Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 1, 47–49

ESTIMATION OF THE DIMENSIONS OF NANO-CAPILLARIES FROM GAS ADSORPTION DATA

J. A. Poulis[1*], *C. H. Massen*[1] *and E. Robens*[2]

[1]Faculty of Applied Physics, Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[2]Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, Duesbergweg 10-14
55099 Mainz, Germany

A new approach is presented to determine the dimensions of cylindrical nanopores from adsorption measurements.

Keywords: *adsorption, capillary, hysteresis, pore size, sorption*

Introduction

The influence of cylindrical and spherical surfaces on the saturated vapour pressure of liquids plays a part in the mechanism of the adsorption of gases in pores. A variety of methods was developed to describe the effects [1–5]. In this paper we present a new approach based on a simple adsorption model. We shall discuss the possibility to use this mechanism for the estimation of the dimensions of cylindrical pores.

We shall discuss experiments, which consist of two parts, under isothermal conditions. We shall use the expression ‘up period’ when the sample is surrounded by a gas the pressure which is increased and use the expression ‘down period’ when the pressure of the gas is lowered. During the ‘up period’ the adsorption takes place in the pores (we consider the gas molecules which are adsorbed inside the pores). When at the end of this ‘up period’ the pores are completely filled, the gas pressure is decreased. Then desorption will start at the ends of the pores, from where the desorbing molecules will leave spherical surfaces of the condensate.

‘Up period’

We consider a hollow cylinder with inner radius, r_{cyl} and length, l_{cyl}. We consider the adsorbate molecules as spheres of radius r_{mol}. We define dimensionless quantities:

$$R_{\mathrm{c}}=r_{\mathrm{cyl}}/(2r_{\mathrm{mol}}) \text{ and } L=l_{\mathrm{cyl}}/(2r_{\mathrm{mol}})$$

The number, n_1, of adsorbed molecules in the first layer has a maximum value, $n_{1\,\mathrm{full}}$’, satisfying:

$$n_{1\,\mathrm{full}}=2\pi(R_{\mathrm{c}}-1/2)L \qquad (1)$$

the i^{th} layer can contain maximally $n_{\mathrm{i\,full}}$ molecules

$$n_{\mathrm{i\,full}}=2\pi(R_{\mathrm{c}}+1/2-i)L \qquad (2)$$

We shall make use of a simplified adsorption model, where we consider only either fully occupied layers or empty layers. The surface tension of the i^{th} layer will be referred to by σ_{i}. We assume that the i^{th} layer is only attracted to molecules in the adjacent $(i-1)^{\mathrm{th}}$ layer so by $n_{\mathrm{i-1\,full}}$ molecules. This number is larger than would have been the case if both the i^{th} and the $(i-1)^{\mathrm{th}}$ layer were flat instead of cylindrical, in which case the attractive force would have been caused by $n_{\mathrm{i\,full}}$ molecules. So for the surface tension σ_{i} of the i^{th} layer in relation to the surface tension σ_∞ of a flat surface we can write:

$$\frac{\sigma_{\mathrm{i}}}{\sigma_\infty}=\frac{n_{\mathrm{i-1\,full}}}{n_{\mathrm{i\,full}}}=\frac{R_{\mathrm{c}}+3/2-i}{R_{\mathrm{c}}+1/2-i} \qquad (3)$$

In order to describe the relation between this surface tension and the saturated vapour pressure p_{si}, we use the optimisation of the Gibbs free enthalpy. Thereby we equalise the specific free energies of the gas phase and of the adsorbed phase and assume that this equality survives a variation of surface tension and gas pressure. We get:

$$(\sigma_{\mathrm{i}}-\sigma_\infty)A_{\mathrm{Av}}=-R_{\mathrm{g}}T\ln(p_{\mathrm{si}}/p_\infty) \qquad (4)$$

where p_∞ stands for the saturated vapour pressure for a gas in contact with an adsorbate with a flat surface, A_{Av} stands for the surface area of a monolayer of the adsorbate which contains a number of molecules equal to Avogadro’s number and where R_{g} stands for the gas constant.

