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An Improved Method of Pore Size Distribution Analysis

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An improvement over the method of pore size distribution analysis has been made in this work. The improved method is based upon the idea of the micro pore analysis of Mikhail, Brunauer, and Bodor, and utilizes the V-t curve of nitrogen adsorption. Two pore models are assumed, and the deviation of the initial slope of the V-t plot is ascribed to the pore filling and to the adsorption on the wall of unfilled pores. The improved method of this work is very convenient in that the analysis starts from the small pore regions. The method of this work is however quite distinct from the similar V-t plot method proposed by Sellevold and Radjy. The proposed method is applied to a few adsorbents, and very satisfactory results are obtained. The cumulative surface area calculated by this method also agrees very well with those obtained by the BET plot or by the t-method.

Introduction

The t-method, put forward originally by Lippens and deBoer¹, has been applied quite extensively in evaluating the surface area of solid adsorbent. The method was further developed to apply to the micro pore analysis by Mikhail, Brunauer, and Bodor², and later to the meso pore distribution analysis by Sellevold and Radjy^{3,4}. The meso pores are assumed to be either slate-shaped or open-ended circularly cylindrical in their work. In this meso pore analysis method, like in any other adsorption isotherm methods^{5,6}, the volume of nitrogen adsorbed in a small finite pressure range is assumed to consist of two contributions, one due to the pore condensation if any and the other due to the adsorption on empty pore walls. In case of slate-shaped pores, the surface area of the adsorbent decreases with increase in vapor pressure of the adsorbate gas as a consequence of the pore filling by the growing statistical thickness. In case of cylindrical pores on the other hand, the pore condensation takes place. It is necessary therefore to know the average radius of pores in which the condensation takes place as a function of the vapor pressure and the statistical thickness just prior to the condensation. Sellevold and Radjy made a few assumptions in order to calculate these. First of all, they introduced an idea of effective thickness. The thickness of the physisorbed layer calculated from this effective thickness is expected to give an unreasonably small value, and moreover they ignored the curvature effect of adsorbent surface on the thickness of physisorption. They assumed furthermore a fictitious distinction between the condensate and the physisorbed layer. Nevertheless, this method is quite attractive in that the analysis starts from small pore regions rather than from the large pore regions.

In the improved method, the average radius of the pores in which the condensation takes place in a given small vapor pressure range and the average statistical thickness just prior to the condensation may be calculated using any one of the universal adsorption isotherms in which the Kelvin condensation term is introduced^{7,8}. The Frenkel-Hill-Halsey equation⁹ is used as an universal isotherm in this work.

Meanwhile the volume of the pore condensate can be estimated from the deviation of the slope of initial straight line of the V-t plot. These knowledges will be sufficient to know the volume and the wall area of the pores in which the condensation takes place.

The improved method proposed in this work is based upon the idea of the micro pore analysis by Mikhail, Brunauer, and Bodor, and will provide a means by which the pore volume distribution can be estimated as a function of the pore radius in the meso pore range. The improved method assumes none of above assumptions made by Sellevold and Radjy, and the results of analysis by this method are quite satisfactory when they are compared with the results obtained by conventional adsorption isotherm method.

Theory and Results

The Slope of the V-t plot. Experimental isotherms of nitrogen physisorption on high energy non-porous solid surfaces (such as metal oxide) at the liquid nitrogen temperature are found to be very similar in shape¹⁰. It stimulated many investigators to seek for an universal adsorption isotherm. The FHH equation in the following form can be regarded as one of them.

$$\ln (p^0 / p) = b / \theta^s \quad (1)$$

Table 1. Parameters of the FHH Equation

Sample	γ -Alumina	BN	Davidson 59	Davidson 81
b	2.29	2.65	2.24	2.26
s	2.00	2.37	2.15	2.06

Here, θ is the fractional coverage, and b and s are adjustable parameters. The fractional coverage is related to the statistical thickness by the expression

$$t = \theta \sigma, \quad (2)$$

where σ is the average diameter of nitrogen molecules, which is usually taken as 3.54×10^{-10} m. The parameters are adjusted in this work so as to make the equation fit the lower vapor pressure part of the experimental isotherm, where no capillary condensation is expected to take place. The adjusted values in this work are given in Table 1.

