Journal of Engineering Physics and Thermophysics, Vol. 78, No. 6, 2005

HEAT AND MASS TRANSFER IN DISPERSIVE AND POROUS MEDIA

DESCRIPTION OF THE NONINERTIA OF MICROPOROUS CARBON ADSORBENTS IN INTERACTION WITH GASES

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UDC 541.183

The issue of description of adsorption equilibrium with allowance for the noninertia of the adsorbent is considered. The model of elastic adsorption deformation of microporous carbon adsorbents in a wide range of pressures and temperatures is proposed. The results of modeling of adsorption deformation based on the model proposed are given.

Introduction. Despite the intense progress made by adsorption science, problems calling for solution are still quite numerous. One such problem, faced even in the early 20th century, is the noninertia of the adsorbent; this noninertia must be taken into account in considering adsorption phenomena.

Of considerable current use is a method of description of adsorption equilibrium that is given, for example, in [1]; in it, the role of the adsorbent surface is reduced only to the creation of an adsorption field. Thus, the adsorbent is assumed to be absolutely inert, which enables one to consider a one-component system, i.e., the adsorbate, rather than a two-component system.

The assumption that the adsorbent is absolutely inert is not adequate from the physical viewpoint. Even in the simplest case — that of adsorption on a plane homogeneous surface — the surface tension of the adsorbent inevitably changes as a result of the interaction of adsorbate molecules and surface atoms. Uncompensated forces applied to the surface adsorbent atoms decrease, which leads to a deformation of the adsorbent. The value of such a deformation depends on the specific properties of the adsorption system. However, even small deformations may exert a substantial influence on the thermodynamic characteristics of adsorption systems that are determined by adsorption and calorimetric experiments.

No investigations of adsorption (adsorptive) deformation have been carried out at present. The sole exception is provided by experiments with clay minerals [2, 3] and polymers [4, 5]. That is why there are actually no equations adequately describing adsorption equilibrium with allowance for the noninertia of the adsorbent. Therefore, experimental dilatometric investigations (given in [6]) of the adsorption deformation of microporous carbon adsorbents in a wide range of pressures and temperatures are particularly worth noting. For such systems we have proposed a model of elastic adsorption deformation, whose essence is presented below.

Model of Adsorption Deformation of Microporous Adsorbents. The pressure deforming the adsorbent is generally determined by both internal and external factors. However, we may disregard the external pressure in considering microporous adsorbents, since the dominant role is played by the internal pressure. This is shown by simple evaluations by the experimental dependences of the relative linear deformation on the pressure $\Delta l/l = f(P)$ (adsorption–deformation isotherms) and the Young modulus E. The experimental isotherms of adsorption deformation for the case of CO_2 adsorption by AUK-type coal are shown in Fig. 1.

The internal pressure may be represented as the difference of two pressures — the pressure related to the impacts of adsorbed molecules with micropore walls P_2 and the pressure P_1 compressing the adsorbent due to the effect

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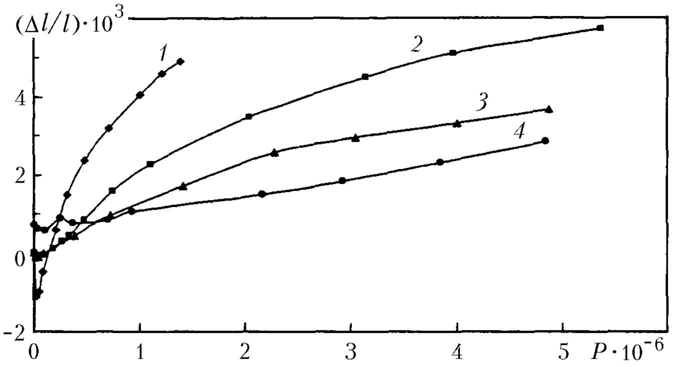

Fig. 1. Experimental isotherms of relative deformation of an AUK microporous carbon adsorbent in adsorption of carbon dioxide: 1) T = 243; 2) 293; 3) 313; 4) 393 K. P, Pa.

of decrease in the surface tension of the adsorbent in adsorption and interaction of the adsorbate molecules and the walls of micropores comparable to the molecular diameter in size:

$$P = -P_1 + P_2 . \tag{1}$$

The pressure P_1 may be expressed by the force f causing contraction upon the penetration of one adsorbate molecule into the micropores:

$$P_1 = \frac{fN}{S} .$$

To pass to the adsorption a in the expression written we must multiply the numerator and the demoninator of the fraction by the mass of an adsorbate molecule m_{mol} and the mass of the adsorbent m_{ads}:

$$P_1 = \frac{fa}{S_{\text{sp}} m_{\text{mol}}} . \tag{2}$$

The pressure P_2 is determined by the concentration of adsorbed molecules colliding with micropore walls on a free-volume basis and by the kinetic energy. Assuming that the adsorbed molecules, penetrating into the micropores, act similarly to an ideal gas, in molecular-statistical analysis we obtain [7]

$$P_2^{\text{id}} = \frac{2}{3} n \bar{\varepsilon} \quad \text{or} \quad P_2^{\text{id}} = \frac{2}{3} n \frac{ikT}{2} .$$

