

Sorbostriction of AR-V Carbon Adsorbent in Organic Vapor Adsorption

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Deformations of granulated recuperative activated carbon AR-V (produced in granulated form from coal dust (coals mixture) and adhesion agents by steam treatment at the temperature of 1100 — 1200K) upon carbon tetrachloride adsorption has been studied; this adsorbent (produced by company "Sorbent", Perm, Russia) has high adsorption capacity for vapors of organic substances.

To solve this problem a dilatometer was used. Its main part was a line differential transformer, the core of which was connected to the adsorbent by means of a rod. Any changes in the adsorbent height caused a change in the core position in the transformer, which influenced the signal recorded from its secondary winding. High sensitivity of the dilatometric method has been shown. The dilatometer used allowed the measurement of absolute deformations in the range $1 \cdot 10^{-7}$ to $3 \cdot 10^{-3}$ m. These results were compared with the adsorption isotherms.

Also the model and the equation of elastic adsorptive deformation of microporous adsorbents have been presented at their interaction with gases and vapors. The results of the modeling for the system activated carbon AR-V - carbon tetrachloride are compared with the experimental data.

1. Introduction

As early as (Meehan 1927), it was established that solid bodies change their size when adsorbing gases or vapors. Even now, however, it has not yet been generally accepted that the adsorbent is being deformed, i.e. is not inert, in the process of adsorption. Nevertheless from a physical viewpoint it can be stated that there can be no inert adsorbents at all. In fact, if we consider the simplest adsorption on the flat uniform surface of an adsorbent, even here the surface tension of the adsorbent declines when adsorbate molecules interact with the surface atoms. Thus, the uncompensated force affecting the surface atoms of the adsorbent decreases and this causes deformation of the adsorbent. It is clear that the deformation degree will be different in different cases: it depends on the properties of particular adsorptive systems. Nevertheless, even minor deformations of the adsorbents contribute considerably to the total thermodynamic characteristics determined from adsorption and calorimetry experiments (Tvardovskiy 2006). Despite this, direct measurements of adsorptive deformation essentially are not conducted nowadays.

Only measurements of structural characteristics of clay minerals (Tvardovskiy et al. 1997; Tvardovskiy et al. 1999; de la Calle et al. 1988), polymeric materials (Keller et al. 1999; Zhang et al. 1997) carbons (Bangham et al. 1937; Haines et al. 1947; Wiig et al. 1949; Yakovlev et al. 2003; Yakovlev et al. 2004; Fomkin 2005) and zeolites (Krasilnikova et al. 1988) and some theoretical works (Coudert et al. 2016; Balzer et al. 2015) are performed.

For a long time the progress of research in this direction was hampered by the lack of theoretical concepts and by considerable experimental and methodical difficulties. However, studying the deformation of solids in the process of adsorption and absorption is of great importance, as mentioned, for both the progress of thermodynamics and practical applications.

This work presents model designed to describe the elastic adsorptive deformation of carbon microporous adsorbents and dilatometric investigations of the adsorptive deformation of adsorbent AR-V upon carbon tetrachloride adsorption. A description with the help of the presented model and equations for the experimental data presented has been given.

2. Model

Supposing that the microporous adsorbents have a homogeneously microporous structure, the adsorbent can be considered in the first approximation as a parallelepiped with regularly distributed non-intersecting and spontaneously bent. Here it is assumed that the slot-like micropores have the same sectional area, and the distance between the centers of neighboring micropores is a constant. A schematic picture of the adsorbent is given in Figure 1.

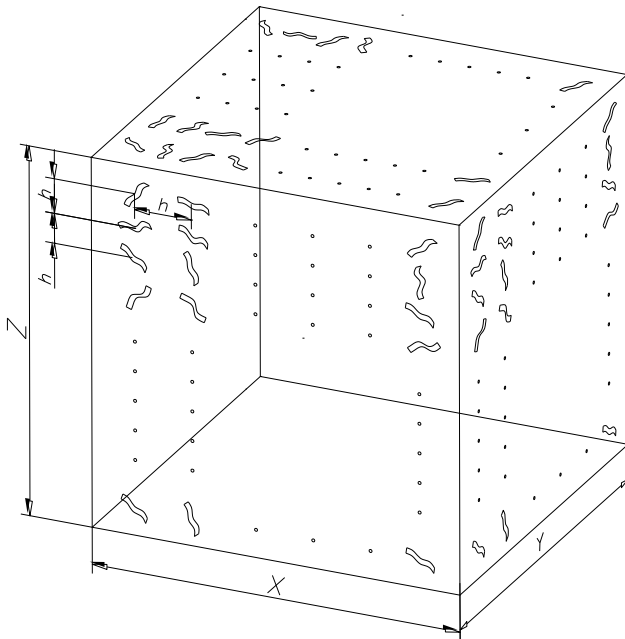


Figure 1: Model of microporous adsorbent.

