Contribution to characterization of microstructure of a carbon molecular sieve based on coal

Z. SPITZER, V. BÍBA, and J. HRNČÍŘ

Fuel Research Institute
CS-250 97 Prague

By comparing the experimental activation energies of diffusion of O_2 and N_2 with the theoretically calculated Lennard—Jones interaction potential, the characteristic dimension of pores of a carbon molecular sieve was calculated. The values of the characteristic dimension of communication micropores thus obtained were tested by the method of small-angle X-ray scattering.

На основании сравнения экспериментально измеренных величин энергий активации диффузии O_2 и N_2 с теоретически рассчитанным интеракционным потенциалом Леннарда—Джонса был вычислен характеристический размер пор углеродного молекулярного сита. Эти величины характеристического размера коммуникационных микропор были проверены методом малоуглового рассеяния рентгеновского излучения.

The increased interest in properties and separating ability of carbon molecular sieves based on coals has recently been evoked by the fact that a new method, the so-called adsorption separation of air, was developed. This method enables us to obtain by means of carbon sorbents air enriched with oxygen up to 55 volume % by the use of a one-stage technology or almost pure oxygen and nitrogen by the use of a multistage technology [1]. At present, four main types of carbon sorbents with molecular sieve properties are known: coal, carbonization products of charcoal or brown coal (chars), cokes from bituminous coal and polymer carbon materials prepared by thermal treatment of polymers.

For the purpose of adsorption separation of O_2 and N_2 from air, a carbon sorbent with molecular sieve properties enabling us to obtain air with the content of O_2 increased up to 80 volume % at a pressure of 2—3 MPa [2, 3] was developed in the Fuel Research Institute. We may assume that it will be of good use in technologies employing air oxygen for oxidations, *e. g.* in processing of sewage and waste waters, combustion processes, gasification of coal, medicine, food industry, chemi-

cal industry, *etc.* A field of future use which is not less important is represented by technology of the production of pure hydrogen because the carbon sorbent can under convenient technological conditions enable us to separate undesirable components, such as methane, carbon monoxide, carbon dioxide, and water vapour [4].

The preparation of the sorbent with molecular sieve properties according to our procedure is based on slow pyrolysis of the granulated raw material made of the finely ground high volatile bituminous coal of Kladno and tar at a pressure of 25 MPa. This pyrolysis is to be performed in nitrogen or argon atmosphere, the final temperature of pyrolysis being 650—950 °C. At present, the separating properties of the sorbent with respect to air oxygen at a pressure of 5 MPa are tested on a laboratory scale. In connection with measurements of the separating ability of the developed sorbent in technological conditions, attention is also given to the study of characterization of the developed sorbents from the view-point of their microstructure.

Though considerable progress in the development of the methods of the micropore analysis based on adsorption isotherms of carbon sorbents has recently been achieved [5, 6], these methods do not yet enable us real evaluation of the structure of pores of the size near to the kinetic dimensions of gas molecules. As other methods, such as electron microscopy, small-angle X-ray scattering, and high-pressure mercury porosimetry do not always allow to measure microporous structure unambiguously, we have tried to use a theoretical calculation for this characterization. In this study we started from the fact that the diffusion coefficient D_e obtained by measuring the diffusion of gases on chars from coal exhibited temperature dependence of the Arrhenius type. It results from this fact that the rate-determining step of mass transport is activated diffusion in the system of pores of molecular dimensions [7]. According to *Walker* [7], the activated diffusion on chars takes place provided the distance between the pseudographitic fundamental planes of sorbent is smaller than the sum of the critical diameter of a diffusing gas molecule and the value of 0.16 nm. According to this author, a slight change in the width of a slot (pore) produces a great change in the activation energy of diffusion and in the value of diffusion coefficient which results from the fact that the repulsion potential is inversely proportional to the twelfth power of distance in the sense of the Lennard—Jones potential. Thus we may explain that *e. g.* the diffusion of O_2 with kinetic diameter of 0.28 nm proceeds only if the diameter of pores (slots) is smaller than 0.44 nm.

Roques and *Bastick* ascertained by calculation that the magnitude of radii of communication micropores in a carbon molecular sieve from French high volatile bituminous coal was 0.26—0.28 nm [8].

