Adsorption of Gases, Vapors and Liquids by Microporous Adsorbents

A.A. FOMKIN

Institute of Physical Chemistry of Russian Academy of Sciences, 119991 Moscow, Russia, Leninskii prospect 31

Abstract. Adsorption of Xe, Kr, Ar, N_2, O_2, H_2 CH_4, CO_2, He, and freons by PAU-10 and ACC microporous carbon adsorbents as well as by A and X zeolites was investigated over a wide range of pressures (0.1 Pa – 20 MPa) and temperatures (77, 120–600 K). The amount of gases, vapors and liquids adsorbed by microporous adsorbents increases steadily with increasing pressure and does not change dramatically if phase transitions occur in the adsorptive. Isosteres of adsorption constructed as a curve of ln P against $f(1/T)_a$ retain a linear form over a wide range of pressures and temperatures. The slope of isosteres does not vary on going through the critical temperature of the gaseous phase. At high pressures, due to non-ideality of the gaseous phase and non-inert behavior of the adsorbent the differential molar heat of adsorption is dependent on temperature. At high fillings of micropores the differential molar isosteric heat capacities of adsorption systems show maxima that indicate the occurrence of structural rearrangements in the adsorbate.

Keywords: adsorption, isosteres, gas, vapor, liquid, microporous adsorbents, heat of adsorption, adsorption deformation, heat capacities of adsorption systems

Introduction

This article is devoted to the memory of Professor Wolfgang Schirmer, Germany. Under his supervision at the Central Institute of Physical Chemistry of the Academy of Sciences of the GDR, Berlin, and that of Professor Michail M. Dubinin at the Institute of Physical Chemistry of the Academy of Sciences of the USSR, Moscow, a vast research of adsorption on microporous adsorbents had been conducted during the 1970–85 years.

Physical adsorption of gases, vapors and liquids in microporous adsorbents is significantly different from the adsorption on open surfaces. A classification proposed by Dubinin (1975) defines micropores as pores with the effective diameter or the width less than $3.2 \div 3.6$ nm, values comparable with effective dimensions of the sorbed molecules. Adsorption fields of neighboring walls overlap and adsorption potential of such pores is sufficiently enhanced. Based on the classification adopted by IUPAC the upper limit to micropores is 4.0 nm (IUPAC, 1972). XRD investigations indicate that in the adsorbents with a high developed micropore structure, like carbon adsorbents and zeolites (Breck, 1974), micropores are formed by the system of cavities connected through channels and windows. The energy barriers developed near the entrance to cavities apparently screen the influence of the equilibrated gaseous phase and molecules of neighboring cavities on adsorbate. These features of the microporous system dramatically change the properties of adsorbed species. The adsorption field of microporous adsorbents imposes its structure on adsorbed molecules and distributes these to exclude the first-order phase transitions like condensations. However as the amount adsorbed increases, rearrangement of structure, similar to second type phase transitions, becomes possible.

Adsorption interaction between adsorbate molecules and solid surface generally modifies the state of the solid (Bankham, 1937; Bering et al., 1970). The magnitude of this modification depends on the degree of development of the solid surface, the occurrence of high-energy adsorption sites capable of specific interactions, and, finally, on the energetic level of the intermolecular bounds between atoms of the solid. Adsorption on microporous adsorbents involves the adsorbent

and the adsorbate as equal partners of the adsorption process.

Specific features that characterize the adsorption in microporous adsorbents are markedly displayed in the contours of isotherms and isosteres of adsorption, in the phenomenon of adsorption deformation and thermodynamic functions of adsorption systems. This type of behavior can be observed in investigations extended over wide range of pressures and temperatures.

Experimental

Isotherms of Absolute Adsorption

The features that govern adsorption of Xe, Kr, Ar, N_2, O_2, H_2, CH_4, CO_2, He, CF_3Cl on microporous carbon adsorbents PAU-10, ACC as well as on A and X zeolites were investigated over wide range of pressure (0.1 Pa–20, 150 MPa) and temperature (77, 120–600 K). In addition, adsorption of liquids such as n-C_4H_{10}, n-C_5H_{12}, n-C_9H_{20}, CF_3Cl H_2O, C_6H_6, C_2H_5OH was investigated on NaX zeolite. Under isothermal conditions a monotonous increase in the amount adsorbed with pressure is quite common for all these systems. Isotherms of adsorption and desorption of standard benzene vapor on PAU-10 adsorbent produced from polyvinylidenechloride, and ACC adsorbent produced from silicon carbide exhibit no hysteresis loop over the entire range of relative pressure measured up to $P = P_s$. Parameters of the pore structure calculated by the Dubinin-Radushkevich equation are presented in Table 1.

W_o—micropore volume; E_o—characteristic energy of adsorption; x_o—effective half-width of micropores.

Prior to experiments, adsorbents were treated in vacuum at 673 K and a pressure of 0.01 Pa for 5 hr until no further weight loss could be recorded. The amount adsorbed was measured by a volumetric technique (Fomkin et al., 1974) with an error not exceeding 1%. Temperature was maintained with an accuracy near 0.1 ÷ 0.2 K; pressure was measured by a class 0.01 gauge. Ultra-pure gases with purity not lower than 99.99%
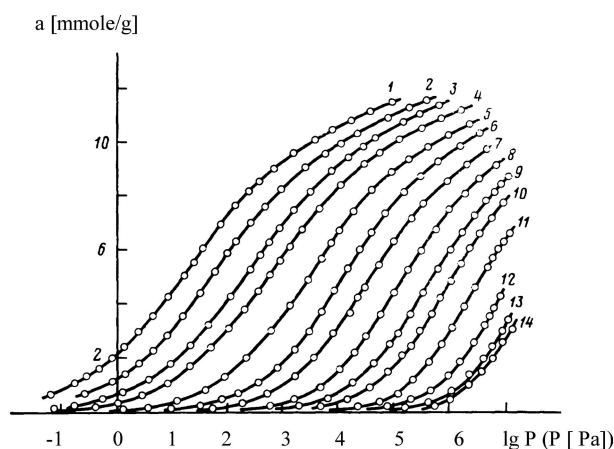

