

Adsorption of carbon dioxide on microporous carbon adsorbents

S. V. Potapov,* A. A. Fomkin, and V. A. Sinitsyn

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.

Fax: +7 (495) 952 5681. E-mail: s_potapov@list.ru

Adsorption isotherms of carbon dioxide on microporous carbon adsorbents prepared by activation with potassium sulfide in water vapor were measured. The measurements were carried out in the pressure interval from 1 Pa to 0.1 MPa at temperatures from 216.2 to 293.15 K. Based on the theory of volumetric filling of micropores, the main structural and energetic parameters of the microporous carbon adsorbents were calculated. The adsorption isosters of carbon dioxide were calculated from the adsorption isotherms in the same pressure and temperature ranges and approximated by linear dependences. The plots of the differential mole isosteric heats of adsorption vs amount adsorbed were constructed by using the adsorption isosters.

Key words: adsorption, microporous carbon adsorbent, adsorption isotherms, adsorption isosters, carbon dioxide, theory of volumetric filling of micropores.

Industrial production, increasing the amount of automobile transport, and, as a consequence, the increase in the fuel consumption result in the continuous increase in the content of the atmospheric CO₂.^{1,2} Carbon dioxide, being a greenhouse gas, is considered to favor the constant increase in the average temperature on the Earth.³ The problem of sequestration and storage of CO₂ is important for the development of new systems for life sustenance and purification of industrial exhaust gases.^{4,5}

Therefore, it seems of interest to study adsorption of carbon dioxide on microporous carbon adsorbents. Their hydrophobicity makes it possible to selectively solve the problem of adsorption of carbon dioxide from the gas flow that usually contains the water vapor. In addition, it is important to take into account that the recovering temperatures of the carbon adsorbents are low,⁶ as a rule, which decreases energy expenses.

Dubinin's theory of volumetric filling of micropores (TVFM) is often used for the description of equilibrium adsorption over wide temperature and pressure ranges.⁷ The Dubinin–Radushkevich thermal equation of adsorption takes the form

$$a = a_0 \exp[-(A/E)^2], \quad (1)$$

where $a_0(T) = W_0 \rho_0$ is the limiting amount adsorbed of vapor under the pressure $p = p_s$, W_0 is the specific micropore volume of the adsorbent, ρ_0 is the density of the adsorbate under the pressure equal to the saturation vapor pressure ($p = p_s$), E is the characteristic energy of adsorption, $A = RT \ln(f_s/f)$ is the differential mole work of adsorption, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, T is temperature, and f and f_s are the volatility of the vapor and saturation vapor, respectively.

In Eq. (1) adsorption is defined as the total content of the substance in micropores. It is accepted in calculations that $E = \beta E_0$, and E_0 is the characteristic energy of adsorption of the standard benzene vapor, and β is the similarity constant.

It is seen from Eq. (1) that the amount adsorbed increases with an increase in W_0 and E under other equivalent conditions. However, the increase in the micropore volume during synthesis of active carbons increases the diameters or half-width of the adsorbent pores.⁸ It follows from the X-ray data^{9,10} that the effective half-width of pores of the adsorbents x_0 is related to the characteristic energy of adsorption of the standard benzene vapor E_0 through the equation $x_0 = 12/E_0$. Therefore, E_0 usually decreases with an increase in W_0 . According to Eq. (1), the amount adsorbed depends linearly on the micropore volume, and its dependence on the characteristic energy of adsorption is exponential. For the analysis of the dependence of the amount adsorbed on W_0 and E_0 , it is necessary, in the general case, to study these regularities for the adsorbents differed in the characteristic energy and volume. The analysis of literature data showed that active carbons of the SKT type with the highest W_0 and E_0 values are of greatest interest among industrial adsorbents. In this work, we present the results of studies of CO₂ adsorption on these carbon adsorbents.

Experimental

Laboratory samples of the granulated microporous carbon adsorbents SKT-4B and SKT-6A, obtained by chemical activation with potassium sulfide in water vapor at 1123 K, were used.¹¹

The structural and energetic characteristics of the microporous carbon adsorbents SKT-4B and SKT-6A were determined on the basis of the TVFM by the adsorption isotherm of the standard benzene vapor at the experimental temperature 293 K. For this purpose, the experimental adsorption isotherms were constructed in the coordinates $\ln a = f(A^2)$. The adsorption isotherms on the carbon adsorbents SKT-4B and SKT-6A in the coordinates $a-f(p)$ are reversible and display a pronounced saturation region at the benzene vapor pressure close to the pressure of its vapor at saturation. The desorption branch of the isotherms coincides with the adsorption branch and the absence of an upward turn at high relative pressures associated with capillary condensation indicates that the porous adsorbent structures contain no noticeable volume of mesopores. The structural and energetic characteristics of the adsorbents are given in Table 1.

