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PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

Temperature Dependence of Adsorption on Microporous Adsorbents

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Abstract—Different ways to theoretically calculate the temperature dependence of the adsorption isotherms of individual substances on activated charcoals in a wide range of temperatures below and above critical temperatures are examined.

Keywords: adsorption, microporous charcoals, adsorption isotherms, molecular dynamics, standard states

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INTRODUCTION

To solve many problems of adsorption technologies, the adsorption isotherms of gases or vapors of individual substances and their mixtures in a wide range of temperatures below and above the critical temperatures for the corresponding adsorbates are required. The available experimental data have been collected in an adsorption computer databank [1], but the practical needs are much wider. In this connection, theoretical calculation of the adsorption-temperature dependence is a critical problem that has been repeatedly discussed in the literature. In this paper, we discuss the most promising, in our opinion, ways to solve this problem.

DESCRIPTION OF ADSORPTION ISOTHERMS AT TEMPERATURES BELOW AND ABOVE CRITICAL TEMPERATURES

Optimization of adsorption technologies is associated with the necessity not only to formally describe the adsorption isotherms, but also to obtain, on the basis of such a description, the characteristics of the corresponding adsorption systems (limiting adsorption, volume of micropores, slit width of slitlike carbon pores, adsorbate–adsorbent interaction energies, adsorption heat, etc.). In addition, it is important that such equations will make it possible to calculate the adsorption isotherms at different temperatures.

As was noted upon the creation of the adsorption computer databank [1], such equations were available, until very recently, only for the description of the adsorption isotherms of vapors (the equations of the theory of volumetric filling of micropores (TVFM) and the lattice model equations). These equations were obtained using the equilibrium-consistent standard states of components in the phases (limiting adsorption and saturated adsorbate vapor pressure equilibrated with it).

Only in recent years was it shown based on molecular dynamics calculations of the adsorption isotherms of methane on PAU-10 activated carbon in a wide temperature range that the same equations can be used to describe adsorption isotherms at temperatures above the critical temperature. At the same time, it was experimentally proved that one should use pressures determined by linear extrapolation of the graph of the saturated vapor pressure logarithm versus inverse temperature to the supercritical temperature range as equilibrium-consistent standard pressures [2–4]. These conclusions were confirmed in [5, 6] using examples of description of adsorption isotherms of different gases on microporous adsorbents.

The modified Dubinin–Radushkevich equation obtained within the theory of volumetric filling of micropores upon the description of adsorption isotherms on activated carbons is presented below [7]:

$$\ln a = \ln a_0 - \left(\frac{RT}{E_0}\right)^2 \ln^2 \frac{P^*(T)}{P}. \tag{1}$$

The corresponding Tolmachev–Aranovich equation set (lattice model) for a two-layer model is of the following form [4]:

$$\ln \frac{X_1(n)[1 - Y_1]}{Y_1[1 - X_1(n)]} + 1.12\frac{\varepsilon_{01}}{kT} - \frac{\varepsilon_{11}}{kT} 9X_1(1) - \frac{\overset{*}{\varepsilon}_{11}}{kT} 12Y_1 = 0, \tag{2}$$

