CONCLUSIONS

1. Discussion is given of the relation between the enthalpy of liquid immersion of activated carbons and the characteristic energy $E_0$ of the Dubinin–Astakhov equation.

2. The enthalpy of immersion in benzene at 307 K varies from $-90$ to $-140$ mJ/m² equivalent micropore surface area. There is no standard value which can be used for determining micropore volumes and surface areas, the situation here being different from that met in the nonporous solids.

LITERATURE CITED


THE ADSORPTION OF WATER VAPOR ON NaX
ZEOLITES IN THE PRESENCE OF HYDROCARBONS

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The fact that the zeolites are extremely powerful dehydrating agents itself hinders any attempt to study the adsorption of water vapor on zeolites at low degree of filling.

Investigation of the extended dehydration of organic compounds by zeolites involves the study of adsorptio-al equilibrium in zeolite–water–hydrocarbon systems containing water at very low concentrations, and presupposes a knowledge of the precise adsorption of each component in such a system. The problem in question here was therefore that of designing a system which could be used for measuring the adsorption of water vapor on zeolites at concentrations of the order of 2–5 adsorbed molecules per cavity, and the adsorption of binary hydrocarbon–water mixtures as well.

The fact that the initial heat of adsorption of water on zeolites is high (100–125 kJ/mole) [1, 2] is an indication that some 30–50% of the zeolite adsorption space must be filled at pressures of the order of 1 Pa ($10^{-2}$ torr). Most of the manometers commonly used for low-pressure measurements are not suitable for work with water vapor under such conditions.

By using the values of the parameters for the reversible adsorption of water vapor on the NaA zeolite at pressures ranging from $10^{-2}$ to 1 Pa [3, 4], the adsorption of water vapor on the NaX zeolite over this same interval can be measured, the NaA functioning as a special type of "manometer" with the equilibrium water–vapor pressure read off from an adsorption isotherm developed by the torsion–effusion method of [3].
EXPERIMENTAL

The procedure followed here involved determining the adsorption of the NaX zeolite from the loss of water in a microburette and calculating the equilibrium pressure from the adsorption of water on the NaA zeolite inserted in one cup of an adsorption balance.

This made it possible to study both the isotherm for water-vapor adsorption on the NaX zeolite and the partial isotherm for water-vapor adsorption from mixtures, the molecular-sieve effect assuring that the second component of each mixture would adsorb on the NaX zeolite rather than the NaA. Cyclopentane, the second component of the mixtures in question here, could adsorb only on the external NaA crystal surfaces and the adsorption was small in comparison with that of water. The volumetric-gravimetric system shown in Fig. 1 was used to study adsorptive equilibria in the NaX-cyclopentane-water vapor system.

The volume of this system was known to within ±0.25 vol. % from an earlier calibration with He. The larger part of the adsorption space was taken up by the adsorption tube 1 and the McBain quartz spring balance 2, the latter carrying some 0.2 g of granulated NaA zeolite 3. The balance sensitivity was 7·10⁻⁴ g/mm of spring extension. The mesh box 4 containing some 2 g of the powdered crystalline NaX zeolite was set at the bottom of the adsorption tube. The amount of each of the two vapor components introduced into the system was determined by cathetometer measurements (accuracy of reading ±0.005 mm) on the liquid level in the capillary of the microburette 6, the latter enclosed in the high-precision thermostat 5. Minimal dosing gave no less than a 1-2 mm alteration of the liquid level in the burette. The burette was separated from the measuring section of the system by a mercury bellows lock 7, adsorbate filling being supplemented from the ampul 8. A second burette with its own lock and ampul (not shown in the diagram) was used in the work with cyclopentane. The adsorbate was carried quantitatively into the measuring section of the system by inserting loop 9 into a Dewar flask filled with liquid nitrogen.

The lower equilibrium pressures encountered in the work on water vapor adsorption (10⁻²-50 Pa), and the partial water vapor pressures met in the work on the hydrocarbon-water mixtures, were determined by reading the water-vapor adsorption on the NaA zeolite from the McBain balance, and then calculating the pressures from an adsorption isotherm for this zeolite which had been developed earlier by the torsional-effusion method [4]. Pressures ranging from 50-100 Pa up to saturation at the working temperature were read from the U-manometer 10, the latter being so constructed that the mercury level could be brought exactly up to the constant volume mark. All measured values were reduced to normal conditions, a correction for gas nonideality being introduced at pressures in excess of 1 kPa [5]. Low hydrocarbon pressures were measured on the two-stage MacLeod gauge 12 with the metallic valve 11 open; this part of the system was previously calibrated by volume.

By the use of the metallic vacuum valve 11, and the mercury seals 7 and 13, it was possible to avoid dissolution of the hydrocarbon vapors in the vacuum grease in extended experiments with mixed phases. The adsorption tube was equipped with detachable metallic flange which was packed with Teflon or soft metal.

This entire system was housed in an air thermostat where the temperature could be automatically controlled. The part of the adsorption tube containing the adsorbent was immersed in the auxiliary liquid-flow