Measurement of Pore Distribution by Utilizing Equilibrium Moisture Content Curve

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Abstract

As one of the methods of measuring the pore distributions, the equilibrium moisture content curve of porous powder was investigated owing to the facility in the measurement.

A simple and reasonable method was developed for calculating the distribution from an adsorption isotherm. It was shown that the distribution could be evaluated by an equation which contained two coefficients. The coefficients depend only on the characteristics of adsorbate, and these values can be calculated from a t-curve.

Since it seemed impossible to measure t-curve on the equilibrium moisture content, the t-curve on water vapor adsorption was determined instead of that on moisture content. It was then shown feasible to apply the curve for pore distribution analysis by the equilibrium moisture content curve.

1. Introduction

In the measurements of pore distributions by the adsorption method, the nitrogen isotherm at its own boiling point has been generally used, and the isotherm of water vapor adsorption is also useful in certain cases. The water vapor adsorption isotherm can be usually measured by a spring balance, and this measurement method has some advantages, for example, unnecessity of the special refrigerant such as liquid nitrogen. But the method by water vapor adsorption needs a long time to measure the isotherm because of the reasons that the adsorption rate is slow at room temperature, and that the adsorbed weight is measured stepwise by increasing the relative pressure.

In the measurements of equilibrium moisture contents by a so-called desiccator method, not only moisture contents of various materials can be determined in a run, but it is also possible to measure the moisture contents for different humidities at the same time. Furthermore, neither complex equipment nor tedious experimental operations for completing the adsorption isotherm are required. In spite of these simplicities, only a few studies have been reported on the calculations of pore distributions from moisture content curves, moreover the estimated values on the pore radii have been known to be too small on account of disregarding the moisture adhered to the pore surface.1)

Although complicated calculations are necessary to obtain a pore distribution from an isotherm, this paper describes a simplified and reasonable method for the calculation from an isotherm of water vapor adsorption. Then the equilibrium moisture content curves are shown on several porous materials. The present method on water vapor adsorption was discussed on whether the calculation of pore distributions from the curves is appropriate or not.

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2. Calculation of pore distribution

2.1 Calculation method of pore volume

When an adsorption isotherm is divided into many sections as shown in Fig. 1, pore volumes of porous materials have been calculated on the basis of the concepts as follows: upon increasing relative pressure from \( x_i \) to \( x_{i-1} \), the state of multimolecular layer at the thickness of \( t_i \) changes into that of capillary condensation in the pore with radius \( r_i \) to \( r_{i-1} \). In the pore with radius more than \( r_{i-1} \), the thickness of the adsorbed layer increases from \( t_i \) to \( t_{i-1} \). Then the sum of those is equal to the increment of adsorption volume, \( \Delta V_i \), on an isotherm, that is,

\[
\Delta V_i = \int_{r_i}^{r_{i-1}} \left( \frac{r - t_i}{r} \right)^2 V(r) \, dr
+ \sum_{j=1}^{i-1} \int_{r_j}^{r_{j-1}} \frac{(r-t_j)^2 - (r-t_{j+1})^2}{r^2} V(r) \, dr
\]

where \( V(r) \) is the distribution function of pore volume. The first term of the right hand side of Eq. (1) corresponds to the increase in adsorption volume on account of pore filling, the second term indicates the increase in thickness of the adsorbed layer in the pore not yet filled by capillary condensation.

Complexities of the conventional calculation methods are in the evaluation process of pore volume from Eq. (1), and various methods have been presented. Cranston and Inkley\(^2\), Doolittle\(^3\) assumed that the thickness of adsorbed layer, \( t_i \), in Eq.(1) depends only on relative pressure, and that the values of \( t_i \) are equal to those of \( t \)-curve. On the other hand, Broekhoff and De Boer\(^4,5\) showed on the basis of thermodynamical considerations that \( t_i \) depends not only on the relative pressure but on the pore radius, as indicated on Fig. 2. They calculated the pore volume by employing both average value of \( t_i \) and average pore radius in each section. In the previous paper\(^6\), their method was reasonably modified as follows.