Figure 1. Adsorption isotherms of CH_4 on microporous carbon PAU-10 at (1) 120 K; (2) 130 K; (3) 140 K; (4) 150 K; (5) 170 K; (6) 190 K; (7) 210 K; (8) 240 K; (9) 273 K; (10) 03 K; (11) 370 K; (12) 450 K; (13) 550 K; (14) 600 K.

were used in the experiments. Figure 1 that refers to adsorption isotherms of methane on microporous carbon PAU-10 derived from polyvinylidenechloride provides an illustration (Chkhaidse et al., 1986).

Analogous dependencies of the amount adsorbed on pressure were obtained on zeolites. An example can be found in Fig. 2 that shows adsorption isotherms of Xe on NaX zeolite (Fomkin et al., 1975; Fomkin et al., 1978). Fully crystalline NaX zeolite with composition $0.98Na_2O$-Al_2O_3-$2.36SiO_2$ $0.02H_2O$ and a unit-cell constant of 2.496 nm were used. Prior to experiments the zeolite was treated in vacuum at 673 K and a pressure of 0.01 Pa for 8 hr to reduce the residual pressure to 0.01 Pa.
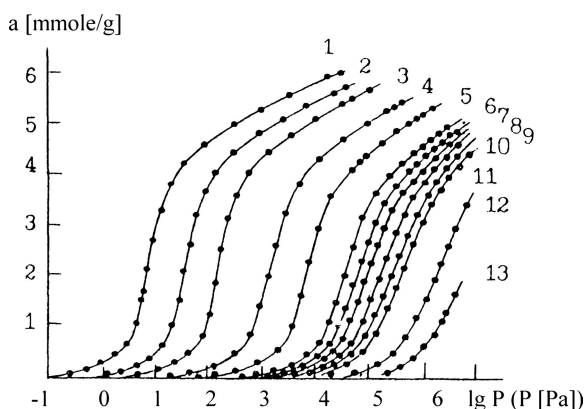
Table 1. Structure parameters of microporous carbon adsorbents.

Adsorbent	W_o (cm^3/g)	E_o (KJ/mol)	x_o (nm)
PAU-10	0.41	27.4	0.44
ACC	0.44	26.0	0.47

Figure 2. Adsorption isotherms of Xe on NaX zeolite at (1) 150 K; (2) 165 K; (3) 180 K; (4) 210 K; (5) 240 K; (6) 280 K; (7) 296 K; (8) 310 K; (9) 330 K; (10) 350 K; (11) 370 K; (12) 500 K; (13) 600 K.

Figures 1 and 2 indicate the absence of condensation effects for the adsorbate as evidenced by the same pattern of temperature dependence revealed by all adsorption isotherms on passing through critical temperatures of adsorptive. Note that $T_c = 190.55$ K for CH_4 and 289.7 K for Xe (Vargaftik, 1972). Similar dependencies were recorded for a number of adsorption systems (Seliverstova et al., 1978; Fomkin, 1983; Fomkin et al., 1974; Chkhaidse et al., 1986; Kharitonov et al., 2001).

Whatever the state of adsorptive, the chemical potentials μ of adsorptive and adsorbate in micropores are the same. Accordingly, the adsorption isotherm $a = f(\mu)_T$ should be described by a common curve not only for the adsorption of gases but also for the adsorption of vapors and liquids (Dubinin et al., 1980; Seliverstova et al., 1982). To test the validity of this suggestion, adsorption systems H_2O—NaX zeolite and C_6H_6—NaX zeolite were investigated (Fomkin et al., 1986). Figure 3 shows relevant adsorption isotherms constructed as plots $a = f(\mu)_T$ obtained by combining the data on adsorption of the vapor, on the adsorption of the liquid that experiences the pressure of its saturated vapor, and, finally, on the adsorption of the liquid that experiences hydrostatic pressures (up to 100 MPa).

The chemical potential of the liquid compressed to hydrostatic pressure P was calculated by the equation

$$\mu(P) = \mu(P_s^0) + \int_{P_s^o}^{P} v(P) dP \qquad (1)$$

where P_s^0 is the pressure of the saturated vapor of the liquid under zero excessive hydrostatic pressure, $v(P)$ is the specific volume of the liquid compressed. A value of $\mu(P_s^0)$ was taken as a reference zero point at a given temperature.
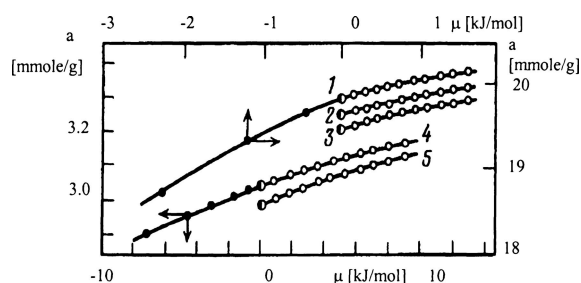

Figure 3. Adsorption isotherms of water (1–3) and benzene (4, 5) on NaX zeolite at (1) 303 K; (2) 313 K; (3) 323 K; (4) 303 K and (5) 323 K.

