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Full Articles

Carbon dioxide adsorption on the microporous ACC carbon adsorbent

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Adsorption isotherms of carbon dioxide on the microporous ACC carbon adsorbent and the adsorption deformation of the adsorbent were measured. The heats of adsorption at temperatures raising from 243 to 393 K and pressures from 1 to $5 \cdot 10^6$ Pa were measured. In the low-temperature region (243 K), an increase in the amount adsorbed is accompanied by adsorbent contraction, and at high micropore fillings ($a > 10$ mmol g^{-1}) the ACC carbon adsorbent expands. At high temperatures, adsorbent expansion is observed in the whole region of micropore filling. At 243 K in the low filling region ($a < 1$ mmol g^{-1}), the heat of adsorption decreases smoothly from 27 to 24 kJ mol^{-1}. The heat of adsorption remains virtually unchanged in the interval 2 mmol g^{-1} $< a <$ 11 mmol g^{-1} and then decreases to 8 kJ mol^{-1} at $a = 12$ mmol g^{-1}. Taking into account the nonideal character of the gas phase and adsorbent deformation the heats of adsorption are strongly temperature-dependent in a region of high pressures.

Key words: adsorption, microporous carbon adsorbent, adsorption deformation, carbon dioxide, high pressures, adsorption isosteres, heats of adsorption.

Fundamental studies of adsorption at high pressures are confined, as a rule, to narrow ranges of pressure and temperature because of experimental difficulties. This impedes the elucidation of general regularities of adsorption and correct description of the thermodynamic properties of adsorption systems. A method for measuring amounts adsorbed is important for analysis of the properties of an adsorption system at high pressures. For adsorbents with a heterogeneous collection of micro-, meso-, and macropores, a method for determination of an amount adsorbed as an excessive value is needed, because the position of an interface between the adsorbed substance and gas phase cannot be determined reliably. Convenient objects for correct determination of the adsorbed phase content are microporous adsorbents, in particular, zeolites and microporous active carbons. For measurements on these materials, the total content of a substance in the adsorption field of a microporous adsorbent is determined. In the

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general case, for adsorption on microporous adsorbents, the volume of the adsorbent with micropores can be determined by helium-liquid picnometry,[1] whereas for zeolites it can be found from X-ray diffraction data. These approaches were used in studies of gas adsorption in wide temperature and pressure intervals on the completely microporous adsorbent PAC-10 obtained from poly(vinylidene chloride).[2—4] Carbon dioxide, methane, and xenone served as adsorbates. Studies in a high-pressure region show that deformation effects of the adsorbent itself should be taken into account for a correct calculation of the thermodynamic characteristics of an adsorption system.[4,5] Non-inert behavior of microporous adsorbents, whose almost all atoms are involved in the adsorption interaction, is of special significance.[6] The adsorption deformation of active carbons induced by adsorption of methanol, carbon dioxide, oxygen, ammonia, sulfur dioxide, and water has previously[7—11] been studied. In the most cases, contraction of a carbon adsorbent at low fillings gives place to expansion in a region of high fillings. The maximum contraction values for water and methanol adsorption approach 0.1%. At high fillings, expansion effects reach several tenths percentage of the initial value, while contraction effects are by an order of magnitude lower. All deformation curves are reversible. In some cases the initial contraction is absent, for instance, for CO_2 adsorption at temperatures higher than ~310 K.[11] Several researchers explain adsorbent contraction by the dissolution of an adsorbate in an adsorbent.[7—9]

An important role of adsorption deformation has been shown[4,5] for the first time for zeolites NaX—Xe and NaX—CO_2.

It is of interest to reveal whether deformation effects appear in other microporous materials. In this work, we studied a carbon microporous adsorbent ACC—CO_2 system. The ACC adsorbent is worth of special attention, because it contains no mesopores and the macropore surface is low, which makes it possible to measure the amount adsorbed as the total content of a substance in micropores.

Experimental

A cylindrical sample (length 54.1 mm and diameter 11.4 mm) was used in experiments. Prior to measurements, the adsorbent was regenerated *in vacuo* for 6 h at 620 K to a residual pressure of 0.8 Pa.