---

[*] Author for correspondence: hannespoulis@hotmail.com

1388–6150/$20.00
© 2006 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

It follows from Eqs (3) and (4):

$$\ln\frac{p_{\mathrm{si}}}{p_{\mathrm{s}\infty}}=\frac{(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)}{R_{\mathrm{c}}+1/2-i} \tag{5}$$

From Eq. (5) we learn that $p_{\mathrm{si}}<p_{\mathrm{s}\,i-1}$, this implies that in the case of our simplified model the full occupation of the first layer immediately leads to a complete filling (n_{full}) of the hollow cylinder. So when:

$$\frac{p_{\mathrm{jump}}}{p_{\infty}}=\exp-\frac{(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)}{R_{\mathrm{c}}-3/2} \tag{6}$$

or

$$\ln\frac{p_{\mathrm{jump}}}{p_{\infty}}=-\frac{(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)}{R_{\mathrm{c}}-3/2} \tag{6a}$$

the adsorbed number of molecules will jump to:

$$n_{\mathrm{full}}=\pi L R_{\mathrm{c}}^{2} \tag{7}$$

‘Down period’

We consider here a hollow cylinder with one open end, completely filled with adsorbed molecules with a flat surface at the open end. At the beginning of the ‘down period’ where we start lowering the gas pressure, desorption starts and the flat surface at the end will change into a spherical surface. Let the radius of this sphere be $r_{\mathrm{sp}}=R_{\mathrm{sp}}2r_{\mathrm{mol}}$, let the height of the desorbed cap of the sphere be: $h_{\mathrm{cap}}=H_{\mathrm{cap}}2r_{\mathrm{mol}}$, we can use

$$(R_{\mathrm{sp}}-H_{\mathrm{cap}})^{2}=R_{\mathrm{sp}}^{2}-R_{\mathrm{c}}^{2} \tag{8}$$

or

$$H_{\mathrm{cap}}=R_{\mathrm{sp}}-(R_{\mathrm{sp}}^{2}-R_{\mathrm{c}}^{2})^{0.5} \tag{8a}$$

We shall calculate the influence of the curvature on the surface tension, by analogy with the explanation, which leads to Eq. (4). We compare the number of molecules in the surface (spherical) layer with the number of molecules one layer lower. The proportion of those quantities will give us the ratio of the value of the surface tension, σ_{sp}, to that of a flat surface:

$$\frac{\sigma_{\mathrm{sp}}}{\sigma_{\infty}}=\frac{(r_{\mathrm{sp}}+2r_{\mathrm{mol}})^{2}}{r_{\mathrm{sp}}^{2}} \tag{9}$$

or

$$\frac{\sigma_{\mathrm{sp}}}{\sigma_{\infty}}=\frac{(R_{\mathrm{sp}}+1)^{2}}{R_{\mathrm{sp}}^{2}} \tag{9a}$$

The special influence on those molecules of the border layer, which are adjacent to the molecules of the cylinder, has been ignored in these equations.

Using thermodynamics, we derive the saturated vapour pressure, p_{sp}, as in the case of Eq. (5):

$$(\sigma_{\mathrm{sp}}-\sigma_{\infty})A_{\mathrm{Av}}=R_{\mathrm{g}}T(\ln p_{\mathrm{sp}}-\ln p_{\infty}) \tag{10}$$

From Eqs (9) and (10) we get:

$$\frac{A_{\mathrm{Av}}\sigma_{\infty}}{R_{\mathrm{g}}T}\,\frac{2R_{\mathrm{sp}}}{R_{\mathrm{sp}}^{2}}=-\ln\frac{p_{\mathrm{sp}}}{p_{\infty}} \tag{11}$$

The last expression we need is one for the number of molecules, n_{des}, desorbed from the cap of the sphere:

$$n_{\mathrm{des}}=\pi R_{\mathrm{sp}}^{2}H_{\mathrm{cap}}-\frac{\pi}{3}[R_{\mathrm{sp}}^{3}-(R_{\mathrm{sp}}-H_{\mathrm{cap}})^{3}] \tag{12}$$

To enable application of the above equation to the number of remaining adsorbed molecules, n, during the ‘down period’ we use:

$$n=n_{\mathrm{full}}-n_{\mathrm{des}} \tag{13}$$

For our computer simulation presented in Fig. 1 we eliminate n_{full}, n_{des}, H_{cap}, $(\sigma_{\mathrm{sp}}/\sigma_{\infty})$ and R_{sp}. In Fig. 1, the quantity $p_{\mathrm{sp}}/p_{\infty}$ has been replaced by p/p_{∞} along the horizontal axis.