Carbon dioxide (special purity grade) was used as an adsorptive. According to the certificate, the gas contained 99.995% CO₂. The thermodynamic properties were determined from the reference data.¹²

The adsorption isotherms of carbon dioxide on SKT-4B and SKT-6A were measured on a vacuum gravimetric setup in the pressure range from 1 Pa to 0.1 MPa. Samples of the studied adsorbents (0.2–0.4 g) were placed on one scale arm of a tute balance. Another arm of the balance includes a counterbalance in which two cores of the magnetic coils perform mutually related functions. The monitoring system consisting of the magnetic coil and one of the cores from the counterbalance provides the generation of magnetic compensation for the compensating electromagnetic system, which consists of the second coil and second core. The electronic system brings the volumetric system to the zero initial state. This regime provides the lowest errors for the measurement of the adsorbent weight during adsorption.

The whole volumetric system was precalibrated using weights for an analytical balance.¹³

The absolute value of the amount adsorbed was determined by a change in the sample weight and the moment when the kinetic curve of the self-recorder, which is the detector, reached a plateau. Changes in the adsorbent weight during adsorption were recorded by measurements in three ranges (100, 10, and 1 mg) with a measurement error of $\pm 1\%$.

The pressures of the studied gases and vapors were measured with M10 and M1000 absolute-pressure manometers. The M10 manometer used for pressure determination in the range 0.13–1330 Pa had a measurement error of ± 0.066 Pa, whereas the M1000 manometer for the determination of pressures in the interval from 13 Pa to 130 kPa had an error of ± 4.0 Pa.

The temperature of the adsorbent samples was maintained constant as follows: the temperatures of the triple points of water, *n*-octane, and *n*-decane equal to 273.15, 243.3, and 216.2 K were used to obtain temperatures of 273.15 K and lower. Biphasic

Table 1. Structural and energetic characteristics of the adsorbents*

Adsorbent	$W_0/\text{cm}^3 \text{g}^{-1}$	$E_0/\text{kJ mol}^{-1}$	x_0/nm
SKT-4B	0.42	22.3	0.54
SKT-6A	0.60	17.8	0.67

* The specific micropore volume (W_0), characteristic energy of adsorption (E_0), and effective micropore half-width (x_0) are given.

systems liquid–solid of given pure substances were formed in a temperature-controlled vessel.

A liquid thermostat with an error of ± 0.05 K was used to maintain the temperature at a level of 293 K.

The adsorbent was regenerated for 3 h (to a constant weight) *in vacuo* under a pressure of 5 Pa and at 400 °C. The time of adsorption equilibration during CO₂ adsorption was ~ 1 h.

Results and Discussion

Adsorption isotherms. The amounts of carbon dioxide adsorbed on the carbon adsorbents SKT-4B and SKT-6A were measured in the pressure range from 1 Pa to 0.1 MPa at the temperatures 216.2, 243.2, 273.15, and 293.1 K (Fig. 1).

Figure 1 shows that the amount of CO₂ adsorbed increases smoothly with pressure at all temperatures. Evidently, the transition of the substance from the gaseous to adsorbed state is not due to the phase transition of the condensation type. As the temperature increases, the isotherms of CO₂ adsorption on SKT-4B and SKT-6A exhibit an almost symmetrical shift to higher pressures. The isotherms of CO₂ adsorption retain the shape upon pass-