Making use of Eq. (1), one arrives at the expression for the pressure of saturated vapor P_s of the compressed liquid as a function of the hydrostatic pressure P

$$\ln P_s = \ln P_s^0 + \frac{1}{RT} \int_{P_s^o}^{P} v(P) dP \qquad (2)$$

Since values of P_s^0 are small, the use of fugacities in Eqs. (1) and (2) is not needed.

The data in Fig. 3 suggests that adsorption isotherms in microporous adsorbents retain their slope on passing from the vapor area to the area of the compressed liquid through the curve of condensation of the saturated vapor.

Adsorption Deformation of Microporous Adsorbents

In general, the phenomenon of adsorption deformation of microporous adsorbents brings about essential corrections to calculations of the amount adsorbed and thermodynamic functions of an adsorption system (Tvardovski, 1994, 1997, 1999, 2001). As to be shown below, to make a reliable account of these corrections, data on adsorption deformation over wide range of pressures and temperatures are needed.

The first report on adsorption deformation (Mechan, 1927), was followed by a number of studies (Bangham et al., 1928, 1932, 1934; Yates, 1952, 1954; Flood, 1954, 1955, 1957, 1963; Kononyuk et al., 1971, 1972; Bering, 1976; Beresin et al., 1980; Krasilnikova et al., 1979). This phenomenon remains the object of recent investigations (Dolino et al., 1996; Gerard et al., 1998; Warne et al., 2000; Young et al., 2000). However due to narrow ranges of the parameters of adsorption equilibrium the data obtained to date can hardly be used to clarify the main features governing the adsorption deformation in microporous adsorbents.

The measurements were conducted with the help of a sophisticated inductive dilatometer that makes it possible to measure the adsorption deformation of solids at pressures that range from 1 Pa to 20 MPa and temperatures that range from 77 to 570 K. The technique of measurements is described earlier (Fomkin et al., 1996). The dilatometer is connected to the high-pressure adsorption unit discussed in more detail previously (Fomkin et al., 1974). The measured values of adsorption deformation range from $1 * 10^{-4}$ to 3 mm. The sensitivity of the dilatometer is 0.06 μ. Figure 4 shows isotherms of adsorption deformation of a crystalline NaX zeolite pelletized at a pressure of 150 MPa.
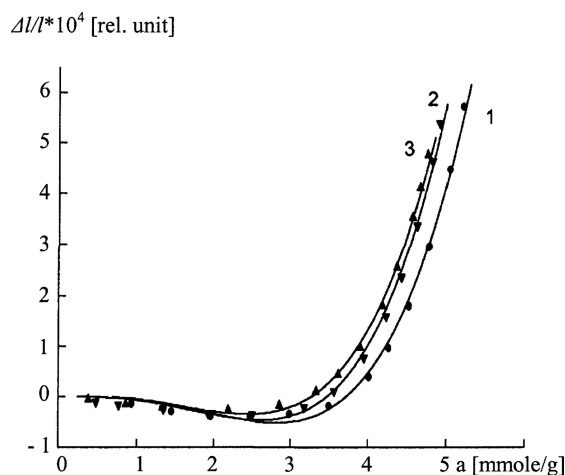
$\Delta l/l * 10^4$ [rel. unit]

Figure 4. The relative adsorption deformation of crystalline NaX zeolite as a function of the amount Xe adsorbed at (1) 273 K; (2) 303 K and (3) 333 K.

The equilibrium pressure of xenon was varied from 1 Pa to 7 MPa. Figure 4 indicates that the general pattern of curves is the same. As the amount of Xe adsorbed increases compression of crystallites is observed, the curves pass then through a maximum, and expansion of crystallites can be recorded. With further adsorption, negative deformation values change the sign, and dramatic expansion of the adsorbent occurs that is nearly one order higher in magnitude than a preceding contraction. With increasing temperature the curves are shifted to the region of lower adsorption values. The highest value of adsorption deformation experienced by NaX zeolite during adsorption of Xe does not exceed 0.06%.

Similar relations were reported (Fomkin et al., 2000) for benzene on microporous activated carbons FAS and ACC at 273°C (Fig. 5). Parameters of the pore structure of activated carbon ACC are given in Table 1. An array of adsorption data indicates that this adsorbent is similar to a monoporous adsorbent.

On the contrary, FAS carbon adsorbent belongs to adsorbents with a bimodal pore size distribution. Using benzene as a standard vapor, characteristic half-widths of 0.35 and 1.0 nm were obtained with micropore volumes amounting to 0.11 и 0.83 cm³/g.

From the data in Fig. 5 it follows that variations in the parameters of the pore structure of adsorbent essentially modify the behavior of curves that describe the adsorption deformation. The differences are particularly pronounced at the initial fillings of micropores. The highest value of deformation induced by ad-
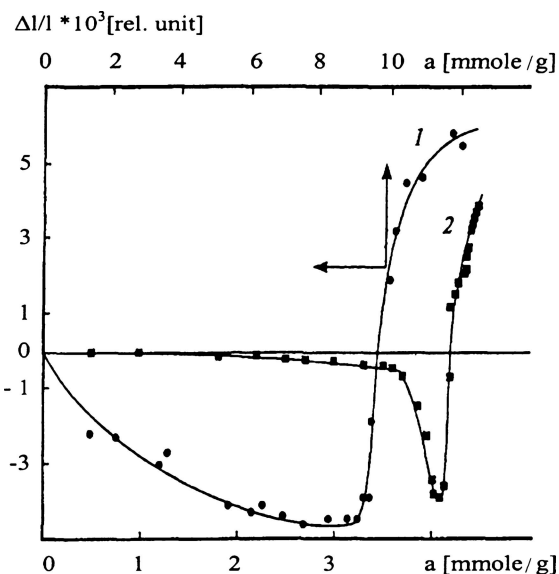
$\Delta l/l * 10^3$ [rel. unit]

Figure 5. The relative adsorption deformation of FAS (1) and ACC (2) microporous carbons as a function of the amount of benzene adsorbed at 293 K.

sorption of benzene on microporous activated carbons reaches a value of 0.6%

The curves of adsorption deformation recorded for adsorption of Xe on NaX zeolite and for adsorption of benzene on microporous FAS and ACC carbons show similar behavior. Again, contraction of the adsorbent is followed by expansion. In general case, however, the dependencies of adsorption deformation on the amount adsorbed and temperature are more complicated.