$$a_1 = a_1^0 \sum_n X_1(n), \tag{3}$$

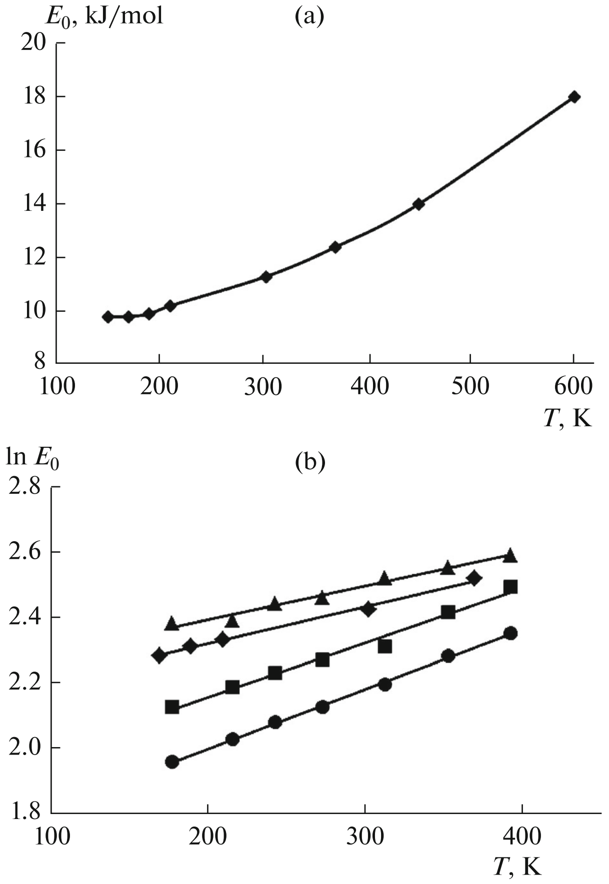

Fig. 1. (a) Temperature dependence of the characteristic adsorption energy of methane on the PAU-10 activated charcoal; (b) temperature dependences of the logarithm of the characteristic adsorption energy of (◆) methane, (■) krypton, (▲) xenon, and (●) oxygen on the AUK activated charcoal.

$$Y_1 = \frac{\rho_{\text{vap}}}{\rho_{\text{liq}}}\frac{P}{P^*}, \tag{4}$$

$$Y_1 = \frac{P}{P^*}. \tag{4a}$$

In Eqs. (1)–(4a) and thereafter, a, a_1, and a_0 are the adsorption values (mol kg^{-1}) equilibrium at the pressure, P, and "limiting" at the standard vapor pressure, $P^* = P_s$, at $T > T_{\text{cr}}$; E_0 (kJ mol^{-1}) is the characteristic adsorption energy; a_1^0 is the monolayer capacity of the first component (mol kg^{-1}); Y_1 and X_1 are the molar fractions of the first component in the equilibrium volumetric (in this particular case, the vacancy solution [8]) and adsorption solutions, and $\varepsilon_{11}, \varepsilon_{11}^*, \varepsilon_{01}$ are the pair-interaction energies in the adsorbate and adsorbed adsorbate and between the adsorbed adsorbate with the adsorbent.

Let us note that Eq. (4), where $\rho_{\text{vap}}, \rho_{\text{liq}}$ are the densities of the adsorbate vapor and liquid adsorbate, determines the molar fraction of the adsorbate in the bulk phase, which is regarded as a binary "liquid" solution of the vacancies and adsorbate [8]. As was shown recently in [9], the constancy of the ε_{11}, ε_{01} parameters of Eq. (2) in a wide range of temperatures below and above the adsorbate critical temperature is obeyed upon the calculation of the molar fraction of the adsorbate in a "vapor" vacancy solution, i.e., according to Eq. (4a).

DESCRIPTION OF THE ADSORPTION-TEMPERATURE DEPENDENCE WITHIN TVFM

To calculate the adsorption-temperature dependence on the basis of one experimental isotherm by Eq. (1), it is necessary to calculate the changes of the P^*, a_0, and E_0 values with temperature. The $P^*(T)$ values are calculated as described above, and the $a_0(T)$ values are determined from the Dubinin–Nikolaev equations [10], as follows:

$$a_0(T) = a_0^0 \exp[-\alpha(T - T_0)], \tag{5}$$

$$\alpha = \frac{\ln(\rho_0/\rho_{\text{cr}})}{(T_{\text{cr}} - T_{\text{boil}})}. \tag{6}$$

In this case, the errors in the calculation of the α value by the empirical formula given in Eq. (6) can give rise, as shown in [11], to errors of about 4–6% in the $a_0(T)$ values.

The $E_0(T)$ dependences in a wide temperature range (below and above the critical temperature) are exponential [12] (see Figs. 1a, 1b) and described by the following equation:

$$E_0(T) = E_0^0 \exp[b(T - T_0)]. \tag{7}$$

The constancy (temperature invariance) of the $E_0(T)$ function in this case is approximately conserved in a range of temperatures below the critical temperature, when the exponent (Fig. 1a) is nearly parallel to the temperature axis.

Changes in the b coefficients for different gases gives rise to errors of about 3–6% in the $E_0(T)$ values upon using an average value of $b = 1.3 \times 10^{-3}$.

Since errors can accumulate or be partially compensated, then the error in the calculation of the $a(T,P)$ values may vary within a range from 2 to 10%.