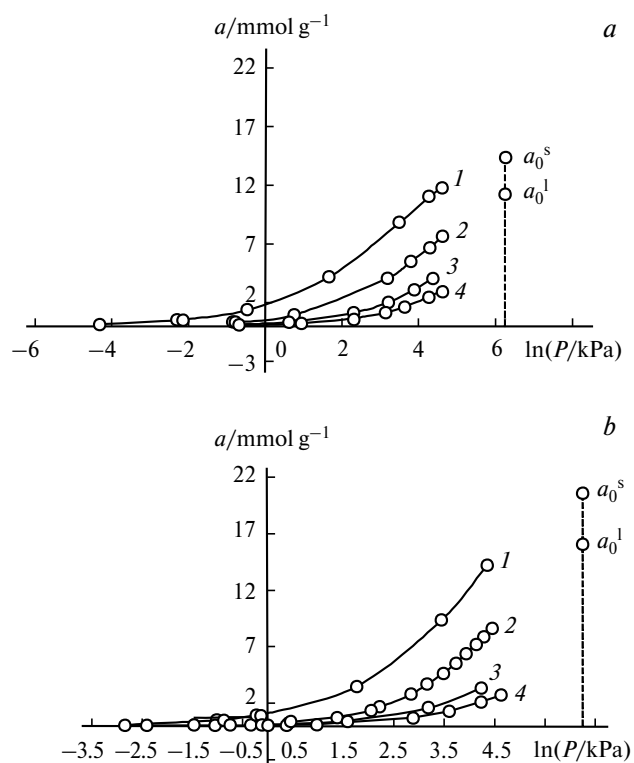


Fig. 1. Dependences of the amount of carbon dioxide adsorbed on the microporous carbon adsorbents SKT-4B (a) and SKT-6A (b) on the logarithm of pressure at 216.2 (1), 243.2 (2), 273.15 (3), and 293.1 K (4). Dashed line is the pressure of saturated CO₂ vapor at the triple point temperature. The amounts adsorbed were calculated assuming that the density of the adsorbate is equal to those of the liquid (a_0^l) and solid phase (a_0^s).

Table 2. Experimental and theoretical values of the amount adsorbed (mmol g^{-1}) for SKT-4B and SKT-6A

Adsorbent	a_{max}	a_0^{l}	a_0^{s}
SKT-4B	11.8	11.2	14.4
SKT-6A	14.3	16.1	20.6

ing through the temperature of the triple point ($T_{\text{tr}} = 216.55 \text{ K}$).

Since the experimental temperature 216.2 K is lower than T_{tr} by only 0.3 K , it seemed interesting to compare the maximum amounts adsorbed with the values calculated in the approximation of equality of the density of the adsorbate to that of liquid or solid CO_2 .

The values of the amounts adsorbed of CO_2 on the studied carbon adsorbent at the saturated vapor pressures of the liquid (a_0^{l}) and solid (a_0^{s}) and the adsorptive under 1.01 kPa (a_{max}) near the triple point are given in Table 2.

As follows from the data in Table 2 and Fig. 1, the maximum amount of CO_2 adsorbed at high coverages for SKT-4B is $a_0^{\text{l}} < a_{\text{max}} < a_0^{\text{s}}$, whereas for SKT-6A $a_{\text{max}} < a_0^{\text{l}} < a_0^{\text{s}}$. According to the TVFM, the adsorbate density in the adsorbent micropores at temperatures in the

interval from the normal boiling point to the triple point temperature is equal to the density of the liquid. For CO_2 adsorption on the carbon adsorbent SKT-6A (see Fig. 2), this condition can be fulfilled at T_{tr} . However, it is not obviously fulfilled for the adsorbent SKT-6A. The maximum amount adsorbed (a_{max}) exceeds a_0^{l} by $\sim 4\%$. This can be due to adsorption in an additional volume of micropores that become accessible due to the adsorption-stimulated expansion of the adsorbent¹⁴ at high coverages.

Another probable reason for the enhancement of the amount adsorbed is adsorption of CO_2 in narrow mesopores, which are likely present in the structure of this adsorbent.¹¹

The amount adsorbed increases fairly smoothly with the pressure increase. This is probably due to an increase in adsorption in narrow mesopores as a consequence of the influence of the curvature of the solid body surface on CO_2 sublimation. The earlier published data¹¹ indicate that the SKT-4B and SKT-6A carbons have almost equal mesopore volumes, whereas the difference in the mesopore volumes is nearly 1.5-fold. Accordingly, the relative contribution of the sublimation effect during adsorption on SKT-4B can be more significant than that in the case of SKT-6A.

Adsorption isosters. The adsorption isotherms of carbon dioxide on the adsorbents SKT-4B and SKT-6A (see Fig. 2, *a* and *b*) were used to plot the adsorption isosters. They indicate that the adsorption isosters of gases and vapors on the microporous adsorbents are well approximated by straight lines, which is a characteristic property of other adsorption systems as well.^{15–17}

Linear approximation of adsorption isosters is practically significant and makes it possible to calculate adsorption isotherms in the region of parameters beyond experimental studies.

Under the conditions of the ideal gas state and inert adsorbent, the differential mole isosteric heat of adsorption was determined from the equation¹⁸

$$q_{\text{st}} = R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_a - \left(\frac{\partial P}{\partial a} \right)_T v_1, \quad (2)$$

where $v_1 = V_1/m_0$ is the specific reduced volume of the adsorbent—adsorbate system, $V_1(a, T)$ is the volume of the adsorbent with micropores, and m_0 is the weight of the regenerated adsorbent.