The universal isotherm equations put forward by deBoer *et al.*⁷ as well as any others can also be used. The improved method proposed in this work is immaterial whichever universal isotherm may be used. The result of pore size distribution analysis is not much affected by the choice of universal isotherms.

It is possible to make a plot of adsorbed volume of gas versus the statistical thickness (t) of adsorbed layer from a universal isotherm. Since the statistical thickness is equal to the adsorbed volume divided by the surface area of the adsorbent, this V-t plot should yield a straight line, the slope of which is usually taken as equal to the surface area of the adsorbent (in square meter) divided by a constant 15.47^{10} .

Most of solids, however, have capillaries in which not only the adsorbate gas can condense below the saturation vapor pressure but also more thick adsorption takes place on the pore wall of small curvature prior to the capillary condensation. Accordingly, the adsorption isotherm for such an adsorbent does not yield a straight line when the V-t plot is made. The pressure at which the capillary condensation takes place and the statistical thickness on a curved surface can be calculated using the following equation;

$$\ln(p^0/p) = b/\theta^s + \bar{V}\gamma/rRT \quad (3)$$

The second term on the right hand side results from the consideration of curvature effect. This kind of correction was attempted by Broekhoff and deBoer⁷, and its validity was shown thermodynamically by Ahn *et al.*⁸. In this equation, γ is the surface tension of the adsorbate liquid, r is the curvature of the adsorbed film, and rest of the symbols have usual meanings. Owing to this second term, if a V-t plot is made using an isotherm for an adsorbent of open-ended cylindrical pores, there results in a positive deviation from a straight line. The positive deviation results in also when the micro pore (MP) filling takes place. The deviation due to this MP filling can be distinguished from the one due to the meso pore condensation, since the MP filling is expected to occur at the t values below ca 8 Å. Fig. 1 is the results of V-t plots for a few adsorbents. The isotherms for alumina and BN powders are obtained recently with a gravimetric BET apparatus, and those for Davidson 59 and 81 are read from literature¹¹. The details of the measurement procedure are omitted since it is not the main interest of this work. In case of adsorbents having slate-shaped pores, pore filling occurs without capillary condensa-

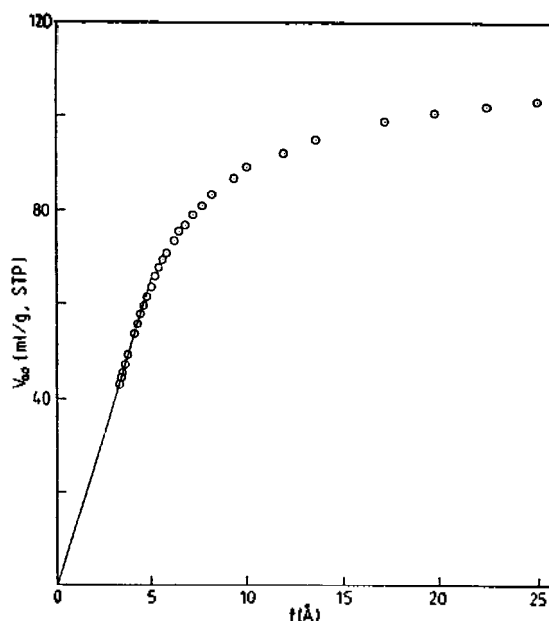
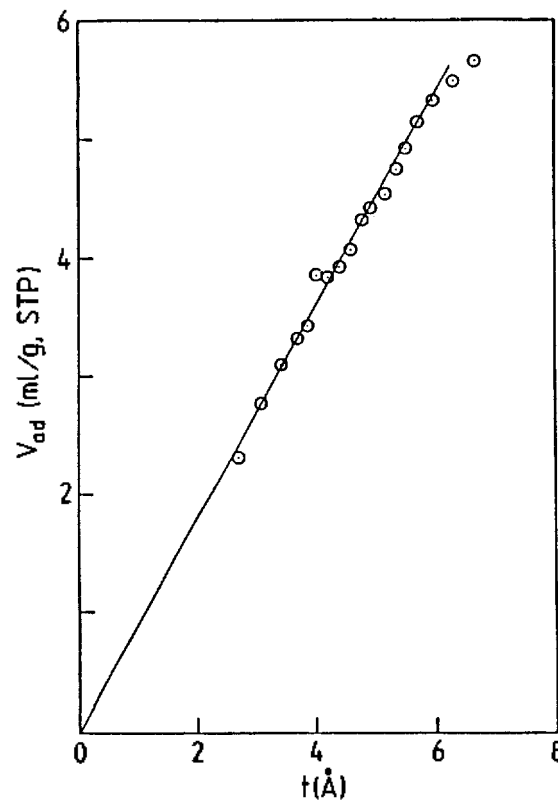
Figure 1. (a) V-t plot for γ -Alumina.