The initial volume of the sample is

$$V_0 = xyz,$$

where x , y , and z are the adsorbent sizes. Assuming that the deformation is isotropic, the volume under the conditions of free expansion (compression) can be written as

$$V = x \left(1 + \frac{\Delta x}{x} \right) \cdot y \left(1 + \frac{\Delta y}{y} \right) \cdot z \left(1 + \frac{\Delta z}{z} \right) \quad \text{or}$$

$$V = V_0 (1 + \Delta l / l)^3,$$

where $\Delta l / l = \Delta x / x = \Delta y / y = \Delta z / z$ is the relative linear deformation of the adsorbent. In this case, the following expression is valid for a change in the adsorbent volume:

$$\Delta V = V_0 \left[\left(1 + \frac{\Delta l}{l} \right)^3 - 1 \right]. \quad (1)$$

The initial volume of micropores in an adsorbent is

$$V_{P,0} = sk_s(N_x N_y z + N_x N_z y + N_y N_z x)$$

where s – cross-sectional area of micropores; k_s is the coefficient that takes account of the tortuosity of the micropores; N_x , N_y , and N_z are the numbers of the micropores in the modeled adsorbent along the axes x , y , z , respectively. Taking into account that $N_x = x/h$, $N_y = y/h$, $N_z = z/h$: $V_{P,0} = k_{P0}V_0$.

where $k_{P0} = 3sk_s/h^2$ is the initial porosity of the adsorbent and h is the initial distance between micropore centers. The current volume of the micropores in the isotropic deformation is

$$V_P = s\left(1 + \frac{\Delta d}{d}\right)^2 k_s \left(N_x N_y z \left(1 + \frac{\Delta l}{l}\right) + N_x N_z y \left(1 + \frac{\Delta l}{l}\right) + N_y N_z x \left(1 + \frac{\Delta l}{l}\right) \right) \text{ or}$$

$$V_P = V_0 k_{P0} \left(1 + \frac{\Delta d}{d}\right)^2 \left(1 + \frac{\Delta l}{l}\right).$$

where d - effective width of a micropore; $\Delta d/d$ - relative linear deformation of a micropore.

Correspondingly, the change in the volume of the micropores is

$$\Delta V_P = V_0 k_{P0} \left[\left(1 + \frac{\Delta l}{l}\right) \left(1 + \frac{\Delta d}{d}\right)^2 - 1 \right], \quad (2)$$

If the density of the solid phase of the adsorbent is the same, then the equality of the right-hand sides of the expressions (1) and (2) is true:

$$\left(1 + \frac{\Delta l}{l}\right)^3 - 1 = k_{P0} \left[\left(1 + \frac{\Delta l}{l}\right) \left(1 + \frac{\Delta d}{d}\right)^2 - 1 \right]$$

or

$$\left(1 + \frac{3\Delta l}{l} + 3\left(\frac{\Delta l}{l}\right)^2 + \left(\frac{\Delta l}{l}\right)^3\right) - 1 = k_{P0} \left[\left(1 + \frac{\Delta l}{l}\right) \left(1 + \frac{2\Delta d}{d} + \left(\frac{\Delta d}{d}\right)^2\right) - 1 \right].$$

Assuming that the relative linear deformation is small (Yakovlev et al. 2003; Fomkin 2005) we can ignore the sizes $(\Delta l/l)^2$ and $(\Delta l/l)^3$. Therefore we can write

$$\frac{\Delta l}{l} = \frac{2k_{P0} \frac{\Delta d}{d}}{3 - k_{P0} \left(1 + 2\frac{\Delta d}{d}\right)} \quad (3)$$

Consequently, it can be stated that the relative linear deformation of the modeled specimen is quasi-linearly related to the relative change in the size of micropore. Using Equation (3), we can reduce to detailed consideration of just a single micropore. Having calculated deformation in a single micropore, we can evaluate the whole adsorbent deformation. In work (Zalivin et al. 2009) the similar approach for slot-like-pore has been presented by us.