In the general case, the mutual impacts of the molecules and the impacts of the molecules with adsorbent walls are inelastic; therefore, we must introduce the coefficient A characterizing this inelasticity into consideration. Also, we should take into account that the concentration of adsorbed molecules must be calculated on a free-volume basis, i.e., with allowance for the size of the molecules themselves (it is denoted as n_*). Therefore, we have

$$P_2 = A \frac{2}{3} n_* \frac{ikT}{2} .$$

The concentration of adsorbed molecules on a free-volume basis in accordance with the Boltzmann distribution may be found in the form

$$n_* = n_{\text{gas}} \exp\left(\frac{-(\varepsilon_{\text{eq}}^{\text{ad}} - \varepsilon_{\text{eq}}^{\text{gas}})}{RT} \right) .$$

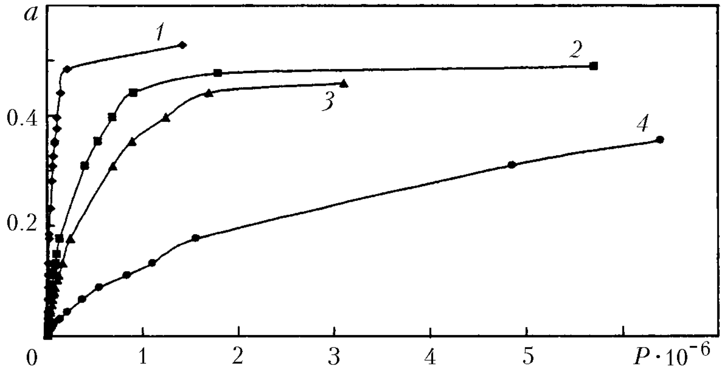

Fig. 2. Experimental isotherms of adsorption of carbon dioxide on an AUK microporous carbon adsorbent: 1) T = 243; 2) 293; 3) 313; 4) 393 K. P, Pa.

Thus, in the model proposed, by n_* we mean the concentration of adsorbed molecules found in the adsorbent field and in the intrinsic-interaction field on a free-volume basis.

If the equilibrium gas phase is ideal, we have $\varepsilon_{\text{eq}}^{\text{gas}} = 0$ and may write

$$P_2 = A\frac{i}{3}\exp\left(\frac{-\varepsilon_{\text{eq}}^{\text{ad}}}{RT}\right)P_{\text{gas}}^{\text{id}},$$

where $P_{\text{gas}}^{\text{id}} = n_{\text{gas}}kT$.

If the equilibrium gas phase is nonideal, then, taking into account that

$$P_{\text{gas}} = zP_{\text{gas}}^{\text{id}},$$

we finally obtain

$$P_2 = A\frac{i}{3}\exp\left(\frac{-\varepsilon_{\text{eq}}^{\text{ad}}}{RT}\right)\frac{P_{\text{gas}}}{z}. \tag{3}$$

Assuming that the adsorbent deformation is elastic, we may use the following expression for description of the deformation of microporous adsorbents with account for (1)–(3):

$$\frac{\Delta l}{l} = \frac{-P_1 + P_2}{E}$$

or

$$\frac{\Delta l}{l} = -Ca + B\frac{i}{3}\exp\left(\frac{-\varepsilon_{\text{eq}}^{\text{ad}}}{RT}\right)P_{\text{gas}}, \tag{4}$$

where $B = A/(Ez)$ and $C = f/(ES_{\text{sp}}m_{\text{mol}})$.

Formally, the deformation (under the assumption that the parameters B and C are constant) is a function of two variables a and P_{gas}, according to expression (4), but actually it is a function of only one variable, since a and P_{gas} are functionally related to each other.

Microporous carbon adsorbents have a homogeneous microporous structure. Thus, this adsorption situation is very similar to a Langmuir one, since the size of the micropores is comparable to the size of the molecules adsorbed. This is confirmed by the experimental isotherms presented in Fig. 2 for the case of CO_2 adsorption by AUK-type coal. At the same time, there is a certain inhomogeneity of the adsorbent, lateral interactions of the adsorbed molecules, and the adsorption deformation of the adsorbent. Therefore, based on the interphase-equilibrium equation [8] and the model premises similar to Langmuir ones, we have obtained the following relation:

$$\theta = \frac{P_{\text{gas}}}{Ka_{\max} + P_{\text{gas}}} = \frac{K_* P_{\text{gas}}}{1 + K_* P_{\text{gas}}}, \tag{5}$$

where $K_* = \dfrac{1}{Ka_{\max}}$ and $K = \dfrac{RT}{V_{\text{sp.max}}\mu} \exp\left(-\dfrac{q_{\text{is}}}{RT}\right)$.