It is clear that at least two isotherms at significantly different temperatures are necessary to calculate the adsorption-temperature dependence correctly and to find the α and b values corresponding to a particular adsorbate. In this case, it is possible to calculate the adsorption-temperature dependence in a wide range of temperatures with an error that does not exceed the experimental error, as shown by the data given in Table 1.

As is seen from the above data, the relative errors (D^*) in the description of adsorption isotherms calcu-

Table 1. Relative errors in the description of adsorption isotherms of krypton and methane at 216.2 K by the Dubinin–Radushkevich equation using the isotherms at 353 (Kr) and 458 (CH_4) K: calculation 1 corresponds to the experimental isotherms at 216.2 K, calculation 2 to the isotherms calculated using the experimental α and b values, and calculation 3 to the isotherms calculated using the theoretical α and b values

Adsorption isotherm of Kr on ACC activated carbon at 216.2 K				Adsorption isotherm of methane on AUK activated carbon at 216.2 K			
calculation 1		calculation 2	calculation 3	calculation 1		calculation 2	calculation 3
a_{exp}, mol/kg	D, %	D^*, %	D^{**}, %	a_{exp}, mol/kg	D, %	D^*, %	D^{**}, %
1.57	−1.42	−6.4	−10.1	1.00	1.6	4.1	2.6
2.08	−0.73	−2.9	6.2	1.50	−1.7	1.0	2.0
2.74	0.65	−1.1	−1.8	2.00	−2.4	1.1	3.6
3.30	1.67	0.0	0.9	2.50	−1.3	1.2	3.8
3.87	2.20	0.9	2.8	3.00	−1.5	1.5	4.8
4.55	3.03	2.0	5.3	3.50	−0.4	1.7	6.0
5.09	3.54	2.7	6.9	4.00	0.8	2.5	6.8
5.48	4.20	0.5	8.2	4.50	1.6	3.1	7.6
5.89	4.60	3.9	9.2	5.00	2.0	4.0	7.2
6.22	4.58	3.9	9.6	5.50	2.0	2.5	7.5
7.27	−7.41	−7.7	9.0	6.00	1.8	3.0	7.6
8.20	−6.7	−6.7	3.0	6.50	1.7	2.7	7.3
9.00	−6.0	−6.0	4.6	7.00	1.4	1.5	6.6
9.75	−5.9	−5.6	5.3	7.50	0.8	1.5	6.0
10.68	−3.6	−3.3	8.2	8.00	−0.1	−08	4.9
11.10	−2.7	−2.3	9.0	8.50	−1.4	−0.9	4.7
11.44	−1.5	−1.1	9.8	9.00	−1.7	−1.4	5.2
11.65	−0.8	−3.4	9.6	9.50	−1.5	−1.3	5.1
11.83	0.1	−0.4	12.0	10.00	−1.4	0.9	5.8
12.45	0.1	0.3	11.5	10.50	−0.8	0.8	−6.8

lated using the experimental α and b values (determined using two isotherms) practically do not differ from the relative errors (D) in the description of experimental adsorption isotherms, and the corresponding errors in the description of isotherms calculated using Eq. (6) and in the mean value of the b coefficient (D^{**}) increase markedly (2–10%).

CALCULATION OF THE TEMPERATURE DEPENDENCE OF ADSORPTION ISOTHERMS BY THE LATTICE MODEL EQUATIONS

The lattice model equations (Eqs. (2), (3), and (4a)) can be used to calculate the temperature dependence of the adsorption isotherms on microporous

Table 2. Relative errors in the description of the experimental adsorption isotherms of CH_4 and CO_2 on activated charcoal (AC) at 212 and 301 K (D, %) by the lattice model equations and the same isotherms calculated using the adsorption isotherms of CH_4 and CO_2 at 260 K (D*, %)

