Adsorption studies of organosubstituted laminated silicates
2.* Hysteresis phenomena in sorptive deformation studies

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The hysteresis of sorptive deformation of sorbents has been studied for the first time. Based on the results obtained, it is assumed that the deformation of sorbents could be the universal reason for the sorptive hysteresis.

Key words: clay minerals; sorptive hysteresis; non-inertness of sorbent, sorbent deformation.

The reasons for the appearance of sorptive hysteresis in adsorption of polar substances by clay minerals have previously[2] been analyzed. Taking into account the literature data, the following reasons can be presented[2] as the main factors: (1) chemical changes in the structure of minerals; (2) the effect of steric factors; (3) the nonequilibrium character of the process (it is evident that items 2 and 3 are to a certain extent interrelated); (4) swelling of the sorbent; (5) a change in the hardness of crystals (this in fact corresponds to the first factor); (6) the irreversible fixation of sorbate molecules in micropores; *etc.* The reasons leading to capillary hysteresis[3] are also clear from the physical viewpoint. In principle, none of the factors mentioned can be neglected. The same applies to the sorption of nonpolar substances. In particular, the process can in fact be nonequilibrium in microporous structures. For example, low-pressure hysteresis in the cyclopentane—active carbon system has been studied,[4] and the conclusion has been drawn that the phenomenon of low-pressure hysteresis in this system is mainly related to the slow penetration of an adsorbate into the carbon pores, which are similar in size to adsorbate molecules. It is likely that the most serious reason for hysteresis in any systems is non-inertness (or swelling) of a sorbent. Even zeolites with rigid structures undergo experimentally observed deformations during interaction with gases.[5,6]

To make a conclusion about the effect of deformations of a sorbent on hysteresis phenomena, deformation curves, including desorption branches, should be considered in addition to isotherms. The results of such an originally performed study are presented in this work.

Experimental

A dilatometer, which had been described in detail previously,[1,7] was used for measuring sorptive deformation of sorbents. A linear differential transformer, whose core was attached to the sorbent by a plunger, was the main part of the dilatometer. Any changes in the height of the sorbent changed the position of the core in the transformer, which exerted an effect on the signal taken from its secondary winding. The calibrated dilatometer was placed in a liquid thermostat at a specified temperature and was attached to a measuring component (an electron-counting frequency meter, a digital voltmeter, or a generator). Calibration and measurements were performed at the frequency ν = 1000 Hz. The dilatometer used made it possible to measure absolute deformations in the 10^{-7} to $\sim 3 \cdot 10^{-3}$ m range. Equilibrium pressures were measured by M10 and M1000 bellows manometers.

Organosubstituted montmorillonite (Pyzhev) and synthetic fluorohectorite with exchange capacities of $1.00 \cdot 10^{-3}$ and $0.82 \cdot 10^{-3}$ kg-eq. kg^{-1}, respectively, were used. Cetyl pyridinium cations were used as organic cations instead of inorganic cations. The detailed data on sorbents, their crystal chemical formulas, and conditions of preparation for experiments are presented in Ref. 1. We only mention that sorbents were prepared under $\sim 10^8$ Pa as pellets with the surface area of the base of $(52.4 \text{ to } 58.6) \cdot 10^{-6}$ m^2 and the height of $(8.17 \text{ to } 8.60) \cdot 10^{-3}$ m. Samples were nonoriented and swelled isotropically, which was caused by the method of preparation. Before measurements organosubstituted laminated silicates were dehydrated *in vacuo* at T = 353 K and $\sim 10^{-2}$ Pa for 8 h. Isotherms were recorded by the weighing method. Water,

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[*] For Part 1, see Ref. 1.

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hexane, and benzene vapor were used as sorbates, and the interaction between each of them and organosubstituted laminated silicates has rigorously specific character.[1]

Results and Discussion

Detailed sorption calorimetric and dilatometric data for the systems mentioned have been presented previously.[1] In addition, information related to hysteresis phenomena in an experimental study of sorptive deformation of organosubstituted laminated silicates has been presented in Ref. 8. The experimental results for the organosubstituted synthetic fluorohectorite—benzene vapor system are presented in Fig. 1 as an example.