Theoretical

In connection with our preceding works [9, 10], we have compared in this study the experimental activation energies of O_2 and N_2 measured on the carbon sorbent of the Fuel Research Institute with the theoretically calculated potential of forces (Φ) operating between diffusing gas molecules and the solid phase. The calculation was based on the idea that the value of q (i. e. the size of the communication pores to be found) may be determined from the function $\Phi = (q)$ provided the values of the coefficients f_A, f_B, C_A, and N (characterizing the adsorbent—adsorptive system) are known and the values of the activation energy of diffusion E and the potential Φ are assigned to each other. The knowledge of the values f_A and f_B involves assumption concerning the shape of pores and expression of the potential of adsorption forces. The values of C_A and N are based on the assumption of the sorbent structure.

The resulting values of the parameter of microstructure of the carbon molecular sieve were compared with independent data obtained from small-angle X-ray scattering.

According to *Barrer* and *Stuart* [11], the value of the potential consists of four terms

$$\Phi = \Phi_D + \Phi_R + \Phi_P + \Phi_Q \qquad (1)$$

where the individual symbols stand for dispersion, repulsion, polarization, and quadrupole interactions. Provided the diffusing molecules have no quadrupole moment, the term Φ_Q for these interactions can be omitted. Similarly, if the polarization interactions are small in comparison with dispersion interactions, the term Φ_P can also be omitted. The potential interaction energy is usually expressed in the form of the (6—12) Lennard—Jones potential

$$\eta = -C_A R^{-6} + C_B R^{-12} \qquad (2)$$

where R is the distance of molecules, C_A is the constant in the Kirkwood—Müller equation, and C_B is a constant expressed by the equation

$$C_B = \frac{1}{2} r_0^6 C_A \qquad (3)$$

(r_0 is the equilibrium distance of an adsorbed molecule from the surface of adsorbent) [12, 13].

The dispersive forces are much stronger in micropores than over flat surface. In protruding parts, they are the weakest. According to *de Boer* and *Custers* [14], the maximum increase of the potential is to be expected in long and narrow pores and small spherical cavities. A molecule localized on the top of a projecting part has the lowest value of interaction potential. According to this idea, the adsorption takes place preferably in micropores [15].

As the detailed atomic structure of microporous carbon molecular sieves is not known, a model image of the form of pores should be chosen for the adsorbent. Since the separating ability of carbon molecular sieves is usually attributed to the existence of nonclosed communication pores [12, 16], the types T-a and T-b, *i. e.* short and long bilaterally open cylindrical pores [9, 10], are used as models of these constrictions in this study.

As shown in preceding paper [17], the value of the potential of adsorption forces in the middle of micropores is given for these shapes of pores by the expression

$$\Phi_{AB} = -NC_A\pi(f_A q^{-3} - \tfrac{1}{2} r_0 f_B q^{-9}) \qquad (4)$$

The values of the coefficients f_A and f_B are given for selected shapes of pores in Table 1. The parameter q stands for the radius of the cross section of pores.

Table 1

Values of the coefficients f_A and f_B for the models of pore shape T-a and T-b

Pore shape	f_A	f_B
T-a	0.643	0.169
T-b	0.714	0.171

Besides the values of f_A and f_B, the calculation of the potential Φ_{AB} according to eqn (4) requires the knowledge of the constants N, C_A, and r_0, as well. For carbon materials we use the value $N^{-1/3} = 0.207$ nm [14]. According to *Avgul et al.,* the parameter r_0 is given by the equation [18]

$$r_0 = r^x + \frac{d}{2} \qquad (5)$$

where r^x is the effective van der Waals radius and d is the interplanar distance of the graphite lattice ($d = 0.352$ nm) [19]. The necessary values of r^x and r_0 for O_2 and N_2 are summarized in Table 2.

Table 2

Van der Waals radii r^x and calculated values of r_0

Adsorptive	$\dfrac{r^x}{\text{nm}}$	$\dfrac{r_0}{\text{nm}}$
O_2	0.145	0.321
N_2	0.157	0.333

The values of C_A were determined by means of the Kirkwood—Müller formula [18]

$$C_A = -6 \, m_e c^2 \alpha \alpha_s \cdot 10^{32}/(\alpha \chi_m^{-1} + \alpha_s \chi_m^{-1}) \qquad (6)$$

where m_e — electron mass $(m_e = 9.109534 \times 10^{-28} \text{ g})$ [20];

     c — velocity of light $(c = 299792.5 \times 10^5 \text{ cm s}^{-1})$ [20];

     α — molar polarizability of adsorptive;

     α_s — polarizability of the atoms of adsorbent (carbon);

     χ_m — molar magnetic susceptibility of adsorbent (carbon).