The processing of the benzene adsorption isotherm at 293 K by the Dubinin—Radushkevich equation[12] gave the following parameters of the porous structure: the total volume of adsorption system $W_0 = 0.47$ cm^3 g^{-1}, a characteristic adsorption energy $E_0 = 30$ kJ mol^{-1}, and a characteristic micropore half-width $x_0 = 0.4$ nm. An inductive-type dilatometer designed for measuring low deformations of solids during adsorption was used in pressure and temperature intervals of 1 Pa—5 MPa and 243—393 K, respectively.[13,14] The dilatometer was connected to a high-pressure adsorption setup, which has been described in detail previously.[14]

The temperature in the dilatometer compartment with a sample was maintained constant with an accuracy of 0.2 K. The temperature of the remaining volume of the dilatometer with an inductive transducer and the high-pressure setup was also maintained at 303 K using an air thermostat.

Adsorption of CO_2 was studied on a gravimetric-type vacuum adsorption setup with electron compensation of the weight in three ranges with limits of 1, 10, and 100 mg. The measurement error did not exceed 1%. The gas pressure was determined with two (M10 and M1000) bellows pressure gauges with measurement intervals of $1—1 \cdot 10^3$ and $10—1.5 \cdot 10^5$ Pa and errors of ±0.1 and ±1 Pa, respectively.

Gaseous CO_2 with the admixture content ≤0.05% was used in experiments.

Results and Discussion

The isotherms of CO_2 adsorption on the ACC microporous carbon adsorbent in a pressure range of $1—5 \cdot 10^6$ Pa and at 178—423 K are presented in Fig. 1.

The points in the adsorption isotherms were obtained by direct experimental measurements at 101 kPa ($\ln p = 11.52$). The adsorption isotherms at higher pressures were calculated, using the linear character of the adsorption isosteres. Linearity of the adsorption isosteres was experimentally found[15—18] to fulfill over wide temperature and pressure ranges in the sub- and supercritical regions of the gas phase states. In particular, for the adsorption of carbon dioxide, methane, and xenon[2—4] on the PAC-10 microporous carbon adsorbent, the adsorption isosteres are linear at 120—600 K and in a pressure range of $0.1—20 \cdot 10^6$ Pa. Linearity of the isosteres is re-

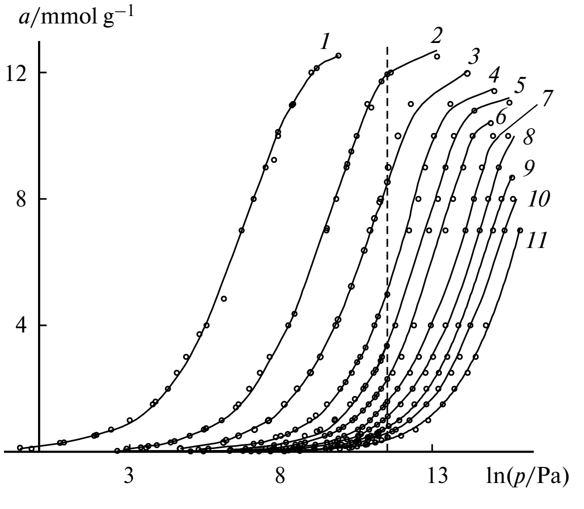

Fig. 1. Adsorption isotherms of CO_2 on the microporous carbon adsorbent ACC at 178 (*1*), 216 (*2*), 243 (*3*), 273 (*4*), 293 (*5*), 313 (*6*), 333 (*7*), 353 (*8*), 373 (*9*), 393 (*10*), and 423 K (*11*) (*a* is the amount adsorbed; points are experiment, lines are calculation; dotted line corresponds to a pressure of 101 kPa).

tained to 150 MPa for the SF_6—microporous carbon adsorbent AC71 system.[18]

The Dubinin—Nikolaev method[12] was used to calculate the limiting amount adsorbed (a_0) along the line of saturated vapor pressure.

The results of calculation of the CO_2 amount adsorbed along the saturation line are presented below. These data were used for the calculation of adsorption isotherms in an interval of 243—313 K.

T/K	216.55*	243	273	293	304.19**
a_0/mmol g^{-1}	12.59	11.975	11.414	11.054	10.98

* Temperature of the triple point. ** Critical temperature.

The adsorption isotherms (see Fig. 1) are reversible and have an inflection point in the region of moderate fillings. The adsorption isotherms in the a—p coordinates have no inflection point, and they are convex towards the pressure axis. The time of adsorption equilibration at low pressures (<100 kPa) is temperature-dependent, for instance, at 178 K it is ~5 h. The adsorption isosteres presented in Fig. 2 were plotted using the adsorption isotherms.

In the whole region of measured pressures and temperatures, the adsorption isosteres are well approximated by linear plots (see Fig. 2). Linearity of the isosteres is retained on going over the critical temperature of CO_2 (T_{cr} = 304.19 K) and triple point temperature ($T_{tr.p}$). The isostere slope ratios depend on the degree of filling of the volume of the ACC adsorbent micropores.