When the section divided in Fig. 1 is so small that \( V(r) \) is regarded as constant, the pore volume corresponding to the \( i \)-th section, \( V_i \), is denoted by

\[
V_i = V(r)(r_{i-1} - r_i).
\]

Now

\[
R_{c,i} = (r_{i-1} - r_i) \int_{r_i}^{r_{i-1}} \left( \frac{r - t_i}{r} \right)^2 \, dr
\]

and

\[
M_{i,j} = \int_{r_j}^{r_{j-1}} \frac{(r-t_j)^2 - (r-t_{j+1})^2}{r^2} \, dr \frac{1}{(r_{j-1} - r_j)}
\]

are defined, then the pore volume is given by

\[
V_i = R_{c,i}(\Delta V_i - \sum_{j=1}^{i-1} M_{i,j} V_j).
\]

By means of Eq. (5), each pore volume may be estimated by starting with the first section, and in each step making use of the value of \( V_j \) ob-

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Fig. 1 Division of an isotherm. The vertical axis indicates the adsorption volume converted into liquefied volume of adsorbate.

Fig. 2 The relations among thickness of adsorbed layer, pore radius and relative pressure.
The method above-mentioned is based on the calculation of pore volumes from an adsorption branch. In the case of desorption branch, the decrease in adsorption volume on account of capillary evaporation with decrease of relative pressure from $x_i$ to $x_i$ can be similarly represented by the first term of the right hand side in Eq. (1). Decrease of adsorbed layer is also indicated by the second term. Therefore, the calculations of pore volumes from desorption branch also refer to Eq. (5).

According to Broekhoff et al. 4), although the thickness of adsorbed layer in a pore is not necessarily the same as that of t-curve which depends only on adsorbate, it is possible to evaluate the thickness from t-curve.

Since $R_c$ and $M$ defined by Eqs. (3) and (4) respectively are the functions of both pore radius and thickness of adsorbed layer, the values of $R_c$ and $M$ can be calculated from t-curve for a given radius, regardless of the characteristics of adsorbents. If these values have been prepared, the calculation of pore volume can be reduced merely to that of Eq. (5).

2. 2 Calculation method of $R_c$ and $M$

When the pore volumes are calculated by means of Eq. (5), the relative pressure at which capillary condensation takes place, $R_c$ and $M$ must have been known in advance.

The relative pressure can be evaluated on the basis of the method proposed by Broekhoff et al. 4) When the adsorption branch of a porous material is used for measuring the pore volume, the thickness of an adsorbed layer in a pore, for example, $t_{c,i}$ shown in Fig. 2 is given by

$$RT \frac{df(t_{c,i})}{dt} = \gamma M_v / (r_i - t_{c,i})^2$$

for a given radius, $r_i$, where $f(t)$ means t-curve, while using the desorption branch, $t_{c,i}$ is given by

$$2RT \int_{t_{c,i}}^{r_i} f(t)(r-t)dt = RT f(t_{c,i})(r_i - t_{c,i})^2$$

$$= \gamma M_v (r_i - t_{c,i})$$

instead of Eq. (6). By the use of these $t_{c,i}$, the relative pressure, $x_i$ is obtained from

$$RT f(t_{c,i}) - RT \ln x_i = \gamma M_v / (r_i - t_{c,i}).$$

After $x_i$ has been determined, the curve, $T$ in Fig. 2 is drawn by

$$RT f(t) - RT \ln x_i = \gamma M_v / (r - t)$$

for $r$ over $r_i$. Since the curve, $T$ means $t_i$ in Eqs. (3) and (4), $R_c$ and $M$ can be evaluated for a given pore radius.

2. 3 Measurement of t-curve of water vapor adsorption

There are many studies on the pore distributions by the water vapor adsorption method, and a few t-curves have been reported 7). But these t-curves may not be useful for calculating $t_i$ in Eq. (3) or (4) because of insufficient measured points in neighborhood of the saturated pressure. Therefore, the t-curves were measured at 25°C.

Making use of the nonporous materials shown in Table 1, the isotherms of water vapor adsorption were measured by a volumetric adsorption apparatus. Since BET's plot gave a good straight line, specific surface area, $S_{H_2O}$

| Material   | $S \times 10^{-3}$ [m²/kg] | BET-C [-] |
|------------|-----------------------------|-----------|
| H₂O        | 2.42                        | 120       |
| N₂         | 3.39                        | 210       |
| H₂O/ H₂O   | 0.71                        | 300       |
| BaSO₄      | 10.5                        | 11.5      |
| anatase    | 16.3                        | 14.1      |
| rutile     | 65.6                        | 71.8      |
| Ca₃(PO₄)₂  | 0.48                        | -         |
| graphite   | 11.2                        | 1.10      |

Table 1 Specific surface area, $S$ and BET's constant $C$ of nonporous materials.