Table 3 contains the calculated values of the constants C_A (kJ nm^6 mol^{-1}) for carbon—adsorptive systems and the corresponding values of polarizabilities and

Table 3

Values of the constants C_A — polarizability and molar magnetic susceptibility

Adsorptive	α	χ_m	C_A
	10^{-25} cm^3	10^{-6} cm^3 mol^{-1}	kJ nm^6 mol^{-1}
O_2	16.0	+3410.0	4.72972×10^{-3}
N_2	17.6	−12.0	2.70648×10^{-3}

Table 4

Adsorption potentials Φ of oxygen and nitrogen for the models of pore shape T-a and T-b

q	Φ_{AB}			
nm	kJ mol^{-1}			
	T-a		T-b	
	O_2	N_2	O_2	N_2
0.215	49.8	52.5	37.5	45.9
0.216	44.9	48.7	32.8	42.1
0.217	40.2	45.0	28.3	38.6
0.218	35.7	41.6	24.0	35.2
0.219	31.5	38.3	19.9	32.0
0.220	27.5	35.2	16.1	29.0
0.221	23.7	32.2	12.5	26.1
0.222	20.1	29.4	9.1	23.4
0.223	16.8	26.8	5.9	20.8
0.224	13.6	24.2	2.9	18.3
0.225	10.5	21.8	0.0	16.0

magnetic susceptibilities of O_2 and N_2. The values of polarizabilities were taken from tables given in [21] and the values of magnetic susceptibilities were taken from tables in [20].

The course of the potential of adsorption forces for O_2 and N_2 in dependence on the pore size of the carbon sieve developed by the Fuel Research Institute was calculated according to eqn (4). The coefficients given in the preceding tables were used. The course of the potential Φ_{AB} for O_2 and N_2 is given as a function of radius of the particular models of pore shape in Table 4.

Experimental

Diffusion of O_2 and N_2

The kinetics of sorption of O_2 and N_2 in the molecular sieve of the Fuel Research Institute was measured with a BET apparatus at 0 and 25 °C. The measurements were carried out by using the so-called volumetric method at a constant gas volume and variable pressure. The initial pressure of O_2 and N_2 was equal to 33.5 kPa. The results of measurements were processed in the sense of the power law of diffusion

$$\frac{Q_t}{Q_d} = f(t^{\frac{1}{2}}) \tag{7}$$

where Q_t is the quantity of gas sorbed at the time t and Q_d is the quantity sorbed after 24 h establishing of equilibrium.

The effective diffusion coefficients $D_e/\text{cm}^2\,\text{s}^{-1}$ were calculated by the Crank method modified by *Kayser* and *Peters* [22]. The reproducibility of the D_e determination was better than $\pm 10\%$. The size of sorbent particles of a narrow sieved ($L = 0.12$ cm) fraction was inserted for the grain radius L. A detailed structural characterization of the molecular sieve used was presented in preceding paper [2]. The values of the effective diffusion coefficients D_e found for certain temperatures (0 and 25 °C) were inserted in the Arrhenius equation and plotted as log D_e against reciprocal absolute temperature. The slope of this plot was used for calculating the value of activation energy.

Small-angle X-ray scattering

The radii of characteristic micropores were determined from small-angle X-ray scattering (SAXS) by using the procedures and methods described earlier [23, 24]. The small-angle scattering was used for calculating the mean value of line segments in the pores. This value is equal to the diameter of pore supposing the cylindrical shape of pores. These measurements were carried out by *J. Baldrian* in the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences.

Results and discussion

The values of the effective diffusion coefficients of O_2 and N_2 measured on the carbon sieve of the Fuel Research Institute at 0 and 25 °C are given in Table 5. The

Table 5

Effective diffusion coefficients of O_2 and N_2 for the carbon sieve of the Fuel Research Institute

Adsorptive	T	$D_e \cdot 10^7$
	K	cm^2 s^{-1}
O_2	273	20.1
	298	37.5
N_2	273	1.8
	298	5.2

values of activation energy resulting from these data for the investigated specimen of carbon sieve and O_2 or N_2 are $E_{O_2} = 16.8$ kJ mol^{-1} and $E_{N_2} = 28.9$ kJ mol^{-1}.