Figure 1. (b) V-t plot for BN.

tion, and the negative deviation in the V-t plot is expected due to the diminishing surface area. This pore filling takes place at the vapor pressure at which the statistical thickness becomes one half of the pore separation.

Two pore models are assumed in this work, too. The adsorbent which gives a positive deviation in the V-t plot as Davidson 59 or 81 is assumed to have open-ended cylindrical pores, and the one which gives a negative deviation as alumina is assumed to have a slate-shaped pores. This

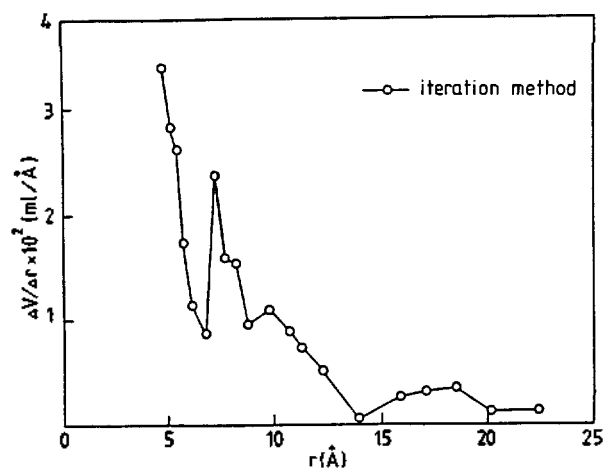
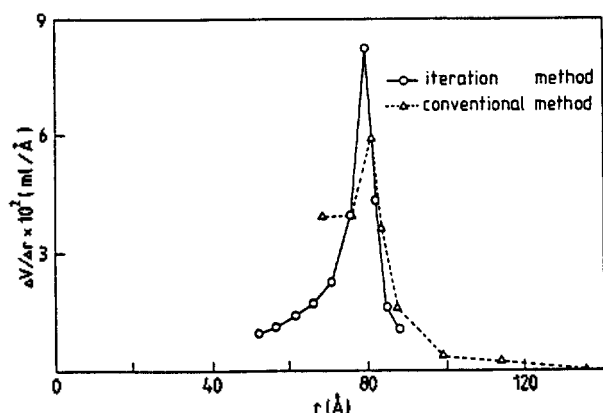
Figure 3. (a) Pore volume distribution curve of γ -Alumina.

Figure 3. (b) Pore volume distribution curve of Davidson 59.

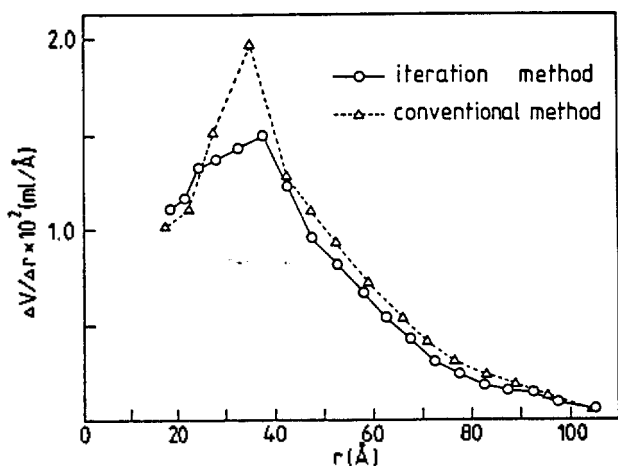


Figure 3. (c) Pore volume distribution curve of Davidson 81.

