules and enthalpy effects due to the isolation of sorbate molecules in the subsystems.

Energetic parameters of the coal structure and sorption system are evaluated for different sorbates on the range of coal samples (Table 1).

TABLE 1

SELECTED ENERGETIC PARAMETERS OF THE SORPTION SYSTEM

C^{daf}	δ_c	δ_p	χ_A	δ_p	χ_A	δ_p	χ_A	δ_p	χ_A
		H_2O		CH_3OH		CO_2		CH_4	
75.16	28.40	46.4	1.87	28.8	4.81	-	-	-	-
80.88	24.00	46.4	-0.17	-	-	16.0	4.82	10.3	5.49
82.51	24.08	46.4	3.03	28.8	4.67	-	-	-	-
83.31	24.10	46.4	2.69	28.8	7.25	-	-	-	-
84.90	23.82	46.4	1.51	28.8	5.30	-	-	-	-
86.55	22.50	46.4	-1.90	-	-	16.0	3.66	10.3	4.17
86.85	22.80	46.4	3.35	28.8	5.37	-	-	-	-
88.95	22.53	46.4	2.40	28.8	5.22	-	-	-	-
91.49	22.58	46.4	1.98	28.8	6.83	-	-	-	-
92.40	22.86	46.4	1.51	28.8	7.09	-	-	-	-
92.41	23.00	46.4	-2.52	-	-	16.0	5.05	10.3	5.17

The tendency of irregular decrease of the cohesion energy density δ_c is observed up to carbon content 85% subsequently the little increase of this parameter is viewable. This fact has important influence on the sorption energy χ_A as it is an effect of the estimation from the Berthelot Rule:

$$\chi_A \approx \zeta_a \cdot 2\sqrt{\chi_{ph} \cdot \chi_{ch}} \qquad (4)$$

where: χ_A – energetic parameter of the sorption in the system, ζ – geometric parameter of molecule fitting to the pore together with specific interactions for polar sorbates, χ_{ph}, χ_{ch} – energetic parameters related to the cohesion energy density of sorbate δ_p and coal substance δ_c, respectively.

Thus, the cohesion energy of arene domains and molecules on its surface is important issue for the sorption modeling in hard coals and further development is necessary.

Conclusion

Development of the new methods of coal structure parameters estimation and sorption system description is in progress. In particular, the issue of more precise cohesion energy evaluation of sorbate for more complicated system like hard coal is under considerations. It is well understood that complex description of the diverse coal structure is almost virtually impossible. Nevertheless, on the basis of identified coal components parameters it is possible to improve the adsorption system analysis.

In particular it was shown that the formulas elaborated in approach aimed at adsorption mechanism identification may be of practical significance when applied to the MSM. On the basis of evaluated adsorbate properties more adequate insight into the modeling of multiple sorption of different sorbates may be obtained. This comes from the equivalent interpretation of the energy profiles, see. Eqs. (2), (3) and (4), in both presented approaches.

Despite less precise treatment of the coal structure diversity in adsorption mechanism identification approach, the discreet representation of the arene domain structure enable to get an insight into the adsorption mechanism. Hence, it may be found as a possible linking of the presented approaches, especially when analyzing the information gained in adsorption mechanism identification approach as an attempt to predict the particle behavior in more complex systems like hard coals.

Acknowledgements

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