Solving expression (5) for the adsorption

$$a = \frac{P_{\text{gas}} a_{\max}}{Ka_{\max} + P_{\text{gas}}}$$

and substituting into (4), we obtain an equation describing the deformation of microporous carbon adsorbents as a function of the pressure in the gas phase P_{gas}:

$$\frac{\Delta l}{l} = -C \frac{P_{\text{gas}} a_{\max}}{Ka_{\max} + P_{\text{gas}}} + B \frac{i}{3} \exp\left(\frac{-\varepsilon_{\text{eq}}^{\text{ad}}}{RT}\right) P_{\text{gas}}, \tag{6}$$

Expressing, in (5), the pressure by the adsorption

$$P_{\text{gas}} = \frac{a}{K_* a_{\max}(1 - \theta)}$$

and substituting it into (4), we obtain an equation describing the deformation as a function of the adsorption:

$$\frac{\Delta l}{l} = -Ca + \frac{Ya}{1 - \theta} \exp\left(\frac{Q}{RT}\right),$$

where $Y = \dfrac{BiRT}{3V_{\text{sp.max}}\mu}$ and $Q = -\varepsilon_{\text{eq}}^{\text{ad}} - q_{\text{is}}$.

To adequately describe the deformation in the range of high pressures we must also allow, in the expression obtained, for the existence of a free volume in the case of close filling of the micropores [9]. Then the equation takes its final form:

$$\frac{\Delta l}{l} = -Ca + \frac{Ya}{1 - g\theta} \exp\left(\frac{Q}{RT}\right). \tag{7}$$

Results and Their Discussion. Modeling of the adsorption deformation and checking of the adequacy of Eqs. (6) and (7) have been carried out based on the experimental data given in [6]: the isotherms of adsorption deformations of an AUK microporous carbon adsorbent and the molecular isosteric heats of adsorption. The isotherms of adsorption deformations (in the linear deformation–adsorption coordinates) and the isosteric heats of adsorption (together with the results of modeling) for the case of CO_2 adsorption are given in Figs. 3 and 4.

For convenience of calculations we took Eq. (7) as the basis. The calculations were carried out based on the assumption that the parameters C and Y in the equations were virtually constant at a constant temperature with allowance for the small deformation of the adsorbent. The parameter g was taken to be unity. This enabled us to use experimental data at two points, solving a system of two equations with two unknowns, for determination of the parameters C and Y.

The calculated values of the parameters C and Y were used for finding such values of the potential energy of interaction in the adsorbed state $\varepsilon_{\text{eq}}^{\text{ad}}$ for which the coincidence of the calculated and experimental $\Delta l/l = f(P)$ curves was observed.

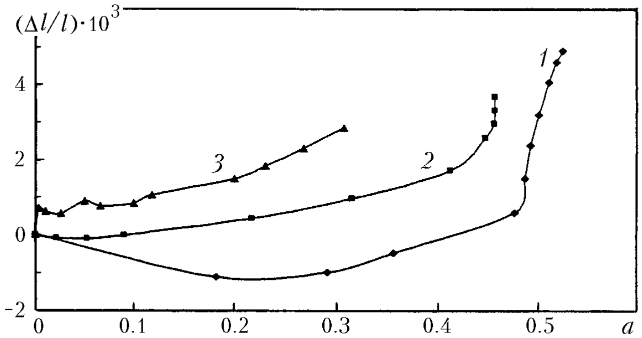

Fig. 3. Experimental isotherms of relative deformation of an AUK microporous carbon adsorbent in adsorption of carbon dioxide: 1) T = 243; 2) 313; 3) 393 K.