The analysis shows that if the horizontal straight line parallel to the axis of the relative pressure of adsorbate vapor p/p_s is drawn for some sorption value "*a*" in any of figures of the type of Fig. 1, it intersects sorption—desorption isotherms in two points. Pressures p_1 and p_2 correspond to these points (p_1 is referred to the desorption branch and p_2 is referred to the sorption branch). These pressures on curves $\eta = f(p/p_s)$ (η is the relative linear deformation of the sorbent) relate to different deformations of the sorbent, *i.e.*, at p_1 the η_1 deformation is observed on the desorption branch and p_2 on the sorption branch corresponds to the η_2 deformation. The inequality $\eta_1 > \eta_2$ is always fulfilled (see Fig. 1), and the higher internal pressure in the sorbent structure thus corresponds to the η_1 value. One very important moment should be mentioned in this connection.

The following simple criterion of elastic deformations is accepted in solid state physics: when the external loading is removed, the solid body returns to the initial state, *i.e.*, takes the original shape and size. We have performed similar experiments, which show that geometric sizes of sorbents return to initial values after dehydration. However, it follows from Fig. 1 that there is a residual deformation at $p/p_s \approx 0$, but the internal pressure is not removed in this state. The internal pressure is eliminated during the thermal dehydration in the regime of preparation of sorbents to experiments, and the height of the sorbent sample returns to the initial value.

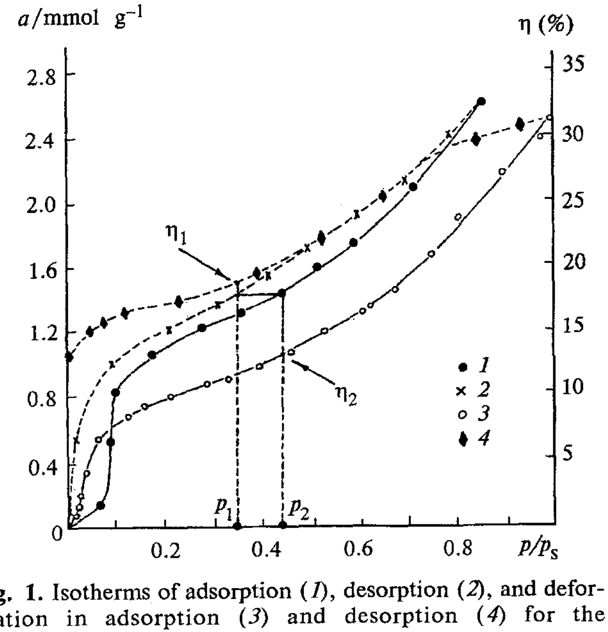

Fig. 1. Isotherms of adsorption (*1*), desorption (*2*), and deformation in adsorption (*3*) and desorption (*4*) for the organosubstituted synthetic fluorohectorite—benzene vapor system at $T = 298$ K.

Thus, when $\eta_1 > \eta_2$ the higher internal pressure in the sorbent structure than that corresponding to η_2 corresponds to the η_1 value. This important result means that when "*a*" values are equal, a redistribution of sorbent molecules in the sorbate is needed to create different internal pressures. It is likely that due to swelling of the system the adsorbate in desorption is redistributed in the adsorbent in such a way that the changes, for example, $\Delta\bar{H}_{ads}$ and $\Delta\bar{S}_{ads}$, result in a lower value of $\Delta\bar{G}_{ads}$ ($\Delta\bar{H}_{ads} = \bar{H}_{ads} - \tilde{H}_{liq}$, $\Delta\bar{S}_{ads} = \bar{S}_{ads} - \tilde{S}_{liq}$, $\Delta\bar{G}_{ads} = \bar{G}_{ads} - \tilde{G}_{liq}$, where $\bar{H}_{ads}$, $\bar{S}_{ads}$, and $\bar{G}_{ads}$ are partial molar enthalpy, entropy, and Gibbs energy, respectively; $\tilde{H}_{liq}$, $\tilde{S}_{liq}$, $\tilde{G}_{liq}$ are the molar enthalpy, entropy, and Gibbs energy of the liquid at the considered temperature, respectively). It is evident that the regions of the sorbent that the sorbate could not penetrate become accessible to the latter in the desorption process due to swelling of the sorbent structure. Taking into account the fact that all sorbents are deformed to different extents in sorption processes, this explanation can be universal for hysteresis phenomena of any systems, including weakly swelling systems. For example, Fig. 2 presents deformation