| Material   | $x_i$ [nm] |
|------------|------------|
| BaSO₄      | 0.0       |
| anatase    | 0.1       |
| rutile     | 0.2       |
| Ca₃(PO₄)₂  | 0.3       |

Fig. 3 The relations between thickness of adsorbed layer and relative pressure.
Table 2  \( R_c \) and \( M \) values for calculation of the pore volume from adsorption branch, which has BET's constant \( C \) over about 50.

| \( r \) [nm] | \( x \) [-] | \( R_{c,t} \) [-] | \( M_j \times 10^3 \) [-] |
|---|---|---|---|
| 15.0 | 0.956 | 1.28 | 51.7 |
| 10.0 | 0.931 | 1.39 | 21.7 |
| 7.5 | 0.904 | 1.49 | 21.7 |
| 6.0 | 0.875 | 1.60 | 26.4 |
| 5.0 | 0.846 | 1.73 | 6.91 |
| 4.5 | 0.826 | 1.78 | 12.1 |
| 4.0 | 0.801 | 1.84 | 27.0 |
| 3.5 | 0.768 | 1.91 | 40.5 |
| 3.0 | 0.723 | 2.00 | 44.3 |
| 2.5 | 0.660 | 2.11 | 31.5 |
| 2.0 | 0.566 | 2.20 | 35.8 |
| 1.5 | 0.420 | 2.26 | 41.9 |
| 1.0 | 0.203 | 2.26 | 47.3 |

Fig. 4  \( t_f - \ln x \) relations obtained from the isotherms of graphite etc.

was calculated by employing 0.108 nm\(^2\) as the molecular cross-sectional area of water. The areas obtained and those by nitrogen adsorption method were shown in Table 1 together with BET’s constant \( C \).

The thickness of adsorbed layer on the surface of an adsorbent, \( t_f \), is evaluated as the ratio of an adsorbed volume of water to the specific surface area, \( S_{\text{H2O}} \). The relations between \( t_f \) and the relative pressures are shown in Figs. 3 and 4. Although the plots in Fig. 3 (a) shift to the right in lower pressure range, the regions over two dotted lines are useful for calculations of the pore distributions from the adsorption and desorption branches. We regarded that measured points fell on a straight line in this regions, and then determined

\[
\ln x = 0.08 - 0.132/t_f^{2.3}
\]

as \( t \)-curve. For higher pressure range, the following relation can hold from Fig. 3 (b).

\[
\ln x = -0.069/t_f^{3.25}
\]

Eqs. (10) and (11) agree with each other at \( t_f = 0.73 \) nm, that is, \( x = 0.825 \).

These two equations are based on the isotherms which have the values of BET-C over about 50 as shown in Table 1. On the other hand, the values became about 20 when silicic anhydride and graphite\(^a\) were employed as adsorbent. The relationships between \( t_f \) and \( \ln x \) for these samples are shown in Fig. 4. The straight line in the figure gives

\[
\ln x = 0.85 - 0.708/t_f
\]

Eq. (12) agrees with Eq. (10) at \( t_f = 0.52 \) nm.

2. 4 Values of \( R_c \) and \( M \)

In order to carry out the integrations in Eqs. (3) and (4), each section in Fig. 2 was divided further into twenty, and \( t_f \) for the each divided point was evaluated with the aid of Eqs. (9) to (12). Integral values were then calculated by

\(^a\) Value of \( S_{\text{H2O}}/S_{\text{N2}} \) of graphite depends on the state of oxidation of its surface. Since the value of the graphite used in this study is 1.01, it may be suitable as the adsorbent for measuring \( t \)-curve.
Simpson's method. The values obtained are shown in Tables 2 to 4.

By reading of the adsorption volumes at the relative pressures shown in the second column of each table, the pore volumes can be easily evaluated by using of Eq. (5), and the calculations of the pore distributions refer to Eq. (2).

3. Equilibrium moisture contents

3.1 Measurement methods

The equilibrium moisture contents of the porous materials were measured by the desiccator method.

Weighing bottles in which sample was contained were placed in a box made of stainless steel instead of the desiccator. The box was then submerged in a thermostat to keep it at a constant temperature. Humidity in the box was controlled by the use of saturated aqueous solution of a salt. A small fan was attached in the box, so as to keep humidity in the box uniform. According to the results of a few preliminary experiments, it was known that the weights of samples which were dried for 24 hours under the conditions of about 13 Pa and 130°C were able to regard as the weights of dry basis. The moisture contents of the samples laid in the box for two weeks, though they reached constant values for 3 to 7 days, were regarded as the equilibrium values.

