

# SORPTION OF WATER BY ACTIVE CARBONS

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## Introduction

The two major approaches concerning the theoretical treatment of the adsorption of water by microporous active carbons are compared. The theories based on capillary condensation [1] give a simple explanation for the sharp rise of the isotherm at an intermediate pressure range, and for hysteresis, but do not give a satisfactory explanation for the occurrence of capillary condensation in pores with widths below the mesoporous range. The theories based on coalescence of water aggregates [2], take into consideration the well known fact that water is adsorbed at selected sites on the pore surface, however the results they predict are not always consistent with the actual features of experimental isotherms [3]. An improved model exempt of these difficulties is obtained, if both capillary condensation and adsorption at a fraction of the pore walls surface are assumed. It can be shown by simple thermodynamic arguments that when adsorption is limited to a fraction of the pore walls surface, the pore width capable of inducing capillary condensation decreases, and a microporous carbon producing isotherms of type 1 with hydrocarbons produces an isotherm of type 5 with water. The model also explains other known properties of the experimental isotherms.

## Theoretical Model and Basic Equations

Capillary condensation, is generally treated on the basis of properties of the liquid - vapor

interface within the pore, and explained by the fact that this interface is concave. The ratio  $P^c/P^s$  between the condensation pressure and the saturation pressure is related by the Kelvin equation, to the surface energy at this interface and to the radius of the core of the pore. However capillary condensation, can also be treated on the basis of properties of the solid - liquid interface at the pore walls, and related to energy parameters characteristic of this interface including parameters of the adsorption process. Eq 1 gives a relation between  $P^c/P^s$  and the change in energy at the solid surface  $\gamma_{sal} - \gamma_{sav}$  that results from condensation.

$$RT \ln \left( \frac{P^c}{P^s} \right) = \frac{2v_l(\gamma_{sal} - \gamma_{sav})}{r_k} \quad (1)$$

$\gamma_{sav}$  is the energy of the solid surface when covered with a layer of adsorbate in contact with the vapor phase at the condensation pressure,  $\gamma_{sal}$  is the energy of the solid surface covered with a layer of adsorbate in contact with a liquid condensate,  $v_l$  is the molar volume of the adsorbate and  $r_k$  the radius of the core of the pore. Eq 1 can be derived by applying to the sorbent - sorbate system, an equation analogous to the Gibbs adsorption isotherm or by combining the Kelvin equation with the Young Dupre equation [4, 5].

Eq 1 can be modified and applied to the adsorption of water by an active carbon by introducing the assumption that a fraction  $y$  of the pore walls surface has the ability to adsorb, and the rest of the surface,  $1-y$ , is non-adsorbing. At the adsorbing regions,

condensation is associated with the change  $\gamma_{sal} - \gamma_{sav}$  of the surface energy. The surface energy at the non-adsorbing regions does not vary as the result of condensation, however the presence of such an inert solid surface, forces the occluded sorbate to acquire an additional area with a surface energy corresponding to that of a liquid-vapor interface  $\gamma_{lv}$ . The resulting equation is

$$RT \ln \left( \frac{P^c}{P^s} \right) = - \frac{2v_l \gamma_{lv} \sigma}{r_k} \quad (2)$$

where  $\sigma$  is defined by

$$\sigma = \gamma(1 + \cos \theta) - 1 \quad (3)$$

where  $\theta$  is the contact angle

### Discussion

Eq 2 is analogous to the Kelvin equation, however the relation between the condensation pressure and the pore radius depends on the factor  $\sigma$  instead of the factor  $\cos \theta$ . It is noted that  $\sigma$  is determined by the fraction of the surface capable of adsorbing, it can vary at various locations on the pore surface, it is likely to be positive and consistently smaller than 1, or negative, it depends on the pretreatment of the carbon. Various observed properties of the isotherm for the adsorption of water can be accounted for by Eq 2.

1) The pore width associated with any given value of the condensation pressure decreases

as  $\sigma$  decreases, thus capillary condensation takes place in narrower pores.

- 2) For a given distribution of  $\gamma$  at the pore walls surface, it is likely that some part of the pore space is enclosed by walls with  $\sigma$  negative. This results in inapplicability of the Gurvich rule.
- 3) A variation of the concentration of the sites capable of adsorption along the pore walls surface has an effect analogous to the one produced by a variation of the pore width and is capable of causing hysteresis
- 4) Experimental data were fitted by isotherms derived by combining Eq 2 with a Gaussian distribution of  $\gamma$  along the pore walls surface, neglecting variations of the pore radii.
- 5) Models for the coadsorption of water with other sorbates can be derived. The vapor pressure of a non-miscible component increases in the presence of water and the vapor pressure of a miscible component decreases.

### References

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