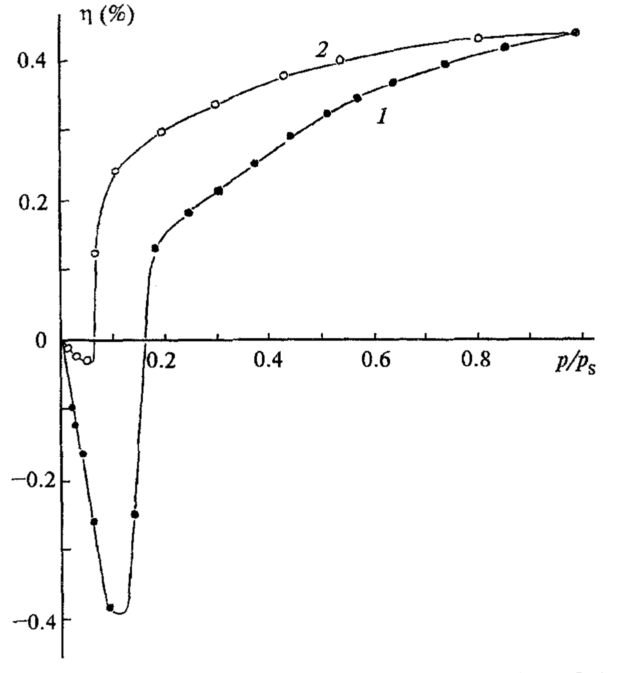

Fig. 2. Dependence of the relative linear deformation of the sorbent (η) on p/p_s in adsorption (*1*) and desorption (*2*) for the microporous active carbon (AC)—benzene vapor system at 293 K.

curves for the microporous active carbon (AC)—benzene vapor system. In this case, a broad hysteresis loop is also observed even with relatively small deformations.

Microporous active carbon kindly supplied by G. K. Ivakhnyuk (St. Petersburg Technological University) was prepared by high-temperature chlorination of Silit pipes in a flow-type quartz reactor. When the chlorination process was completed, which was determined by the cessation of $SiCl_4$ production, the reactor was purged with helium for 1 h to remove traces of chlorine and tetrachlorosilane. The yield of sorption-active carbon was 30 % by weight. The sorption-active carbon synthesized is grouped with microporous AC (the characteristic adsorption energy for benzene $E_0 = 21.2 \cdot 10^3$ J mol^{-1}; the volume of micropores is $(0.37$ to $0.41) \cdot 10^{-3}$ m^3 kg^{-1}). This sorbent was used as a cylinder with height $h = 8.19 \cdot 10^{-3}$ m and diameter of the base $d = 7.63 \cdot 10^{-3}$ m. Prior to the experiment the sample was dehydrated *in vacuo* at $T = 573$ K until a pressure of $\sim 10^{-2}$ Pa was achieved.

Thus, the results presented testify that the fixation of sorbate molecules in the sorbent structure is irreversible due to its deformation.

References

1. A. V. Tvardovskii, Yu. I. Tarasevich, A. I. Zhukova, A. A. Fomkin, and V. V. Serpinskii, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1979 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1537 (Engl. Transl.)].
2. Yu. I. Tarasevich and F. D. Ovcharenko, *Adsorbtsiya na glinistykh mineralakh* [*Adsorption on Clay Minerals*], Naukova Dumka, Kiev, 1975 (in Russian).
3. L. I. Kheifets and A. V. Neimark, *Mnogofaznye protsessy v poristykh sredakh* [*Multiphase Processes in Porous Media*], Khimiya, Moscow, 1982 (in Russian).
4. O. N. Kabanova, T. S. Yakubov, and V. V. Serpinskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1486 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1311 (Engl. Transl.)].
5. O. K. Krasil'nikova, Ph. D. (Chem.) Thesis, Institute of Physical Chemistry Akad. Sci. USSR, Moscow, 1976 (in Russian).
6. A. A. Fomkin, S. Z. Muminov, A. L. Pulin, and I. M. Guseva, *VII Mezhdunarodnaya konf. po teoreticheskim voprosam adsorbtsii* [*VII International Conf. on Theoretical Problems of Adsorption*], Eds. M. M. Dubinin and V. V. Serpinskii, Nauka, Moscow, 1990, 151 (in Russian).
7. A. V. Tvardovski, A. A. Fomkin, Yu. I. Tarasevich, I. G. Polyakova, V. V. Serpinski, and I. M. Guseva, *J. Coll. Interface Sci.*, 1994, **164**, 114.
8. A. V. Tvardovskii, D. (Phys.-Mat. Sci.) Thesis, Institute of Physical Chemistry RAS, Moscow, 1992 (in Russian).

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