The adsorption deformation of the ACC active carbon for CO_2 adsorption at 243—393 K and pressures 1—5 • 10^6 Pa was measured in parallel with the amount adsorbed. The plots of the relative linear deformation of the ACC microporous carbon adsorbent $vs.$ CO_2 amount adsorbed at different temperatures are presented in Fig. 3.

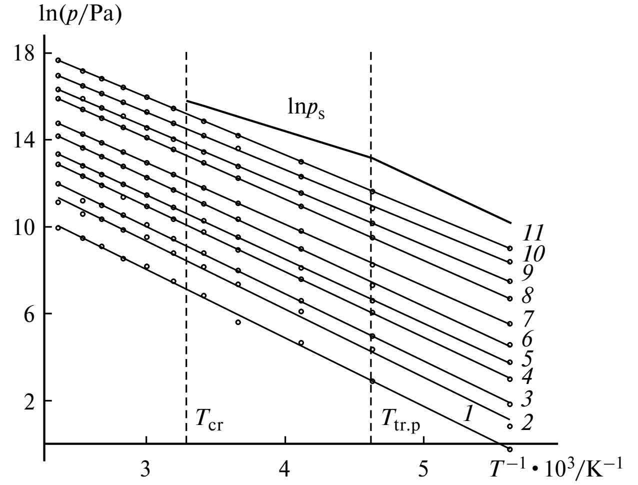

Fig. 2. Adsorption isosteres of CO_2 on the microporous carbon adsorbent ACC at different amounts adsorbed: 0.1 (*1*), 0.3 (*2*), 0.5 (*3*), 1 (*4*), 1.5 (*5*), 2.5 (*6*), 4 (*7*), 7 (*8*), 9 (*9*), 11 (*10*), and 12 mmol g^{-1} (*11*); T_{cr} and $T_{tr.p}$ are the temperatures of the critical and triple points, respectively; lnp_s is the line of saturated CO_2 vapor pressure.

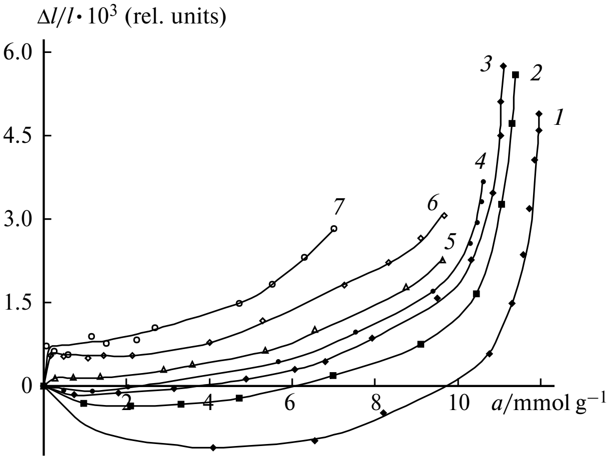

Fig. 3. Relative linear deformation of the microporous carbon adsorbent ACC (Δl/l) $vs.$ CO_2 amount adsorbed (a) at 243 (*1*), 273 (*2*), 293 (*3*), 313 (*4*), 333 (*5*), 353 (*6*), and 393 K (*7*).

The contraction and expansion regions are observed in the low-temperature range (243—313 K). The maximum contraction (0.117%) is achieved at 243 K;[14] with the temperature increase the region of contraction shifts toward lower fillings. The sample expands sharply at the highest degrees of filling of the micropores. No contraction region is observed at temperatures from 333 to 393 K.

In the initial region of micropore fillings, attractive forces brought about by interaction of adsorbed molecules with opposite micropore walls predominate at low temperatures.[19] It is known[20] that the maximum forces of interaction between adsorbed molecules are developed when the micropore width exceeds the diameter of molecules ~1.5-fold. Knowing that x_0 = 0.4 nm and the CO_2 molecule size is 0.51×0.37 nm according to Pauling,[21] we can assume that adsorbent contraction is a consequence of dispersion forces that arise from the interaction between adsorbed molecules and opposite micropore walls. The further sharp expansion of the ACC adsorbent at a > 8 mmol g^{-1} is caused by a decrease in the average distance between the adsorbed molecules and the related sharp increase in the internal adsorbent pressure in micropores.

No region of negative deformations is observed at relatively high temperatures due, most likely, to a change in the adsorption mechanism. It appears that at T = 243—313 K the adsorption is predominantly localized, whereas at T = 333—393 K it becomes delocalized due to an increase in the kinetic energy of adsorbed molecules.