In order to compare the equilibrium moisture contents with the amounts of water vapor adsorbed, adsorption isotherms were measured with a spring balance and with the glass wares as shown in Fig. 5. A sample was dried and weighed by using the left-halves of the wares. A saturated salt solution was poured into the right-halves to control the vapor pressure of water. After evacuating air in the wares under frozen state of the solution, the wares were maintained at a constant temperature in a thermostat. The adsorbed amount was obtained from the weight increment of the left-halves of the wares.

3.2 Comparison of equilibrium moisture content curves with water vapor adsorption isotherms

Under the controlled humidity by the use of saturated solution of the salt shown in Table 5b), the equilibrium moisture contents of activated aluminas were measured at 25°C. Some of the results are shown by the solid lines in Fig. 6. The equilibrium moisture content of a sample was measured by utilizing three weighing bottles in a run. The solid lines in the figure represent the average values of three runs. The symbols on the lines such as I mean the greatest and least values of measured moisture contents. As is evident from Fig. 6, the magnitudes

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Fig. 5 Glasswares for measuring the amount of water vapor adsorbed.

Fig. 6 Comparison of equilibrium moisture content curves (EMC) with isotherms of water vapor adsorption (H$_2$O)
Table 3  $R_c$ and $M$ values for calculation of the pore volume from desorption branch, which has BET's constant $C$ over about 50.

| $r$ [nm] | $x$ [-] | $R_{c,i}$ [-] | $M_{ij} \times 10^3$ [-] |
|----------|---------|---------------|-----------------|
| 15.0     | 0.925   | 1.18          | 20.4            |
| 10.0     | 0.885   | 1.24          | 12.2 21.6       |
| 7.5      | 0.845   | 1.30          | 9.02 14.4 21.8  |
| 6.0      | 0.805   | 1.36          | 5.05 7.70 15.2  |
| 5.0      | 0.765   | 1.41          |                |
| 4.5      | 0.738   | 1.45          | 5.51 8.32 11.6 15.4 19.5 |
| 4.0      | 0.705   | 1.50          | 5.66 8.44 11.6 15.2 18.8 22.6 |
| 3.5      | 0.666   | 1.56          | 6.25 9.24 12.5 16.2 19.7 23.3 28.6 |
| 3.0      | 0.616   | 1.63          | 7.04 10.3 13.8 17.6 21.2 24.6 29.5 37.3 |
| 2.5      | 0.549   | 1.73          | 8.11 11.8 15.6 19.7 23.4 26.8 31.5 38.5 50.4 |
| 2.0      | 0.459   | 1.86          | 9.74 14.0 18.4 23.0 27.0 30.6 35.5 42.3 52.7 71.9 |
| 1.5      | 0.330   | 1.99          | 12.9 18.4 23.9 29.6 34.4 38.7 44.3 51.9 62.7 79.9 113.7 |
| 1.0      | 0.146   |               |                |

of deviations in the measured values increased with increasing humidities, and the constant values of moisture contents were not obtained at the saturated humidity for powder samples.

The isotherms of water vapor adsorptions were measured by two methods mentioned above. The values obtained from both methods almost agreed. The results were also shown in Fig. 6 by the dotted lines. As shown in the figure, the curves of equilibrium moisture contents fell under the adsorption isotherms for all samples.

In order to obtain the specific surface areas, BET's plot was carried out after the conversion of the moisture weight into the volume of water vapor at the standard condition of gas. The results as well as BET-C were shown in Table 6. The specific surface areas evaluated from moisture content curves were slightly smaller than those from other isotherms.

4. Pore distributions

4.1 Pore distributions from equilibrium moisture content curves

By means of the method described above, the pore distributions were calculated from the curves shown in Fig. 6.

The calculations of pore volumes were carried out by the use of numerical values in Table 2 or 3 from the isotherms of water vapor adsorptions except Wako-1525. From other curves, of which BET-C was less than 50, pore volumes were calculated by utilizing the values in Table 4. Results were shown in Figs. 7 and 8.

In Fig. 7, the pore distributions obtained from ad- and desorption branches of the equilibrium moisture content curves (EMC) compared with those from the water vapor adsorption isotherms ($H_2O$). Fig. 8 shows the comparisons among the cumulative pore volumes evaluated from the adsorption branches.