A comparison of these activation energies with the course of the adsorption potential Φ_{AB} shows that the values of Φ_{AB} found for the radius of pores of 0.22 nm for both investigated shapes of pores correspond to the experimental values of E. The values of Φ and E found for the radius of 0.22 nm are shown in Table 6.

For comparison, we present the values of activation energies found by *Jüntgen et al.* [16] for the diffusion of O_2 and N_2 in a specimen of a molecular sieve on coke from bituminous coal. These values are $E_{O_2} = 19.7$ kJ mol^{-1} and $E_{N_2} = 28.5$ kJ mol^{-1}.

It results from a comparison with the data in Table 4 that this molecular sieve, too, has the characteristic radius of micropores of 0.22 nm for both shapes of pores.

Table 6

Comparison of the theoretical values of adsorption potential Φ with the experimental values of activation energy E for pore shapes T-a and T-b

	q	O_2		N_2		E_{N_2}/E_{O_2}	Φ_{N_2}/Φ_{O_2}
		E_{O_2}	Φ_{O_2}	E_{N_2}	Φ_{N_2}		
	nm	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}		
T-a	0.223	16.8	16.8	28.9	26.8	1.72	1.60
T-b	0.220	16.8	16.1	28.9	29.0	1.72	1.80

This sieve is also applied to separation of O_2 or N_2 from air by the use of the adsorption method.

The sum of the presented findings reveals the fact that a certain value of pore size may be attributed to experimental values of activation energy (as calculated from the temperature dependence of the effective diffusion coefficients). This fact may be regarded as a partial confirmation of the anticipated assumption, *i.e.* attribution of the separating effect of carbon molecular sieves to communication pores of about 0.2 nm radius and existence of repulsion forces in these pores. The data presented in paper [16] also support this idea because one value of the size of communication pore may be assigned in approximation to the values of E_{O_2} and E_{N_2} published in this paper.

As already reported, we tried in this study to verify the results thus obtained by the use of other independent method. For this purpose, we used the results of the small-angle X-ray scattering. The results involving the measurements of the characteristic parameters of the carbon sieve (Fuel Research Institute) by the SAXS method are presented in Table 7.

The characteristic size of micropores obtained by the SAXS method is 0.33 nm while the method involving a comparison of the activation energy of diffusion (E) with the Φ potential gave the value of 0.22 nm. These values are comparable with those (0.27 nm) obtained on an analogous sorbent made from the French high volatile bituminous coal [8]. From this point of view, the sizes of communication micropores found by us are consistent. The difference between the theoretical value 0.22 nm and the value 0.33 nm obtained by SAXS is, besides dissimilarity in determination and method of calculation, likely due to the fact that the first method always includes only open pores (communicating with external surface of sorbent) whereas the SAXS method respects the closed pores, as well.

In this study, the contribution of polarization interaction was omitted in the calculations of interaction energies of individual adsorptives on carbon surface

Table 7

Characteristic parameters of the structure of the sorbent (developed at the Fuel Research Institute) obtained by the SAXS method

Density	Porosity	Superficial density	Pore diameter
g cm^{-3}	volume %	m^2 cm^{-3}	nm
1.931^a	17.1	1029	0.67
1.855^b	17.8	1056	0.67

a) Sample density including ash.
b) Sample density referred to pure carbon.

because the investigated adsorptives did not have any permanent dipole moment. In the first approximation, the contribution of quadrupole interaction was also neglected, which could cause (according to [25]) an error of about 11 % with respect to total potential energy.

We assume that the combination of both presented and used methods should enable us to confront the practical selective properties of individual carbon sorbents with the properties of their microstructure and thus appropriately control the conditions of their technological preparation.