3. Materials and methods

Deformation of the AR-V microporous carbon adsorbent during adsorption of CCl_4 in the temperature interval from 255.5 to 353 K and at pressures of $1-14 \times 10^3$ Pa was studied.

The structure-energy characteristics of AR-V adsorbent were determined based on the adsorption isotherm of the standard benzene vapor at 293 K using the computational apparatus of Dubinin's theory (Dubinin 1971) of the volumetric filling of micropores (TVFM). The following characteristics of the adsorbent sample were obtained: micropore volume $W_0 = 0.26 \text{ cm}^3/\text{g}$, characteristic energy of adsorption $E_0 = 15.8 \text{ kJ/mol}$, and characteristic micropore half-width $x_0 = 0.76 \text{ nm}$.

An inductive-type dilatometer designed for measuring small deformations of solids during adsorption in pressure and temperature ranges of $1-2 \times 10^7$ Pa and 77-570 K, respectively, was used (Tvardovskiy et al. 2011). The dilatometer used allowed measurement of absolute deformations in the range from 1×10^{-7} to 3×10^{-3} m.

Adsorption of CCl_4 was studied using a gravimetric vacuum adsorption installation with the electronic compensation of the weight. The error of measurement did not exceed 1 %. The gas pressure was determined with errors of ± 1.0 Pa.

Prior to the measurements, adsorbent AR-V were degassed by heating at corresponding temperatures in vacuum down to a residual pressure of 1.33×10^{-3} Pa in the system. Carbon tetrachloride was thoroughly purified and dried, after CCl_4 was degassed in vacuum, its vapor pressure corresponded to the tabular value.

In a paper published earlier (Nabiulin et al. 2015) data on variation of linear sizes of AR-V adsorbent granules under physical adsorption of benzene, *n*-hexane, *n*-nonane, tetrachloride carbon, and mixtures thereof within the temperature range of from 423 to 473 K were presented for equilibrium and nonequilibrium conditions. It was shown that waves of adsorption deformation of adsorbents – waves of sorbostriction – appeared at a certain selection of adsorption parameters.

4. Results and discussion

A description with the help of the presented model and equations for the experimental data presented is given below.

This model considers an adsorbent micropore as arbitrarily split into similar fragments, and each of them can have 300 or less molecules. Further on, it considers how an adsorbate gradually fills all the fragments until the whole volume of the micropore is filled up. This model assumes that all the micropores are the same, approximately 1.6 nm wide. Consequently, a micropore section can contain only three or less such adsorbate (carbon tetrachloride) molecules.

Relative linear deformation of the micropore in its elastic deformation during localized adsorption can be evaluated as follows:

$$\frac{\Delta d}{d} = \frac{1}{E} \cdot (\pm \sigma \cdot N), \quad (4)$$

where N is the current number of adsorbate molecules in the micropore fragment, and σ is the resulting pressure created by the adsorbed molecules located in this fragment.

Equation (4) can be written so:

$$\frac{\Delta d}{d} = \frac{1}{E} [-\sigma_1 N_1 + \sigma_2 N_2], \quad (5)$$

where σ_1 is the pressure created by adsorbed molecules N_1 interacting with the micropore walls in this fragment, σ_2 is the pressure caused in this fragment by adsorbed molecules N_2 , which have no direct contact with the micropore walls; and E is the Young modulus. We take the Young modulus value $E = 1 \cdot 10^9 \text{ Pa}$ as one of those possible in the characteristic range for carbon materials. The first term in the right-hand side of Equation (5) is for the adsorbent's contraction in the localized adsorption.

From (3), (5) and experimental data on the relative linear deformation of the adsorbent, values of σ_1 and σ_2 can be calculated for the start and end of the adsorption. Obviously, formula (5) gives $N_2 \cong 0$ at the start of the adsorption and $N_1 = 200, N_2 = 100$ at the end, in the fragment under study.

