

## Microporous Structures of Carbonaceous Adsorbents

M.M.Dubin

In the general case, porous carbonaceous adsorbents contain three varieties of pores: macropores, transitional pores and micropores, which are most prominent in active carbons having a polymodal volume distribution of pores. Vapour adsorption in micropores and on the surface of the larger pore varieties differ radically in their mechanism. Micropores are characterized by the volume filling of the adsorption space, the adsorbate being similar to the condensed phase. The surface of transitional and macropores displays monomolecular and poly-molecular adsorption, i. e. the formation of successive adsorption layers. At high relative pressures, volume filling of the pores occurs as a result of capillary condensation of vapours. The lower limit of the effective radii of transitional pores extends to 15 - 16 Å and corresponds to the limit of applicability of the Kelvin equation. Adsorption equilibria in considerably smaller pores are described quantitatively by the theory of volume filling of micropores in vapour adsorption.

Usually, basic information on the parameters of the microporous structure of active carbons can be obtained from experimental adsorption isotherms corrected for adsorption on the surface of transitional pores. Two typical cases are observed depending on the nature of the initial organic materials, the method and degree of activation. The first case corresponds to the quantitative agreement of the adsorption equation with the theory of volume filling of micropores for the entire volume filling region. This equation includes two constants, namely the limiting volume of the adsorption space,  $W_0$ , expressing the micropore volume, and the constant B determining the shape of the isotherm and associated with the micropore sizes. In this case, small-angle X-ray scattering method indicates the presence in the carbons of micropores with effective radii (inertia radii) of 6 to 7 Å. In the second case, the active carbons possess a more complex microporous structure which may be reduced to the presence in the carbon of two micro-

porous structures with parameters  $W_{01}$ ,  $B_1$  and  $W_{02}$ ,  $B_2$ , whose micropores differ substantially in sizes. For the examples studied the small-angle X-ray scattering method reveals, in addition to micropores of the above-mentioned sizes for the first structure, also micropores having inertia radii within the range from 11 to 13 Å for the second structure.

Methods for calculating the specific surface area of transitional pores with digital computers by using experimental isotherms of vapour sorption have been developed for the determination of corrections for adsorption in the transitional pores, and of the parameters of the microporous structure for the general case of the presence of two microporous structures in the active carbons. This calculation method, which takes into account the temperature invariance of the characteristic curves, yields the most reliable results when the initial isotherms correspond to a sufficiently wide temperature range. The parameters of the microporous structure and the specific surface area of transitional pores of active carbons define their fields of application for adsorption of gases, vapours and solutes with different sizes of molecules or subcolloidal particles.

Institute of Physical Chemistry  
U.S.S.R. Academy of Sciences