Figure 6 gives results of deformation of microporous carbons induced by adsorption of nitrogen as a function of the amount of nitrogen adsorbed at different temperatures (Yakovlev et al., 2003).

Figure 6 implies that the curves describing deformation of the ACC activated carbon induced by adsorption of nitrogen show the region of compression at relatively low temperatures (243–293 K). Such a region cannot be traced on the curves obtained at temperatures as high as 313–393 K. Expansion of the adsorbent caused by the adsorption deformation does not exceed 0.12%. From the data outlined above it can be concluded that the adsorption deformation depends not only on the amount adsorbed but on temperature as well.

Discussion

The lack of dramatic changes on adsorption isotherms indicates that phase transitions of the first type do not
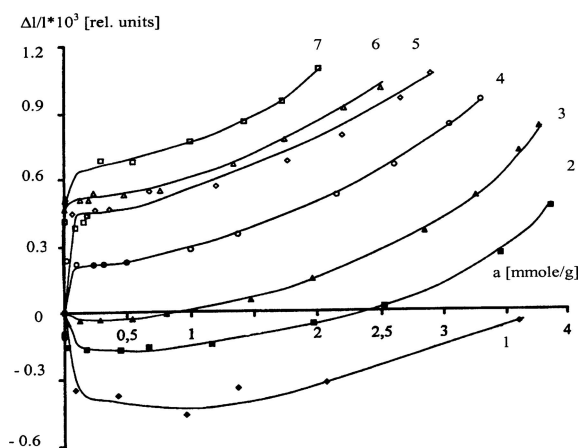
Figure 6. The relative linear deformation of the ACC microporous carbon induced by adsorption of nitrogen as a function of the amount of nitrogen adsorbed at (1)–243 K; (2) 273 K; (3) 293 K; (4) 313 K; (5) 333 K; (6) 353 K; and (7) 393 K.

occur in microporous adsorbents. A uniform distribution of adsorbing species that can place in average dozens of molecules per adsorbent unit cell apparently prevents nucleation of a new phase.

Adsorption Isosteres

Linearity of adsorption isosteres was repeatedly reported (Barrer et al., 1972; Fomkin et al., 1974, 1978, 1982, 1985, 1986; Chkhaidse et al., 1982, 1985; Kharitonov et al., 2001; Bülow et al., 2002). On analyzing the behavior of adsorption isosteres the conclusion can be made that in a good approximation isosteres are linear over wide range of temperatures and pressures. A good example provide isosteres of the adsorption of Xe on NaX zeolite shown in Fig. 7. Based on the figure, the isosteres preserve linearity over the entire range of temperatures and pressures. It should be emphasized that isosteres terminates near the line of saturated vapor pressure and resume their linear pattern in the supercritical area. Dotted lines in Fig. 7 denote an expected pattern of isosteres in the area where the equilibrated phase Фа3а is represented by a compressed liquid. The figure clearly shows that adsorption isotherms commencing in the vapor region resume their linear pattern in the region of the compressed liquid.

This pattern of behavior of isosteres was supported by the data for the systems water —NaX zeolite and benzene —NaX zeolite (Fomkin et al.,1986) obtained
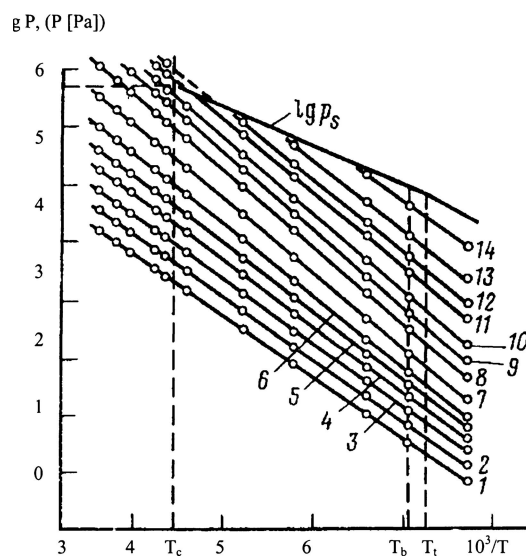

Figure 7. Isosteres of adsorption of Xe on NaX zeolite for the following amounts adsorbed: (1) 0.1; (2) 0.2; (3) 0.4; (4) 1.0; (5) 2.5; (6) 3.5; (7) 4.0; (8) 4.5; (9) 4.7; (10) 4.9; (11) 5.15; (12) 5.3; (13) 5.5 and (14) 5.8 mmol/g. Index $lg\ P_s$ denotes the saturated vapor pressure.
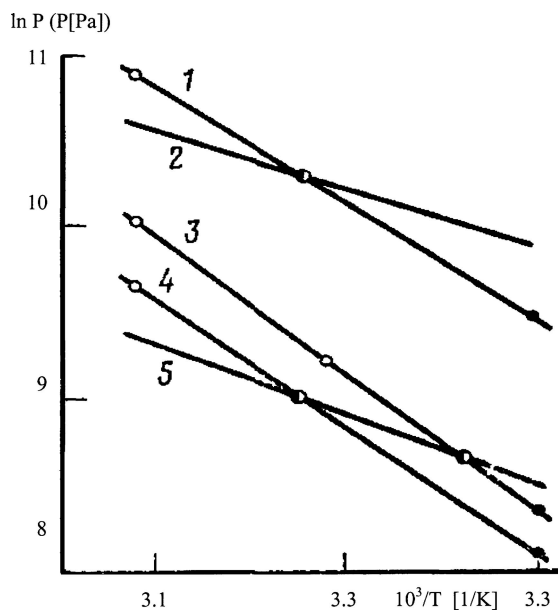