into the consideration upon the basis of preceding result of analysis. The consideration of the curvature effect shifts the point a upward a little, and raises up the virtual slope a little. The second trial pore size distribution can be obtained in this way. The whole of the analysis is iterated until the terminal interval approaches to the last interval. The result converges within a few times of iteration running. The results of the analysis for the adsorbents of this work are shown in Fig. 3. The broken line in Fig. 3 (b) and (c) are the results obtained with a conventional adsorption isotherm method⁵ in which

Table 2. Surface Areas Estimated with Various Methods

Sample	V-t plot	Surface Area (m ² /g)	
		Cumulative	BET
γ -Alumina	200	194	199
BN Powder	14		14
Davidson 59 ¹¹	269	244	273
Davidson 81 ¹¹	410	333	399

the analysis starts from the large pores for the purpose of comparison.

Conclusions

An improvement over the conventional adsorption isotherm method of pore size distribution analysis has been made in this work. This improved method utilizes the V-t curve of nitrogen adsorption in combination with the conventional method which utilizes the full range nitrogen physisorption isotherms. The improved method is very convenient in that the analysis starts from the small pores. This will eliminate the labor of measuring the adsorption isotherm up to the saturation vapor pressure of the adsorbate. The initial straight line through the origin in the V-t plot holds until there arises a change in surface area of the adsorbents. For cylindrical pores, the point of the first departure from this straight line results from the smallest pore of the adsorbent.

The improved method seems similar to the one put forward by Sellevold and Radjy, but it is quite different. The effective thickness is not assumed, and the curvature effect on the physisorption is fully taken into consideration in this method. Furthermore, no fictitious distinction is put between the adsorbed layer and the condensate. The equilibrium thickness of the adsorbed layer increases continuously and then increases infinitely at the appropriate critical pressure. The condensate should be taken as a continuous extension of the adsorbate. The improved method becomes substantially identical to the method of Sellevold and Radjy in case of slate-shaped pores.

The results of the pore size distribution analysis by the improved method for a few adsorbents shown in Fig. 2 are very similar to those obtained by a conventional method in which the analysis starts from the large pore. Moreover, the cumulative surface areas of the pores coincide with the surface areas calculated from the initial slope of the V-t plot and with BET areas as shown in Table 2.

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A True Cholesteric Columnar Liquid Crystal

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A pure columnar cholesterogen based on the octasubstituted phthalocyanine (PcH₂), S-(+)-2,3,9,10,16,17,23,24-octakis[5-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine(**1a**), is described. To evaluate a cholesteric character of **1a**, the corresponding achiral PcH₂ **1b** and the copper complex of chiral PcH₂ **1a** (CuPc), S-(+)-2,3,9,10,16,17,23,24-octakis[4-(dodecyloxy)-2-oxa-pentyl]-phthalocyanine(**2a**) were also prepared. The chiral **1a** exhibited a typical cholesteric texture change in which the transition of platelet (blue phase) to fan-shape texture was observed (K - M - I), whereas the corresponding achiral **1b** showed only a focal conic texture (K - M - I). This is the first instance of a pure columnar cholesterogen observed with discotic liquid crystal systems.

Introduction

Since a new class of liquid crystals formed by disc-like molecules was first reported in 1977,¹ optically active discogens have been investigated in search for the discotic cholesterogens. Destrade *et al.* first reported the discotic cholesteric phase by mixing a known nematic discotic compound (N_D), triphenylene hexa-4-n-heptyloxybenzoate, with several chiral compounds which did not individually behave as cholesterogens.² They also reported the synthesis of the first genuine discotic cholesterogen, (-)-2,3,6,7,10,11-hexa-[S-(4-methyl)-4-n-hexyloxybenzoyloxy]-triphenylene.³ However, it should be noted that the triphenylene derivatives mentioned above are all related to N_D phases (not columnar D-phase) and the resulting N_D^{*} phases exhibited oily streak texture which were similar to those of classical nematic phases.