Adsorption isotherm of CH_4 at 212 and 301 K						Adsorption isotherm of CO_2 at 212 and 301 K					
a_{exp}, 212 mol/kg	*D*, %	*D**, %	a_{exp}, 301 mol/kg	*D*, %	*D**, %	a_{exp}, 212 mol/kg	*D*, %	*D**, %	a_{exp}, 301 mol/kg	*D*, %	*D**, %
1.13	–2.4	1.9	0.47	–1.8	4.0	1.82	0.2	–1.8	1.21	5.0	7.4
1.66	–1.4	–2.7	0.76	–1.7	2.9	2.12	0.2	–1.9	1.89	–1.1	3.0
2.56	1.1	–1.5	0.96	–1.3	2.4	2.75	3.5	–1.5	2.63	–2.9	3.8
2.92	1.2	–1.3	1.29	0.2	3.9	3.00	0.9	–3.8	2.79	–3.2	4.7
3.51	2.2	–3.8	1.64	0.6	2.9	3.26	–1.4	–4.3	3.51	–3.7	3.6
3.73	1.9	–3.8	1.87	0.9	2.8	3.52	–0.4	–3.8	3.73	–3.7	2.4
4.48	1.5	–3.0	2.09	1.1	2.4	4.73	0.5	0.9	4.44	–2.0	3.1
4.63	0.9	–2.1	2.23	1.3	2.5	3.69	–3.5	–9.3	4.52	–3.6	4.6
5.28	0.1	–4.1	2.46	1.3	2.4	4.92	–0.5	0.1	5.05	–2.9	3.3
5.35	–0.1	–3.9	2.56	2.2	3.6	5.22	–1.5	–0.6	5.22	–2.9	2.4
5.7	–0.6	–4.4	2.56	1.2	2.3	5.40	–2.6	–1.8	5.63	–1.8	1.9
5.94	1.3	–1.5	2.74	1.0	2.3	6.26	–0.5	1.9	5.64	–2.1	1.2
6.20	–0.8	–2.2	2.89	1.0	2.4	6.44	–0.2	2.1	5.76	–2.0	0.7
6.22	–1.0	–2.3	3.06	3.0	5.1	6.71	–1.1	0.6	6.05	–0.6	1.3
6.46	–0.9	–1.0	3.06	0.8	2.3	6.92	–1.2	0.3	6.23	–1.1	–0.6
6.49	–1.1	–1.1	3.17	0.7	2.5	7.63	1.2	2.6	6.40	–0.3	–0.4
6.73	0.4	1.3	3.28	0.2	2.0	7.76	1.1	2.3	6.80	1.1	–0.3
6.71	–1.3	–0.2	3.39	0.3	2.4	7.95	0.7	1.2	7.11	1.9	–0.5
7.00	0.3	2.3	3.61	0.7	3.4	9.47	2.0	2.9	7.39	3.2	0.4
7.14	0.2	2.8	3.97	–1.1	2.4	9.57	2.5	3.5	7.64	4.5	1.7
7.25	0.3	3.2	4.04	–3.6	–0.2				7.92	6.4	3.6
7.26	–1.6	1.7	4.19	–3.2	0.7				8.04	6.6	4.0

adsorbents when the $a_0(T)$ values are calculated by Eqs. (5) and (6). However, detailed analysis showed that the ε_{11}^* parameter in the vacancy bulk solution does not retain constant values and the temperature range in which the calculation can be performed with a satisfactory accuracy (3–5%) does not exceed, as a rule, ±100 K from the experimental isotherm, while the intermolecular interaction parameters $(\varepsilon_{11}, \varepsilon_{01})$ in the adsorption solution conserve constant values in a wide range of temperatures (below and above the critical temperature) [14]. This is demonstrated by the data given in Tables 2 and 3 and in Figs. 2 and 3.

In addition, let us note that an increase in the discrepancy between the experimental and calculated initial adsorption values (see Table 3) is connected not with the calculation errors, but with overestimation of the experimental adsorption values due to the presence of small amounts of "active adsorption sites" that are not taken into account in the lattice model equations.