Figure 8. Adsorption isosteres of water and benzene on NaX zeolite: 1-C_6H_6 ($a = 3.05$ mmol/g); 2-$ln\ P_s$ (C_6H_6); 3–H_2O ($a = 19.9$ mmol/g); 4-H_2O ($a = 19.7$ mmol/g); 5-$ln\ P_s$ (H_2O).

at pressures up to 100 MPa. Figure 8 gives isosteres of adsorption for these systems.

Figure 8 confirms that the linearity of adsorption isosteres observed in the region of vapor extends over

the range characterizing the state of the compressed liquid.

The persistence of the adsorption isosteres up to the region in which gases show considerable deviations from linearity along with the linearity of the liquid state of the adsorptive and in the supercritical region favor *the concept of the adsorbate in the microporous adsorbent as a specific state of the substance.*

Some further evidence as to validity of this concept is provided by the data on adsorption of liquids by NaX zeolite conducted along the curve of the saturated vapor pressure (Dubinin et al., 1980; Seliverstova et al., 1982). The main results of the study are as follows. The average density of adsorbed hydrocarbons (CH_4, n-C_4H_{10}, n-C_5H_{12}, n-C_9H_{20}, CF_3Cl) and inert gases (Xe, Kr, Ar) in the region of low temperature is lower and near critical temperature is higher than the density of liquid adsorptive. The temperature at which the densities are equal is $\sim 0,8\ T_c$. Over the temperature range of $273 \div 473$ K the average density of adsorbed polar molecules (H_2O, C_6H_6, C_2H_5OH) exceeds density of liquids and shows a less strong dependence on temperature. Interestingly, the temperature dependence of the density of the adsorbed exhibits no maximum at 277.15 K, common to bulk water.

The Feature that Governs Adsorption by Microporous Adsorbents

Contraction of microporous adsorbents induced by adsorption (Figs. 4–6) is related to interactions of Xe and C_6H_6 molecules adsorbed in the micropores of NaX zeolite and in FAS and ACC activated carbons with opposite walls of micropores. However, an initial contraction of the adsorbent observed at low temperatures can give place to the expansion at higher temperatures. The adsorption of nitrogen on the ACC activated carbon provides a relevant example (Fig. 6). In the case of activated carbons this change appears to be a consequence of the fact that the binding energy between arrays of edge hexagons which make up micropores in carbons decreases with temperature. The binding energy between arrays of edge hexagons in graphite is known to be lower than that between carbon atoms in hexagons (Moelwin-Hughes, 1961). At higher temperatures the interaction of edge hexagons with adsorbed molecules in micropores displaces the hexagons inside micropores to violate the energy balance of the solid that stabilizes the microporosity. The net result would be expansion of the solid. Analogous results were ob-

tained for adsorption of CO_2 and Ar on the same adsorbent (Yakovlev et al., 2003). The same behavior of deformation curves in the case of zeolites can be ascribed to displacement of cations caused by the specific interaction with adsorbed molecules. Results obtained on adsorption of CO_2 on NaX zeolite agree with this interpretation (Pulin et al., 2001).

From the data outlined above, a general conclusion can be made that the extent of adsorption deformation in activated carbons and zeolites is low and can be neglected in adsorption measurements. In industrial processes, however, like PSA processes, adsorption deformation of adsorbents can be an essential factor that determine time-on-stream behavior of adsorbent pellets due to their attrition and destruction. In addition, the extent of adsorption deformation in some cases can influence the efficiency of molecular-sieve separation of adsorbed fluids. Furthermore, as will be outlined below, adsorption deformation of adsorbents can have a significant effect on calculations of thermodynamic characteristics of adsorption systems at high pressures.

Isosteric Heats of Adsorption

The adsorption of gases and vapors by a microporous solid is essentially different from the adsorption by a nonporous sold surface. The first case involves volume filling of the micropores (Dubinin, 1975), whereas in the second case is an adsorbate appears to form an individual phase on the solid surface. In general case, the estimation of the volume of the solid with micropores that contain the adsorbate is a complicated problem. XRD and chemical analyses can be used to determine the micropore volume of crystalline A, X zeolites (Breck, 1974). A general approach to evaluate microporosity in pure microporous adsorbents was described earlier (Fomkin et al., 1985).

Absolute adsorption defined as total amount of substance in the adsorption field of an adsorbent can be given by the expression

$$a = [N - (V - V_1)/V_g(p, T)]/m_o \qquad (3)$$

where N is the amount of adsorbate and adsorptive in the volume $(V - V_1)$ of the system; V is the volume of the system "adsorbent- adsorbate - adsorptive"; V_1 is the volume of the solid including micropore volume.; $V_g(p, T)$ is the molar volume of an adsorptive (gas or liquid); m_o is the weight of the evacuated adsorbent.