Since discogenic phthalocyanine derivatives (Pc) were characterized as columnar D-phases by Piechocki *et al.*,^{4,5} we have focused our attention on these columnar phase and designed a structure of chiral PcH₂ **1a** (Figure 1). We now like to report the synthesis and the optical textures of a new genuine columnar cholesterogen.

The chiral PcH₂ **1a** was prepared according to the procedure⁶ similar to that reported already from S-(+)-1,2-propane-diol (Scheme 1). For the purpose of comparison, achiral PcH₂ **1b** was also synthesized similarly from 1,2-propane-diol.

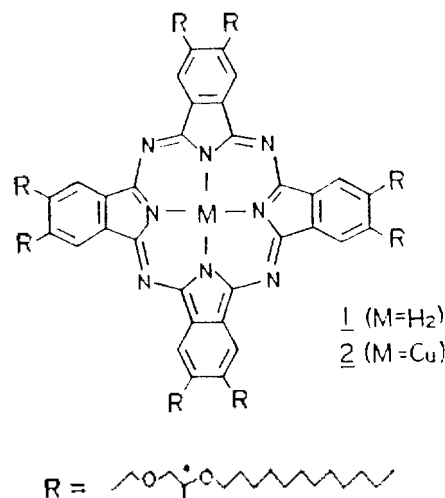
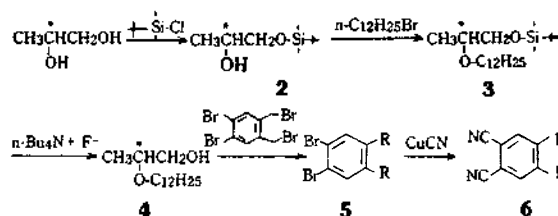


Figure 1. Chemical structure of chiral Pc derivatives: PcH₂ **1a** and CuPc **2a**.



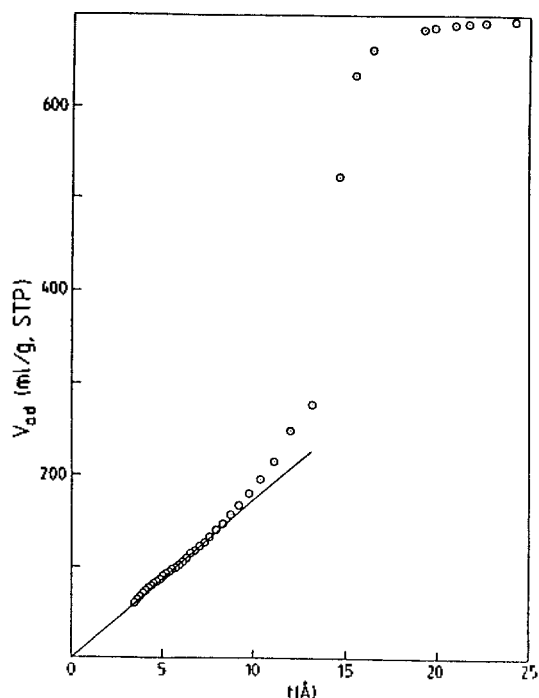


Figure 1. (c) V-t plot for Davidson 59.

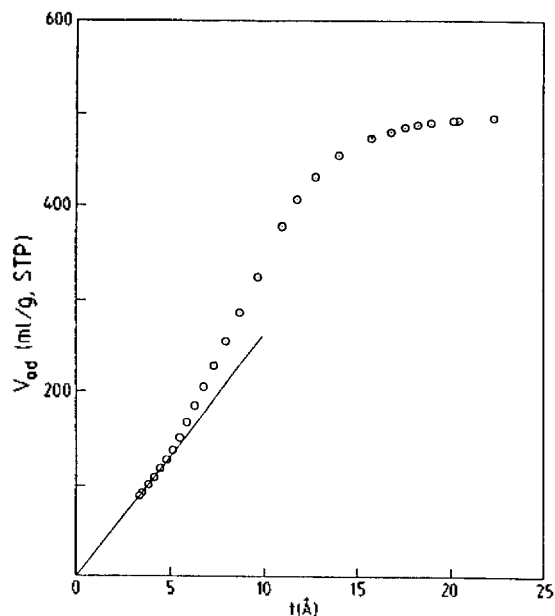


Figure 1. (d) V-t plot for Davidson 81.