CALCULATION OF ADSORPTION ISOTHERMS IN A WIDE RANGE OF TEMPERATURES BY THE METHOD OF MOLECULAR DYNAMICS

As was shown earlier in our works, the adsorption isotherms of different adsorbates on microporous activated charcoals can be calculated by the method of molecular dynamics in quantitative agreement with the experimental data at temperatures below [15] and above [16] the critical temperatures. Detailed procedures for performing molecular-dynamics simulations in constant-volume cells and cells equipped with barostats by using the Tinker and NAMD software

Table 3. Relative errors in the description of the experimental adsorption isotherms of N_2 on AUK activated carbon at 243 and 353 K, and of Kr at 216.2 K (D, %) by the lattice model equations and the same isotherms calculated using the adsorption isotherms of N_2 and Kr at 273 K (D*, %)

Adsorption isotherm of N_2 at 243 K			Adsorption isotherm of N_2 at 353 K			Adsorption isotherm of Kr at 216 K		
a_{exp}, mol/kg	D, %	D*, %	a_{exp}, mol/kg	D, %	D*, %	a_{exp}, mol/kg	D, %	D*, %
1.140	−4.24	13.69	0.58	6.37	−6.49	2.08	−0.95	−8.55
1.25	−6.49	9.92	0.95	0.71	−6.62	2.74	0.75	−7.21
1.73	2.29	6.17	1.30	2.45	−1.84	3.30	1.98	−2.45
2.67	3.45	3.37	1.65	4.22	1.98	3.87	2.69	−3.59
3.25	6.20	5.61	1.97	4.42	3.45	5.09	4.33	−5.81
3.70	−0.62	5.15	2.26	3.17	2.84	5.89	5.54	−0.37
4.50	−1.90	1.80	2.54	3.43	3.79	6.22	5.58	1.08
5.36	−0.51	2.47	2.77	1.85	2.33	7.27	−5.93	−7.66
5.73	−0.45	1.92	3.01	1.16	1.81	8.20	−5.1	−7.21
6.23	−0.05	1.54	3.24	0.95	1.79	9.00	−4.3	−4.30
6.66	0.01	0.65	3.56	4.36	3.29	9.75	−4.1	−3.07
7.02	−0.35	−0.82	3.86	2.89	4.57	10.68	−1.7	−0.08
7.33	−0.54	−1.99	4.15	2.1	3.62	11.10	−0.8	0.50
7.62	−0.3	−2.38	4.41	2.1	3.43	11.44	0.4	1.28
7.85	−0.3	−3.01				11.83	1.9	2.13
8.06	0.0	−3.21				12.18	4.0	3.71
8.13	0.1	−3.29				12.57	6.2	4.79

packages and the OPLS-AA universal force field are given in [2, 15, 16].

The use of an adsorption phase of limited sizes (in the case of microporous activated charcoals, a model slit formed by two carbon surfaces with limited sizes (5 × 5 nm in our calculations)) is an important characteristic feature of the numerical experimental procedures developed in [14, 15], as well as the calculation of the slit width characterizing the adsorption energy by the following equation obtained within the theory of volume filling of micropores, which has been developed by M.M. Dubinin [7]:

$$l = \frac{A}{E_{0,\,\text{benz}}}, \tag{8}$$

where l is the slit width in nanometers, A is the standard energy of 24 kJ, and $E_{0,\text{benz}}$ is the characteristic energy of benzene adsorption (a parameter of Eq. (1)). If the adsorption isotherm of some other adsorbate is available, then the corresponding characteristic energy is normalized to the $E_{0,\text{benz}}$ value by using the parachors of substances [7].

The use of an adsorption phase of limited sizes made it possible to calculate the "limiting" adsorption values, m_s, corresponding to the equilibrium pressure (P_s at $T < T_{\text{cr}}$ and P^* at $T > T_{\text{cr}}$) for each adsorbate in the model pore and to represent the adsorption isotherm in relative coordinates, which eliminated the problem of determining the number of model micropores in 1 kg of the adsorbent, as follows: $m/m_s = a/a_0 - P/P_s(P^*)$.

The use of the slit width calculated by Eq. (8) made it possible to reliably characterize each adsorbent and gave rise to a quantitative match between the calculated and experimental isotherms, which further confirms the experimentally found dependence given by Eq. (8). For example, calculations on the adsorption of ethanol on the AU-1 microporous carbon adsorbent were performed for the pores with widths of 1.6 and 1.0 nm and for a width of 0.8 nm calculated by Eq. (8) (see Fig. 4). As one could expect, the first two adsorption isotherms go below the experimental curve and the calculated and experimental isotherms for the model pore with a width of 0.8 nm are consistent with each other.