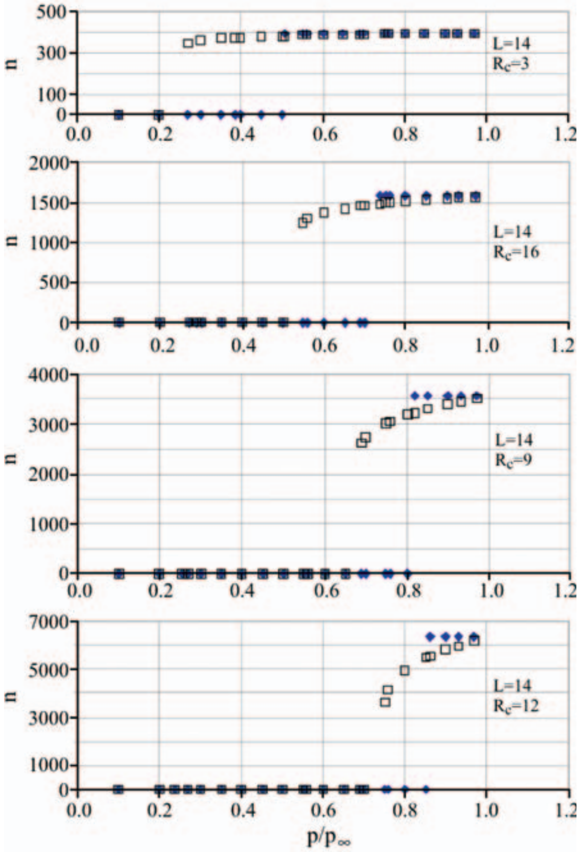

Fig. 1 The influence of the dimensions of nano-capillaries on the ◆ – adsorption (‘up period’) and □ – desorption (‘down period’). The curves refer to water at 293 K and 10^5 Pa leading to: $(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)=1.69$

The curve of the ‘down period’ in Fig. 1 discontinuously falls to zero at pressure, p_{fall}, when $H_{\mathrm{cap}}=R_{\mathrm{c}}$. So according to Eq. (9) when:

$$\sigma_{\mathrm{sp}}/\sigma_{\infty}=(R_{\mathrm{c}}+1)^2/R_{\mathrm{c}}^2 \tag{14}$$

We use when $p=p_{\mathrm{fall}}$:

$$n_{\mathrm{des\,max}}=2/3\pi R_{\mathrm{c}}^3 \tag{15}$$

The remaining number of adsorbed molecules, n_{fall}, just before a pressure of p_{fall} satisfies:

$$n_{\mathrm{fall}}=\pi LR_{\mathrm{c}}^2-2/3\pi R_{\mathrm{c}}^3 \tag{16}$$

and with Eq. (12) we get for the pressure p_{fall}:

$$\frac{p_{\mathrm{full}}}{p_{\infty}}=\exp-\left(\frac{A_{\mathrm{Av}}\sigma_{\infty}}{R_{\mathrm{g}}T}\frac{2R_{\mathrm{c}}+1}{R_{\mathrm{c}}^2}\right) \tag{17}$$

or

$$\ln\frac{p_{\mathrm{full}}}{p_{\infty}}=-\left(\frac{A_{\mathrm{Av}}\sigma_{\infty}}{R_{\mathrm{g}}T}\frac{2R_{\mathrm{c}}+1}{R_{\mathrm{c}}^2}\right) \tag{17a}$$

Conclusions

The unknowns, in which we are interested, are R_{c} and L. Besides in many situations it will be welcome to solve also the quantity $(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)$ while in practice there will be an extra unknown which we did not deal with so far viz. the number of pores. To solve the four unknowns we can use the Eqs (6), (7), (16) and (17). When dividing Eq. (17a) by Eq. (6a) we get an equation with a single unknown viz. R_{c}. When dividing Eq. (16) by Eq. (7) and using the value of R_{c} we can solve L. If one should wish to solve the number of pores or the value of the quantity $(A_{\mathrm{Av}}\sigma_{\infty})/(R_{\mathrm{g}}T)$ one could substitute the values of R_{c} and L into the four Eqs (6), (7), (16) and (17).

References

1 R. M. Barrer, N. McKenzie and J. S. S. Reay, J. Colloid. Sci., 11 (1956) 479.
2 D. H. Everett, in Characterisation of Porous Solids, S. J. Gregg, K. S. W. Sing and H. F. Stoeckli, Eds, Soc. Chemical Industry, London 1979, pp. 229–251.
3 R. S. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces, Wiley, Chichester 1983.
4 L. Bonnetain, J. L. Ginoux and M. Cabedo, In Characterization of Porous Solids, K. K. Unger, J. Rouquerol, K. S. W. Sing and H. Kral, Eds, Elsevier, Amsterdam 1988, pp. 223–232.
5 F. Rouquerol, J. Rouquerol and K. Sing, Adsorption by Powders and Porous Solids, Academic Press, San Diego 1999.

DOI: 10.1007/s10973-006-7593-3