work is concentrated on adsorbents of the cylindrical pores. The analysis for adsorbents of the slate-shaped pores turns out to be identical substantially to the method of Sellevold and Radjy³.

The initial slope of the V-t plot has been used to estimate the overall surface area of adsorbents. The point of first departure from this straight line is assumed to be caused by the condensation in the smallest pore of the adsorbent. Therefore, the increase of the slope has to be interpreted as a diminishing of the surface area. The diminishing continues on until the surface area decreases to the outer surface area of the adsorbent at the onset of a new straight line in the V-t plot. The total diminished area should be equal to the inner

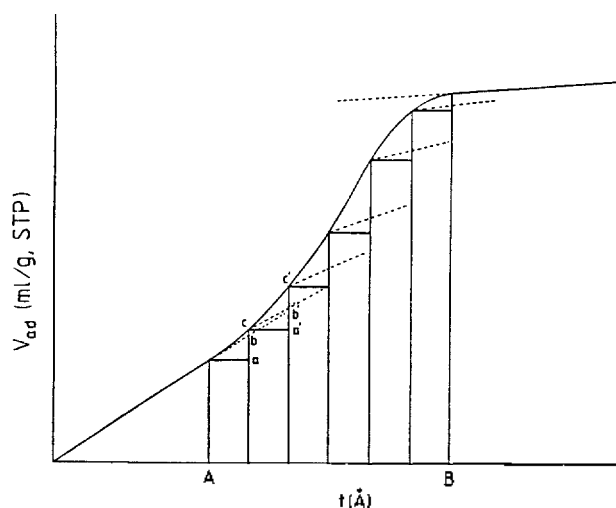


Figure 2. Illustration of the V-t plot analysis.

surface area of the adsorbent.

Pore Size Distribution Analysis. The region of the abscissa in the V-t plot between the point of first deviation (point A in Fig. 2) and the point (B) where the slope resumes a constant value is divided into a small finite intervals at first as in Fig. 2. In the first interval, where the positive deviation begins, the adsorption is considered to be resulted from two causes; the one due to the pore condensation and the other due to the adsorption on the walls of large empty pores. Were it not for the pore condensation and the increased adsorption on the curved surfaces of empty pore walls, the slope of the V-t plot should be unchanged and follow the straight broken line of the first interval in Fig. 2. Accordingly, the volume between the points b and c in the figure can be ascribed to the pore condensation and the increased adsorption resulting from the curvature effect. Since the surface area is unknown as a function of curvature (i.e., radius of the pore) at the beginning, the curvature effect is neglected and the whole volume between the points b and c is ascribed solely to the pore condensation as a first trial. The average pore radius, appropriate for the condensation in this interval, can be calculated from equation 3. Now that the volume of the pore condensate and the average pore radius are known, it is possible to calculate the wall area of this filled pores. In the next interval, the total adsorbed volume can be again ascribed to the pore condensation in the pore of so much increased radius and the adsorption on the so much diminished empty pore walls. Due to the diminished empty pore wall area, the V-t plot in this interval should give a decreased slope, were it not for the further pore condensation. This virtual slope is shown by a broken line in the second interval in Fig. 2. Therefore, the pore condensate in the second interval may be given again by the volume between the points b' and c', and the pore wall area of the pores can be calculated as is done with the first interval. The process of analysis continues to the next interval and so on until the virtual slope becomes equal to the slope at the point B in the figure. This terminal interval usually does not coincide with the last interval of the V-t plot at the first trial. The result of the above analysis as a whole will give the first trial pore size distribution. The whole of the above analysis is run again. The curvature effect on the adsorption on the pore walls is taken at this time