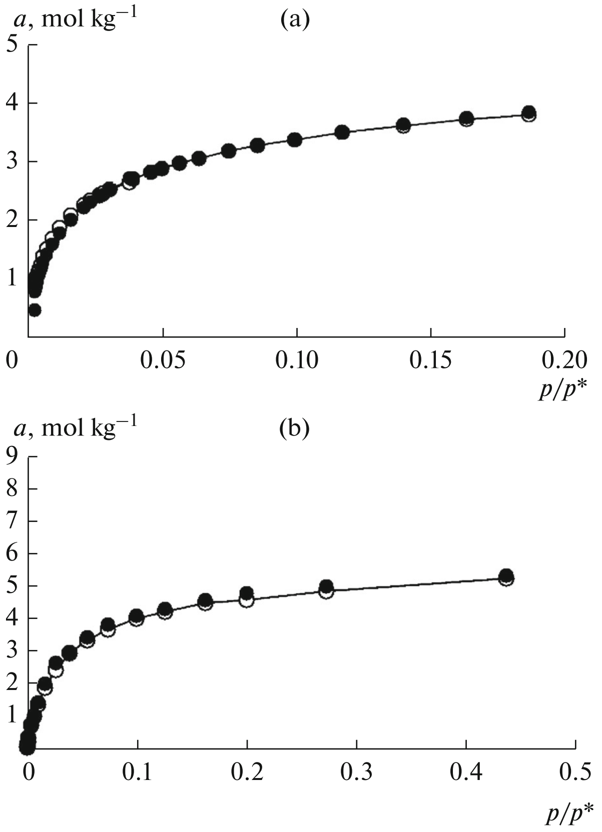

Fig. 2. (a) Adsorption isotherms of propane on the Nuxit activated carbon at 363 K, which are (●) determined experimentally and (○) calculated using the adsorption isotherms at 293 K; (b) adsorption isotherms of methane on the NaX zeolite at 330 K, which are (●) determined experimentally and (○) calculated using the adsorption isotherm at 210 K.

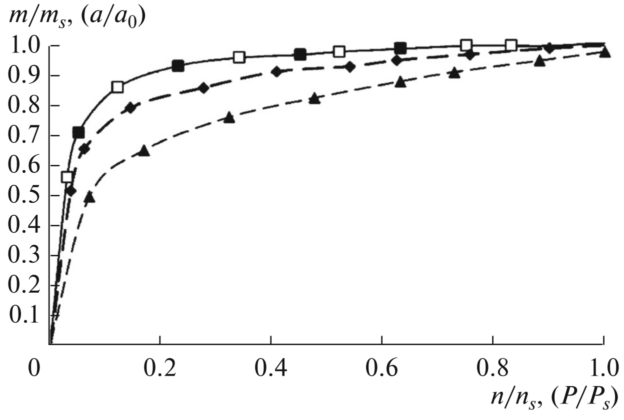

Fig. 4. Adsorption isotherms of ethanol on microporous carbon adsorbent (AU-1), which are (□) determined experimentally (upper smooth curve) [17] and calculated for the pores with widths of (▲) 1.6, (◆) 1.0, and (■) 0.8 nm.