Symbols

C_A	constant in the Kirkwood—Müller equation	[kJ nm^6 mol^{-1}]
C_B	constant in the Lennard—Jones equation	[kJ nm^{12} mol^{-1}]
D_e	effective diffusion coefficient	[cm^2 s^{-1}]
E	activation energy	[kJ mol^{-1}]
L	grain radius	[cm]
N	number of atoms of adsorbent in volume unit	[nm^{-3}]
Q	sorbed quantity	[cm^3 STP]
R	distance of molecules (L.—J. potential)	[nm]
c	velocity of light	[cm s^{-1}]
f	coefficients for individual shapes of pores	
m_e	electron mass	[g]
q	characteristic size of pores	[nm]
r_0	equilibrium distance between an adsorbed molecule and the surface of adsorbent	[nm]
r^x	van der Waals radii of molecules	[nm]
t	time	[s]
Φ	interaction potential	[kJ mol^{-1}]
η	potential interaction energy	[kJ mol^{-1}]
α	molar polarizability of atoms or molecules	[cm^3]
χ_m	molar magnetic susceptibility	[cm^3 mol^{-1}]

Indices

D	dispersion
R	repulsion
P	polarization
Q	quadrupole
A, B	adsorbent—adsorptive interaction
s	adsorbent (Kirkwood—Müller formula)

References

1. Knoblauch, K., Jüntgen, H., and Peters, W., *Erdöl und Kohle-Erdgas-Petrochemie 32,* 551 (1979).
2. Hrnčíř, J., Spitzer, Z., and Lisý, J., *Chem. Prům. 30,* 173 (1980).
3. Spitzer, Z., Hrnčíř, J., and Lisý, J., *Chem. Prům. 31,* 342 (1981).
4. Knoblauch, K., Reichenberger, J., and Schröter, H.-J., *Chem.-Ing.-Tech. 50,* 212 (1978).
5. Mikhail, R. Sh., Brunauer, S., and Bodor, E. E., *J. Colloid Interface Sci. 26,* 45 (1968).
6. Spitzer, Z., Bíba, V., and Kadlec, O., *Carbon* (Oxford) 14, 151 (1976).
7. Walker, P. L., *Fuel 59,* 809 (1980).
8. Roques, M. and Bastick, M., *Fuel 58,* 561 (1979).
9. Bíba, V. and Spitzer, Z., *Chem. Zvesti 34,* 29 (1980).
10. Bíba, V. and Spitzer, Z., *Proceedings of the 5th Conference Porosimetry and its Application.* House of Technology, Prague, 1979.
11. Barrer, R. M. and Stuart, W. I., *Proc. Roy. Soc.* (London) *A249,* 464 (1959).
12. Walker, P. L., Austin, L. G., and Nandi, S. P., in *Chemistry and Physics of Carbon,* Vol. 2. (Walker, P. L., Jr., Editor.) P. 257. M. Dekker, New York, 1966.
13. Bezus, A. G., Kislev, A. V., and Lopatkin, A. A., *J. Chem. Soc., Faraday Trans. II, 74,* 367 (1978).
14. De Boer, J. H. and Custers, J. F. H., *Z. Phys. Chem. 25B,* 225 (1934).
15. Gregg, S. J. and Sing, K. S. W., *Adsorption, Surface Area and Porosity.* Academic Press, London, 1967.
16. Jüntgen, H., Knoblauch, K., Münzer, H., and Peters, W., *Chem.-Ing.-Tech. 45,* 533 (1973).
17. Bíba, V., Spitzer, Z., and Kadlec, O., *J. Colloid Interface Sci. 69,* 9 (1979).
18. Avgul, N. N., Kiselev, A. V., and Poshkus, D. P., *Adsorptsiya gazov i parov na odnorodnykh poverkhnostyakh.* Khimiya, Moscow, 1975.
19. Kiselev, A. V. and Poshkus, D. P., *Trans. Faraday Soc. 59,* 428 (1963).
20. *Handbook of Chemistry and Physics.* CRC Press, Cleveland, 1975.
21. D'Ans-Lax, *Taschenbuch für Chemiker und Physiker.* Springer Verlag, Berlin, 1970.
22. Kayser, H. G. and Peters, W., *Proceedings of the 7th International Conference on Coal Science,* p. 1 62 1, Prague, 1968.
23. Baldrian, J., Pleštil, J., and Štamberg, J., *Collect. Czech. Chem. Commun. 41,* 3555 (1976).
24. Pelzbauer, Z., Baldrian, J., Jansta, J., and Dousek, F. P., *Carbon* (Oxford) 17, 317 (1979).
25. Ponec, V., Knor, Z., and Černý, S., *Adsorpce na tuhých látkách.* (Adsorption on Solids.) Státní nakladatelství technické literatury (State Publishing House of Technical Literature), Prague, 1968.

Translated by R. Domanský