The resulting data enable us to calculate the differential molar isosteric heat of adsorption (q_{st}), which is determined as a difference between the molar enthalpy of the equilibrium gas phase h_g and differential molar enthalpy of the adsorbent—adsorbate system $(\partial H/\partial a)_T$.

$$q_{st} = h_g - (\partial H/\partial a)_T \qquad (1)$$

With allowance for the nonideal behavior of the gas phase and taking into account non-inertness of the adsorbent toward adsorption and temperature, we can write the equation for calculation of q_{st} in the following form[22]:

$$q_{st} = -zR[\partial(\ln p)/\partial T^{-1}]_a[1 - (\partial v/\partial a)_T/v_g] - \\ - (\partial p/\partial a)_T[v - T(\partial v/\partial T)_a], \qquad (2)$$

where $z = pv_g/(RT)$ is the compressibility coefficient of the gas phase at the pressure p, specific volume v_g, and temperature T; R is the universal gas constant; $v(a) = V/m_0$ is the specific volume of the adsorbent—adsorbate system (V is the volume of a microporous solid including micropores that is a function of the adsorption equilibrium parameters (a, p, T); m_0 is the weight of the degassed adsorbent); and a is the amount adsorbed defined as the total content.

It follows from Eq. (2) that the heat of adsorption depends on both the parameters of the adsorption system (a, p, T) and its deformation induced by adsorption ($(\partial v/\partial a)_T$) and thermal motion ($(\partial v/\partial T)_a$). The estimation of the maximum value of $(\partial v/\partial T)_a$ derivative showed that $T(\partial v/\partial T)_a(\partial p/\partial a)_T \ll v(\partial p/\partial a)_T$ in the studied pressure and temperature interval. Therefore, the calculations were performed using the equation

$$q_{st} = -zR[\partial(\ln p)/\partial T^{-1}]_a[1 - (\partial v/\partial a)_T/v_g] - v(\partial p/\partial a)_T. \quad (3)$$

The plots of the differential molar isosteric heats of CO_2 adsorption on the ACC adsorbent *vs.* amount adsorbed are presented in Fig. 4.

The typical dependence of q_{st} on a can be exemplified by the data obtained at 243 K and at low (to 5%) deviations of the equilibrium phase from ideality. At low pressures and, hence, small fillings of the adsorbent surface, the account for the nonideal character of the gas phase and noninertness of the adsorbent contributes insignificantly to the heat of adsorption (see Fig. 4). At low fillings ($a < 1.0$ mmol g^{-1}), q_{st} decreases smoothly from 27 to 24 kJ mol^{-1}. In an interval of 2.0 mmol g^{-1} $< a <$ $<$ 11.0 mmol g^{-1}, the heat of adsorption decreases weakly, remaining at a level of ~24 kJ mol^{-1}. Nearly constant differential molar isosteric heats of CO_2 adsorption on ACC in the range 2 mmol g^{-1} $< a <$ 11 mmol g^{-1}, *i.e.*, in the region of an ideal gas phase, indicate a high homogeneity of the adsorbent. The further increase in filling results in a sharp shortening of the average distance between the adsorbate molecules and an increase in the repulsive forces associated with interactions between neighboring adsorbate molecules and between adsorbate molecules and micropore walls. In this case, the energy of CO_2 adsorption decreases sharply, the adsorbent expands, and the molar heat of adsorption decreases.

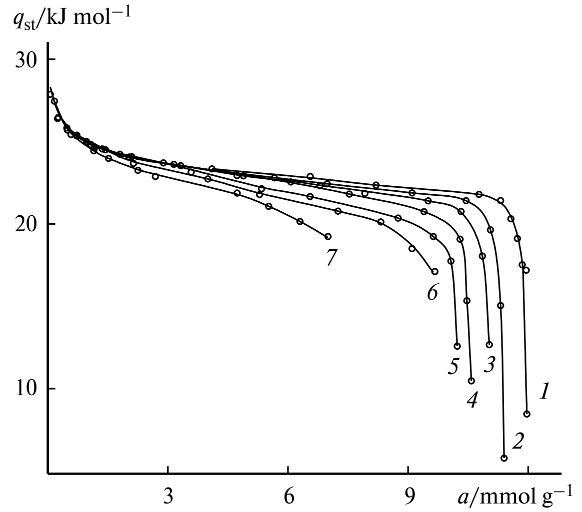

Fig. 4. Differential molar isosteric heat of adsorption of CO_2 (q_{st}) on the microporous carbon adsorbent ACC as a function of the amount adsorbed (a) at 243 (*1*), 273 (*2*), 293 (*3*), 313 (*4*), 333 (*5*), 353 (*6*), and 393 K (*7*).