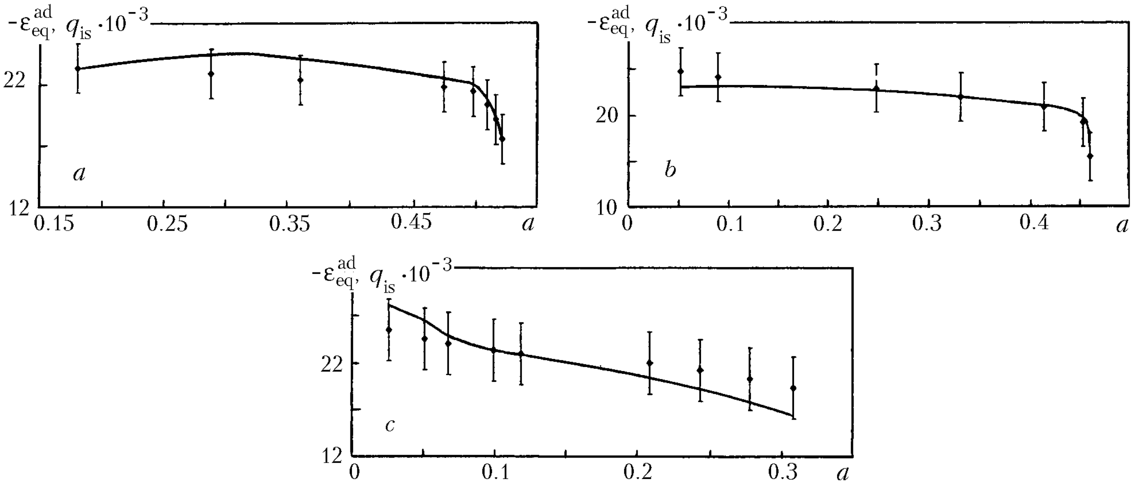

Fig. 4. Comparison of the values of ε_{eq}^{ad} (solid curve) and q_{is} (points) in adsorption of carbon dioxide on an AUK microporous carbon adsorbent: a) T = 243; b) 313; c) 393 K. ε_{eq}^{ad} and q_{is}, J/mole.

The calculation results for the case of CO_2 adsorption are given in Fig. 4. A good correlation of the ε_{eq}^{ad} and q_{is} values is observed; the difference between them is no higher than RT.

Conclusions. Using the thermodynamic approach, we have obtained equations enabling us to describe adsorption equilibrium in adsorption of gases by microporous carbon adsorbents with allowance of the noninertia of the adsorbent. The adequacy of the obtained results of modeling based on the equations proposed to the data of experimental investigations of adsorption deformation enables us to speak of the efficiency of the model proposed.

A detailed analysis of the resultant equations of thermodynamic description of adsorption equilibrium in interaction of microporous carbon adsorbents and gases with allowance for the noninertia of the adsorbent may provide more comprehensive information on the behavior of such systems. This information may be used in solving certain technological problems in the field of environmental protection (for creation of adsorption-trapping and degassing systems and facilities of individual and group protection against toxic substances).

NOTATION

A, semiempirical coefficient characterizing the inelasticity of impacts; a, running value of the equilibrium adsorption, kg/kg; a_{max}, limiting value of the equilibrium adsorption at a given temperature, kg/kg; E, Young modulus, Pa; f, force causing compression (contraction) upon the penetration of one adsorbate molecule into the micropores, N; g, parameter allowing for the existence of a free volume in close filling of the micropores; i, number of degrees of freedom of a molecule; k, Boltzmann constant, J/K; m_{ads}, mass of the adsorbent, kg; m_{mol}, mass of an adsorbate molecule, kg; N, running number of adsorbed molecules; n, molecular concentration, m^{-3}; n_*, molecular concentration on a free-volume basis, m^{-3}; n_{gas}, molecular concentration in the equilibrium gas phase, m^{-3}; P, pressure, Pa; P_1, pressure compressing the adsorbent due to the effect of decrease in its surface tension in adsorption and interaction of the adsorbate molecules and the walls of the micropores comparable to the molecular diameter in size, Pa; P_2, pressure related to the impacts of adsorbed molecules with the micropore walls; the pressure is determined by their concentration on a free-volume basis and by the kinetic energy, Pa; P_{gas}, pressure in the equilibrium gas phase, Pa; $P_{\text{gas}}^{\text{id}}$, pressure in the equilibrium gas phase which is ideal, Pa; P_2^{id}, pressure related to the impacts of adsorbed molecules with the micropore walls under the assumption that they act similarly to an ideal gas, Pa; q_{is}, molar isosteric heat of adsorption, J/mole; R, universal gas constant, J/mole·K; S, area of the interior adsorbent surface, m^2; S_{sp}, specific adsorbent surface, m^2/kg; T, temperature, K; $V_{\text{sp.max}}$, specific maximum volume of filling of the micropores, m^3/kg; z, compressibility factor of the gas phase; $\Delta l/l$, relative linear deformation of the adsorbent; $\bar{\varepsilon}$, mean kinetic energy of one molecule, J; $\varepsilon_{\text{eq}}^{\text{ad}}$, molar potential energy of interaction in the adsorbed state, J/mole; $\varepsilon_{\text{eq}}^{\text{gas}}$, molar potential energy of interaction in the equilibrium gas phase, J/mole; μ, molar mass of the adsorbate, kg/mole; θ, degree of filling of the adsorbent molecules. Subscripts and superscripts: ad, adsorbed; ads, adsorbent; gas, gas; id, ideal; is, isosteric; eq, equilibrium; sp, specific; max, maximum.

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