Having information about σ_1 as well as σ_2 and assuming that these characteristics are practically constant in adsorption at a given temperature, we can calculate the relative linear deformation of the adsorbent directly from the relative linear deformation of a single micropore. In this case formulae (3) and (5) are used. Here, in the course of gradual filling the micropore fragment, N_1 and N_2 values are being set to reach the maximum correlation between the theoretically calculated and experimentally measured data. Obviously, $N = (aN_{\max})/a_{\max}$, where $N = N_1 + N_2$ and $N_{\max} = 300$ are the current and maximum numbers of the adsorbate molecules in the micropore fragment respectively, whereas a and a_{\max} are the current and maximum adsorptions respectively.

Thus, from the experimental data on the relative linear deformation of the adsorbent and using equations (3, 5) we can model filling a micropore fragment with adsorbate molecules in the adsorption.

One of the criteria that the presented model is correct is an agreement between the results of modeling and experiments.

Figure 2 shows modeling the relative linear adsorptive deformation of microporous carbon adsorbent AR-V adsorbing CCl_4 . The figure shows quite a satisfactory agreement between the theoretically calculated and experimentally measured data.

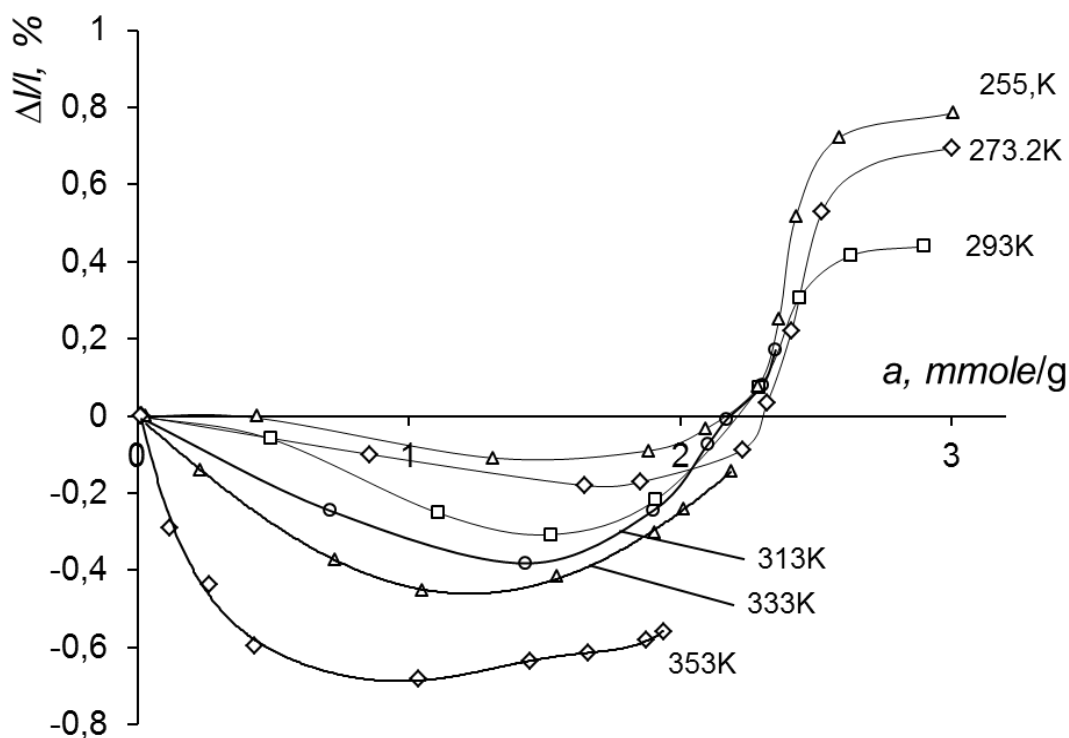


Figure 2: Relative linear deformation of the microporous carbon adsorbent AR-V ($\Delta l/l$) vs. CCl_4 amount adsorbed at different temperatures. Points are experiment, lines are calculation with using Eq.(3,5).

5. Conclusions

A model and equation for the adsorptive deformation of a microporous adsorbent – that allow connecting the value of deformation in a single micropore with size changes in the whole adsorbent – have been proposed. On the basis of the above equation, the adsorptive deformation of microporous carbon adsorbent AR-V in the course of adsorbing carbon tetrachloride (in the ranges of temperature and pressure of 255 to 353 K and 0.001 Pa to 20 kPa respectively) has been modeled. A good correlation of the calculations with the experimental data has been revealed.

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