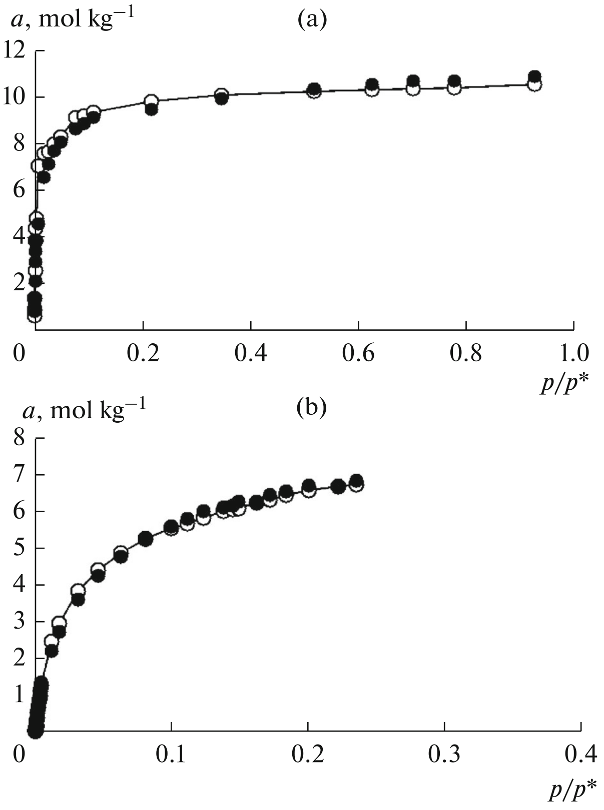

Fig. 3. (a) Adsorption isotherms of xenon on the AUK activated charcoal at 212 K, which are (●) determined experimentally and (○) calculated using the adsorption isotherm at 273 K; (b) Adsorption isotherms of xenon on the AUK activated charcoal at 393 K, which are (●) determined experimentally and (o) calculated using the adsorption isotherm at 273 K.

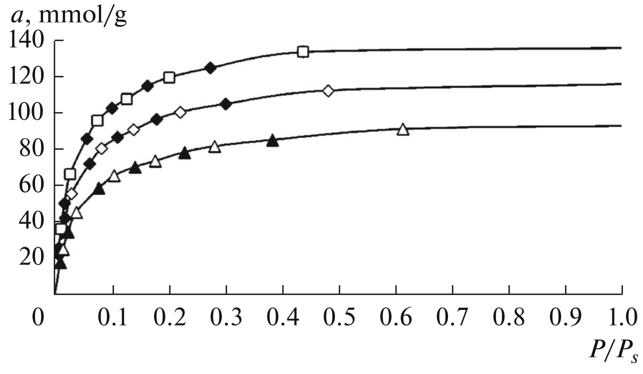

Fig. 5. Isotherms determined experimentally [17] for the adsorption of (■) ethane, (◆) propane, and (▲) n-butane on the Nuxit microporous carbon adsorbent at 293 K, and (□, ◇, △) the corresponding calculated isotherms.

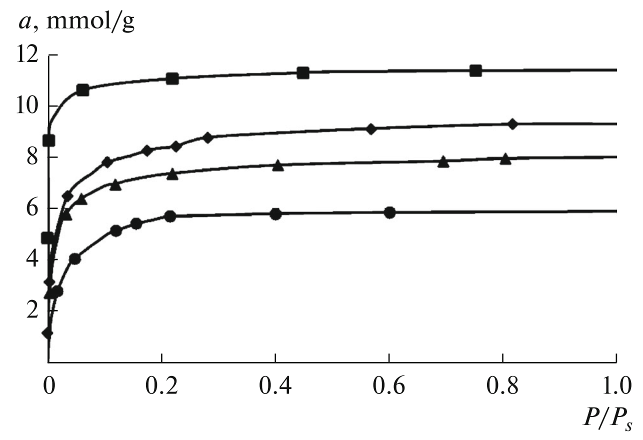

Fig. 6. Experimental (solid lines) and theoretical adsorption isotherms of methane (T_{cr} = 190.55 K) at (■) 120 and (◆) 240 K, and of xenon (T_{cr} = 289.75 K) at (▲) 302 and (●) 427 K.

The following point is quite important for theoretical and practical reasons: for the adsorption on the same adsorbent (Nuxit activated carbon), the effective model pore size determined for one adsorbate (propane in Fig. 5) does not change upon the transition to other adsorbates and temperatures. This is demonstrated by the data for ethane, butane, and propane (the experimental data are obtained from [17]). Obviously, the coincidence of the experimental and calculated curves in relative coordinates allows one to represent them in the a–P/P_s coordinates. The relevant experimental and calculated isotherms are shown in Figs. 4 and 5.

The calculated and experimental adsorption isotherms of methane at temperatures below and above the critical temperature, as well as the adsorption isotherms of xenon at supercritical temperatures, which demonstrate that adsorption isotherms can be calculated in wide temperature ranges, are shown in Fig. 6.

CONCLUSIONS

The obtained data show that the molecular-dynamics simulation of the adsorption isotherms on microporous activated charcoals solves the problem of determining the adsorption-temperature dependence and, at the same time, is effective substitution for laborious physical experiments, especially at temperatures above the critical temperatures and, accordingly, at high pressures. Furthermore, only one experimental adsorption isotherm of the "standard" vapor at temperatures substantially below the critical temperature is required for determining the slit width when performing calculations for any adsorbate.

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