Adsorption is accompanied by heat evolution and deformation of the adsorbent. The thermodynamics of adsorption needs to consider non-inertial behavior of the adsorbent, whereas imperfection of the equilibrated adsorptive needs to be recognized at higher pressures. According to Guggenheim (1941), rigorous thermodynamics of the adsorption equilibrium considers gas phase and adsorbing species as a single thermodynamic system, in which only experimentally found values can be used as thermodynamic variables. This approach was pursued in a number of works (Bakaev, 1971, 1989; Shechvzova et al., 1992; Fomkin, 1993).

Consider a thermodynamic system consisting of N moles of a gas (or a liquid), included in a given volume V at pressure P. The system is in adsorption equilibrium with an adsorbent. The thermodynamic system can be simulated conveniently by a cylinder with a movable piston at the thermodynamic equilibrium with a thermostat at temperature T. The cylinder is a classical object for thermodynamic investigations. We assume further that the system has no hysteresis loop and only quasi-static transitions between equilibrium states can be executed. For these transitions the first and the second low of thermodynamics are given by

$$TdS = dE + PdV \qquad (4)$$

Here S and E are the entropy and the enthalpy of the system. The caloric equation of state may be written as

$$dE = (dE/dT)_v dT + (dE/dV)_T dV \qquad (5)$$

Equations (4) and (5) together give

$$T(dP/dT)_v = (dE/dV)_T + P \qquad (6)$$

When P and T are variables another form of Eq. (6) may be written

$$V - T(dV/dT)_P = (dH/dP)_T, \qquad (7)$$

where $H = E + PV$ is the enthalpy of the adsorption system.

Equations (6) and (7) are well-known equations of classical thermodynamics. In our case they are applicable to the system "adsorbent—adsorbat—gas" positioned under the piston in a cylinder and representing, in this way, a universal adsorption unit suitable

for determining isotherms volumetrically and measuring heats of adsorption. The N, V, P, T parameters derived from the experiments can be converted into the N, a, P, T—form, more useful in adsorption measurements (Bakaev, 1971, 1989). The most general mathematical technique of such transformations is the method of Jakobi-type determinants (Landau et al., 1964).

$$(dE/dV)_T = (dE/da)_T/(dV/da)_T \qquad (8)$$
$$(dP/dT)_v = (dP/dT)_a - (dP/da)_T$$
$$\times (dV/dT)_a(da/dV)_T \qquad (9)$$

Introducing (8) and (9) into (6) and multiplying both sides of resulting equation by $(dV/da)_T$ we arrive at

$$(dE/da)_T + P(dV/da)_T$$
$$= T(dP/dT)_a(dV/da)_T - T(dP/da)_T(dV/dT)_a \qquad (10)$$

We can put

$$V = V_g + V_1 = V_g + V_o + V_a, \qquad (11)$$
$$E = E_g + E_1 = E_g + E_o + E_a, \qquad (12)$$
$$H = H_g - H_1 = H_g + H_o + H_a, \qquad (13)$$

where subscripts "g", "o" and "a" refer to the gas, adsorbent and adsorbate correspondingly.

For an adsorption system, in which the amount adsorbed is defined as the total content implied by Eq. (3), $V_a \neq 0$ and thermodynamic functions can be represented by the following expressions:

(1) Differential energy of the adsorbent-adsorbate system

$$(dE_1/dN_a)_T = h_g + RZ(dlnP/dT^{-1})_a$$
$$\times [1 - (dV_1/dN_a)_T/V_g] - T(dP/dN_a)_T$$
$$\times (dV_1/dT)_a - P(dV_1/dN_a)_T, \qquad (14)$$

where N_a is the amount adsorbed defined as the total content.

If the gas is in equilibrium ($Z = 1$), the adsorbent is an inert solid $V_1 \neq V_1(N_a, T)$, then

$$(dE_1/dN_a)_T = h_g + R(dlnP/dT^{-1})_a \qquad (15)$$

(2) The differential energy of the adsorbent-adsorbate system

$$(dH_1/dN_a)_T = h_g + RZ(d\ln P/dT^{-1})_a$$
$$\times (1 - (dV_1/dN_a)_T / V_g) + (dP/dN_a)_T$$
$$\times [V_1 - T(dV_1/dT)_a] \qquad (16)$$

If $Z = 1$; $V_1 \neq V_1(N_a, T)$, then

$$(dH_1/dN_a)_T = h_g + R(d\ln P/dT^{-1})_a$$
$$+ V_1(dP/dN_a)_T \qquad (17)$$

The differential isosteric heat of adsorption is defined as

$$q_{st} = h_g - (dH_1/dN_a)_T = h_g - h_1, \qquad (18)$$

where h_1 is the differential enthalpy of an adsorption system

Since $a = N_a/m_o$, and the specific reduced volume of an adsorption system $v_1(a, T) = V_1(a, T)/m_o$ then

$$q_{st} = -RZ(d\ln P/dT^{-1})_a[1 - (dv_1/da)_T / V_g]$$
$$- (dP/da)_T[v_1 - T(dv_1/dT)_a] \qquad (19)$$

If $Z = 1$ and the adsorbent does not experience deformation induced by adsorption $v_1 \neq v_1(a, T)$ then

$$q_{st} = -R(d\ln P/dT^{-1})_a + v_1(dP/da_a)_T \quad (20)$$

Since in the region of small pressures ($P < 100$ kPa) the latter term is negligible we arrive at familiar equation for the differential heat of adsorption

$$q_{st} = -R(d\ln P/dT^{-1})_a \qquad (21)$$

Equation (16) allows us to relate the isosteric heat with the differential calorimetric heat of adsorption q_k measured calorimetrically using a reference sample bulb with a suitable nonporous sample (Gusev et al., 1991).