A temperature dependence of the heat of adsorption begins to manifest itself in a region of high pressures, when the gas phase becomes nonideal and $z \neq 1$. As the temperature increases, corrections needed to allow for the nonideal character of the gas phase and adsorption deformation of the adsorbent, increase. All these factors induce a "fan" of curves describing the dependence of q_{st} on the amount adsorbed. Reasons for decreasing q_{st} in the initial region of micropore filling ($a < 1.0$ mmol g^{-1}) are also clear. In this region, the isosteric heat usually decreases once the sites with the highest adsorption energy are filled.

The present studies showed that the microporous carbon adsorbent undergoes rather complex deformation during adsorption. In addition, the character of adsorption changes with temperature. Linearity of the isosteres is confirmed in the whole temperature and pressure range under study. The estimations demonstrated that a correction to the differential molar isosteric heat of adsorption for the CO_2—carbon adsorbent ACC for noninertness of the adsorbent reaches 10—15%.

References

1. A. A. Fomkin, I. I. Seliverstova, and V. V. Serpinskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 280 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 256 (Engl. Transl.)].
2. A. B. Kharitonov, A. A. Fomkin, A. A. Pribylov, and V. A. Sinitsyn, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 566 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 591].

3. E. V. Chkhaidze, A. A. Fomkin, V. V. Serpinskii, G. V. Tsitsishvili, and M. M. Dubinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 929 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 847 (Engl. Transl.)].
4. V. Gusev and A. Fomkin, *J. Colloid Interface Sci.*, 1994, **162**, 279.
5. A. L. Pulin, Ph. D. (Chem.) Thesis, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, 2003, 154 pp. (in Russian).
6. B. P. Bering, A. L. Maiers, and V. V. Serpinskii, *Dokl. Akad. Nauk SSSR*, 1970, **193**, 119 [*Dokl. Chem.*, 1970 (Engl. Transl.)].
7. J. R. Dacey, G. J. C. Fransdorff, and I. T. Gallangher, *Carbon*, 1964, **2**, 41.
8. J. R. Dacey and M. I. Evans, *Carbon*, 1971, **9**, 579.
9. R. S. Haines and R. McIntoch, *J. Chem. Phys.*, 1947, **15**, 28.
10. A. D. Buckinghem and R. L. Dish, *Proc. R. Soc.*, 1963, **A273**, 275.
11. V. Yu. Yakovlev, A. A. Fomkin, and A. V. Tvardovski, *J. Colloid Interface Sci.*, 2003, **268**, 33.
12. M. M. Dubinin, *Adsorbtsiya i poristost´* [*Adsorption and Porosity*], VAKhZ, Moscow, 1972, 128 pp. (in Russian).
13. A. A. Fomkin and A. L. Pulin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 336 [*Russ. Chem. Bull.*, 1996, **45**, 321 (Engl. Transl.)].
14. V. Yu. Yakovlev, A. A. Fomkin, A. V. Tvardovskii, V. I. Sinitsyn, and A. L. Pulin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 338 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 354].
15. A. A. Fomkin, V. A. Avramenko, I. I. Seliverstova, and V. V. Serpinskii, *Dokl. Akad. Nauk SSSR*, 1986, **288**, 678 [*Dokl. Chem.*, 1986 (Engl. Transl.)].
16. N. N. Avgul´, A. V. Kiselev, and D. P. Poshkus, *Adsorbtsiya gazov i parov na odnorodnykh poverkhnostyakh* [*Adsorption of Gases and Vapors on Homogeneous Surfaces*], Khimiya, Moscow, 1975, 384 pp. (in Russian).
17. R. M. Barrer and R. Pahadopoulos, *Proc. R. Soc. London*, 1972, **A326**, 315; 1566.
18. A. A. Pribylov, I. A. Kalinnikova, and N. I. Regent, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 839 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 882].
19. A. A. Fomkin and A. L. Pulin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1887 [*Russ. Chem. Bull.*, 1999, **48**, 1864 (Engl. Transl.)].
20. V. B. Fenelonov, *Poristyi uglerod* [*Porous Carbon*], Izd-vo Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 1995, 453 pp. (in Russian).
21. L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, Cornell University Press, Ithaca, New York, 1939, 429 pp.
22. V. A. Bakaev, Doct. Sci. (Phys.-Math.) Thesis, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1989, 348 pp. (in Russian).

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