Using Eq. (2) and the adsorption isosters, we calculated the differential mole isosteric heats of CO_2 adsorption at different amounts adsorbed for the both adsorbents. The results are presented in Fig. 3. In the initial region of the isotherm, the differential mole heats of adsorption increase with an increase in the amount adsorbed from 29 to 25 kJ mol^{-1} for SKT-4B and from 23 to 21 kJ mol^{-1} for SKT-6A. This decrease in the heats of adsorption is a consequence, most likely, of the energy heterogeneity of

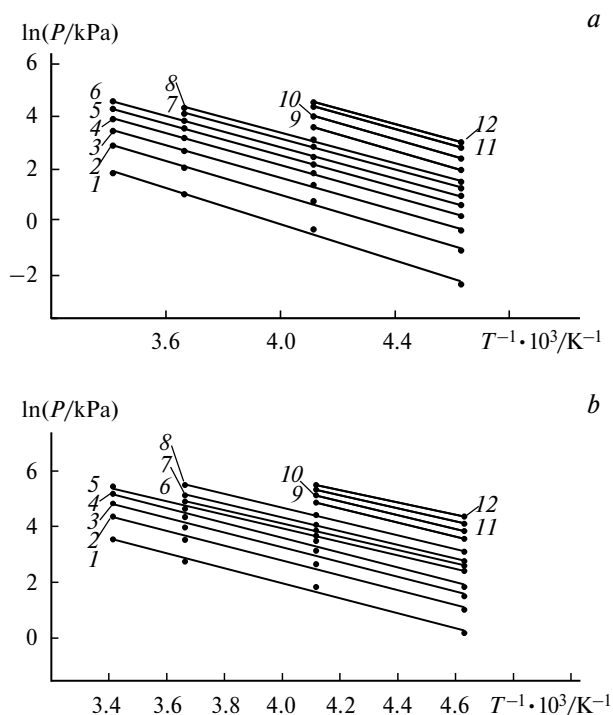


Fig. 2. Isosters of adsorption of carbon dioxide on the microporous carbon adsorbents SKT-4B (*a*) and SKT-6A (*b*) for the amounts adsorbed (mmol g^{-1}): *a*, 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), 3.0 (6), 3.5 (7), 4.0 (8), 5.0 (9), 6.0 (10), 7.0 (11), and 7.5 (12); *b*, 0.5 (1), 1.0 (2), 1.5 (3), 2.0 (4), 2.5 (5), 3.0 (6), 3.5 (7), 4.5 (8), 6.0 (9), 7.0 (10), 8.0 (11), and 9.0 (12). Symbols are the experimental data, and lines are the approximation curves.

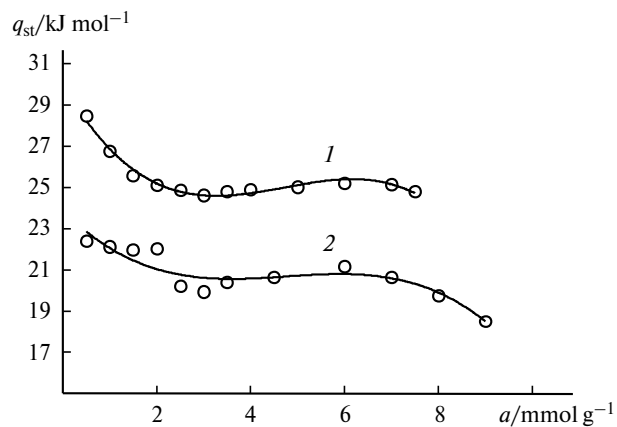


Fig. 3. Dependences of the differential mole heats of carbon dioxide adsorption on the microporous adsorbents SKT-4B (1) and SKT-6A (2) on the amount adsorbed.

the adsorbent surface. This fact also indicates that the surface of the carbons is substantially heterogeneous.

It follows from Fig. 3 that the adsorption field in the micropores becomes fairly uniform after the most active adsorption sites were filled. The energy of the adsorbate—adsorbate interaction increases with an increase in the amount adsorbed, *i.e.*, an increase in the number of molecules in the adsorbent pores.^{19,20} This results in a slight increase in the heat of adsorption. However, further, with an increase in the amount adsorbed, the heat values begin to decrease again, because the average distances between adsorbed molecules decrease and the repulsion forces enhance as pores become filled. As a result, the local maximum is observed in the plots of the differential mole heat of adsorption of the systems studied.

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