$$/q_k/ = q_{st} + V_1(dP/dN_a)_T \qquad (22)$$

It is evident that an alternative setting of the calorimetric experiment would yield some other relation be-
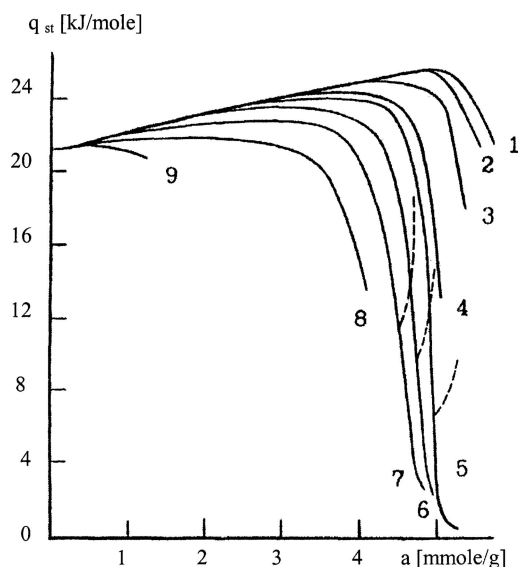

Figure 9. Differential molar isosteric heat of adsorption plotted as a function of the amount of Xe adsorbed by NaX zeolite (full lines) calculated with allowance for the adsorption deformation at (1) 150; (2) 210; (3) 240; (4) 280; (5) 295; (6) 310; (7) 330; (8) 420 and (9) 600K. (The curves obtained by neglecting the adsorption deformation are denoted by dotted lines).

tween the isosteric and calorimetric heats of adsorption (Kington et al., 1951).

Equation (19) suggests that the differential isosteric heat of adsorption depends both on properties gaseous phase in equilibrium with the adsorbent (Z, V_g), and on properties of the adsorbent including magnitude of its deformation induced by adsorption $(dv_1/da)_T$ and increasing temperature $(dv_1/dT)_a$.

Figure 9 shows plots of the differential molar isosteric heat of adsorption against the amount of Xe adsorbed by NaX zeolite (full lines) at temperatures 150–600 K and pressures 0.1 Pa–12 MPa and calculated from Eq. (19). When deformation of the adsorbent is neglected a dependence, is yielded that is denoted by dotted lines. The results given in Fig. 9 imply that the corrections due to the adsorption deformation of the adsorbent introduced into the energetic contribution of the heat of adsorption can be as high as 70–80%. Equation (19) indicates that at high temperatures the dependence of the differential calorimetric heat of adsorption on temperature is due largely to the non-ideality of the gas phase that is given by the compressibility factor Z. A derivative of the type $(dP/da_a)_T$ is also of importance in this region. Similar results were obtained also for other adsorption systems (Fomkin, 1993).

Isosteric Heat Capacity

Temperature differentiation of (18) produces the Kirch-hoff equation

$$\left(\frac{dh_1}{dT}\right)_a = \left(\frac{dh_g}{dT}\right)_a - \left(\frac{dq_{st}}{dT}\right)_a \qquad (23)$$

where

$$C_1 = \left(\frac{dh_1}{dT}\right)_a \qquad (24)$$

is the differential isosteric heat capacity of an adsorption system. Figure 10 shows temperature dependences of the isosteric heat capacity of the adsorption system Xe—NaX zeolite for different amounts of Xe adsorbed.

Similar temperature dependences for isosteric heat capacity were reported for other adsorption systems. Calculations indicate that the occurrence of maxima cannot be ascribed to the effect of properties of gas phase in equilibrium with the adsorbent because heat capacities of gas phase and those of the adsorption system are different both in behavior and in magnitude of values involved. The isosteric heat capacity characterizes generally both a microporous solid (adsorbent) and the fluid adsorbed in its micropores (adsorbate).
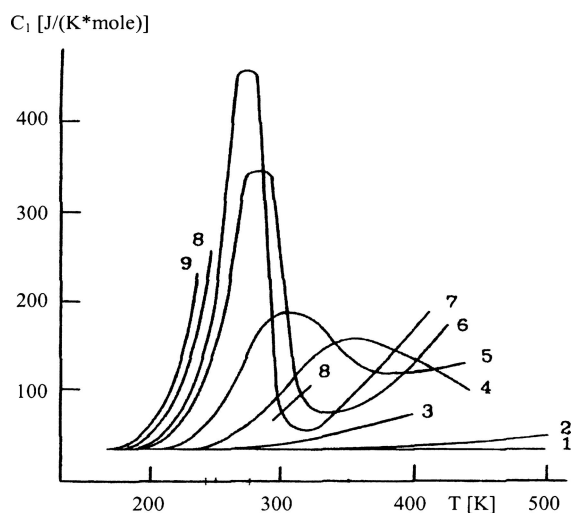
C_1 [J/(K*mole)]

Figure 10. Temperature dependences of the isosteric heat capacity of the adsorption system Xe—NaX zeolite for different amounts of Xe adsorbed: (1) 1.0; (2) 2.0; (3) 4.0; (4) 4.5; (5) 4.7; (6) 4.9; (7) 5.0; (8) 5.15 and (9) 5.30 mmol/g.

Given that the crystalline structure of the adsorbent remains unchanged by adsorption, a microporous solid (NaX zeolite or microporous carbons PAU-10, ACC) cannot be a reason *per se* for the presence of maxima on curves describing the temperature dependence of isosteric heat capacity. In particular, reversibility of the adsorption isotherms, our dilatometer measurements of adsorbents, investigations of zeolite heat capacity, XR diffraction studies of zeolite (Breck, 1974) and activated carbons (Dubinin, 1975) provide proof of evidence for the stability of the micropore structure. The occurrence of maxima on the curves that describe the temperature dependence of isosteric heat capacity seems to be a consequence of specific features that characterize the behavior of the fluid adsorbed in micropores of adsorbents. This follows mainly from the temperature ranges that favor extreme phenomena. As given in Fig. 10, initial formation of maxima occurs in a temperature range that lies about 100–200 K above critical temperature of the gas sorbed. Similar dependences were recorded for other system investigated so far. As the amount adsorbed increases and, correspondingly, the average number of molecules in the cavities of microporous adsorbent increases, maxima on the curves of isosteric heat capacity become more discernable, and their position shifts towards lower temperatures.

From the results of calculations given in a map form with lines that describe the potential energy of interaction in the adsorbent pores (Fiedler et al., 1982) it was found that at low fillings the molecules spend nearly all their time in the deep potential wells. Under isosteric conditions and at moderate and high micropore fillings, an increase in temperature leads to an increase in kinetic energy that favors transition of molecules from single adsorption sites into the micropore volume to form associates. In particular, on analyzing adsorption of He by NaX zeolite, a similar mechanism of adsorption that involves transition from partially localized adsorption to non-localized adsorption could be discovered (Fomkin et al., 1987).

NMR data on Xe^{129} adsorbed in CaA and CaY zeolites at 144 K revealed a rearrangement of the adsorbate structure followed by its ordering (Cheung, 1990). In CaA and CaY zeolites, the chemical shift of Xe^{129} relative to that for the gaseous state increases markedly at a threshold filling of 7 atoms per a cavity while the highest number of Xe^{129} atoms adsorbed per cavity does not exceed 11. This effect can be interpreted as being due to a mutual approach of Xe^{129} atoms. At the

same instant, the NMR signal width decreases to the lowest value, which indicates the ordering in packing of xenon species. From these observations, a "phase transformation" inside the pore systems of A and X zeolites was inferred. To achieve higher loadings in these experiments, it is the usual procedure to reduce temperature rather than to increase pressure. Under isosteric conditions favoring the existence of associates increasing temperatures can promote the destruction of associates with concomitant dramatic increase in the adsorbate heat capacity. The destruction of associates is further accompanied by a marked increase in volume of the adsorbed material. This is well-illustrated specifically by the results derived from computational modeling of Kr and Ar adsorption in cavities of CaA zeolites conducted over wide range of temperatures (Golikov et al., 1989).

Comparing the curves of the differential molar isosteric heat capacity of adsorption systems with relevant curves of the differential isosteric heat of adsorption it is immediately obvious that the highest values of isosteric heat capacity appears in the vicinity of highest values of isosteric heats of adsorption. It appears that the increase in the amount of adsorbed material brings about an increase in the number of molecules in associates, an increase in the contribution of repulsion forces to the intermolecular interaction due to micropore volume limitations and finally an essential diminution in isosteric heat of adsorption. The change in the nature of forces governing the intermolecular interaction of xenon includes the transition from attraction that induces appearance of associates in micropores to repulsion. This development is reflected in the dilatometric curves as evidenced by the shift from the compressive deformation to the tensile deformation NaX zeolite crystalls. For the system xenon-NaX zeolite the maxima on the curves of isosteric heat of adsorption associates with the zero deformations of crystals at higher micropore fillings. In addition to diminutions in isosteric heat of adsorption increase in repulsion forces generates a sudden expansion of zeolite crystals. It appears that similar features are common for all systems involved in the adsorption by microporous adsorbents.

Conclusions

The amount of gas, vapor and liquid adsorbed on microporous over wide range of pressures (0.1 Pa–20 MPa) and temperatures (77, 120–600 K) increases steadily with increasing pressure and is not related to phase transitions in the adsorptive. Isosteres of adsorption constructed as a curve of $\ln P$ against $f(1/T)_a$ retain a linearity over a wide range of pressures and temperatures. The slope of isosteres does not vary on going through the critical temperature of the gaseous phase. At high pressures the differential molar heat of adsorption is dependent on temperature due to imperfection of the gaseous phase and non-inert behavior of the adsorbent. At high fillings of micropores by adsorbed molecules, the differential molar isosteric heat capacity of adsorption systems passes through maxima, which indicates the occurrence of structural rearrangements in the adsorbate.

Nomenclature

a	absolute adsorption (mmol/g)
T	temperature of the system (K)
T_c	critical temperature of gas in equilibriu (K)
T_b	point of conventional boiling (K)
T_t	triple point (K)
P_s^0	saturated vapor pressure over liquid at zero excessive hydrostatic pressure (Pa)
P	pressure of adsorptive in equilibrium, (Pa)
P_s	saturated vapor pressure over compressed liquid (Pa)
$v(P)$	specific volume of the compressed liquid (mol/m³)
$\mu(P_s^0)$	zero reference of chemical potential at a given temperature (kJ/mol)
N	the amount of adsorbate and adsorptive in the volume of the system (mol)
N_a	the amount of adsorbed material (mol)
V	the volume of the "adsorbent- adsorbate-adsorptive" system (m³)
V_1	the volume of a solid including micropores (m³)
v_1	the specific reduced volume of an adsorbent with micropores (cm³/g)
$V_g(p, T)$	the molar volume of adsorptive (gas or liquid) (mol/m³)
m_o	the weight of regenerated adsorbent (kg)
H	the enthalpy of the the thermodynamic system (kJ/mol)
q_k	the calorimetric heat of adsorption (kJ/mol)
S	the entropy of the system (J/[mol∗K])
E	the energy of the system (kJ/mol)
Z	the compressibility factor of gas

q_{st} the differential isosteric heat of adsorption (kJ/mol)

q_k differential calorimetric heat of adsorption (kJ/mol)

C_1 differential molar isosteric heat capacity of an adsorption system (J/[mol/K])

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