Three pore distribution curves almost agreed with each other, despite there were differences between the moisture content curves and the water vapor adsorption isotherms. As the
Table 4 $R_c$ and $M$ values for calculation of the pore volume from an isotherm, which has BET's constant $C$ less than 50.

| $r$ [nm] | $x$ [-] | $R_c$ [J] | $M_{ij} \times 10^3$ [-] |
|----------|---------|-----------|--------------------------|
| 2.5      | 0.660   | 2.11      | 11.0                     |
| 2.5      | 0.566   | 2.20      | 14.4 20.8 27.2 33.9 39.8 45.2 52.6 63.4 81.6 129.0 |
| 1.5      | 0.420   | 2.16      | 20.2 28.8 37.6 46.4 54.1 60.9 69.7 81.6 98.8 126.4 191.0 |
| 1.0      | 0.203   |           |                          |

[adsorption]

[desorption]

Fig. 8 Cumulative pore distribution curves obtained from adsorption branches.

reasons for the agreement, it may be considered that the values of $\Delta v_i$ in Eq. (5) obtained from the moisture content curves were nearly equal to ones from the isotherms in higher pressure range, because both curves were in parallel with each other. In the lower pressure range, since the slope of the moisture content curves were larger than that of the isotherms, the values of $\Delta v_i$ from the moisture content curves also became larger, while the values $R_c$ in Table 4 are smaller than that in Table 2 or 3, and $M$ is in opposite relation to $R_c$. By these effects, it was expected that the pore distribution was agreed with each other also in lower pressure range.

The total pore surface, $\Sigma S$ was calculated from the pore distribution curve. Table 7 shows the comparisons of the results with the specific surface areas from BET's method. The ratio of the two surface areas has been used to judge whether the pore distribution obtained was reasonable or not. It seemed that $\Sigma S$ nearly agreed with the specific surface areas in any method.

4.2 Discussions

In order to calculate the pore distribution from the equilibrium moisture content curve, the $t$-curve of the moisture content must be measured in principle. It is then desirable that $R_c$ and $M$ have been evaluated from the $t$-curve. But the amount of moisture content of nonporous material is very small as that in the case of water vapor adsorption. Although water adsorption isotherm can be volumetrically measured with good accuracy, the moisture contents cannot be measured with enough accuracy as shown in Fig. 6. Therefore, it is very difficult to measure the $t$-curve on the equilibrium moisture content.

If the $t$-curve of moisture contents could be measured on nonporous materials, the curve might differ from that of water vapor adsorp-

Table 5 Relative pressure over the saturated aqueous solution of salt at 25°C.

| salts   | $x$ [-] | salts   | $x$ [-] |
|---------|---------|---------|---------|
| LiBr    | 0.067   | NaBr    | 0.578   |
| LiCl    | 0.111   | NaNO₂   | 0.643   |
| CaBr₂   | 0.162   | KI      | 0.688   |
| CH₃COOK | 0.224   | NaCl    | 0.754   |
| MgCl₂   | 0.328   | KBr     | 0.808   |
| NaI     | 0.378   | KCl     | 0.842   |
| K₂CO₃   | 0.440   | BaCl₂   | 0.903   |
| Co(NO₃)₂ | 0.490   | K₂SO₄   | 0.976   |

4) Blanks in the table mean no available data for the desorption branch. The powder of Wako-1525 is so fine that it scattered when the vapor pressure of water was decreased.
Table 6 Specific surface areas, $S$ and BET's constant $C$ of activated aluminas

| Materials    | $S \times 10^{-3}$ [m$^2$ / kg$] | BET-C [-] |
|--------------|---------------------------------|-----------|
| Merck-1077   | 108 123 130 20 60 102           |           |
| Wako-1525    | 140 146 166 19 28 68            |           |
| Neobead C-4  | 163 184 177 26 53 175           |           |
| Neobead D-4  | 226 283 277 25 53 126           |           |
| Neobead MSD-2| 246 303 270 27 81 253           |           |

Table 7 Comparison of total pore surface areas, $\Sigma S$ with BET's specific surface areas, $S$

| Materials    | $\Sigma S \times 10^{-3}$ [m$^2$/kg]$] | $\Sigma S/S$ [-] |
|--------------|-----------------------------------|------------------|
| Merck-1077   | 126 138 148 1.17 1.12 1.14*       |           |
| Wako-1525    | 160 164 183 1.14 1.12 1.10        |           |
| Neobead C-4  | 164 182 191 1.01 0.99 1.08        |           |
| Neobead D-4  | 165 197 206 1.01 0.97 1.16        |           |
| Neobead MSD-2| 333 332 337 1.47 1.17 1.22        |           |

* upper row: calculated from adsorption branch
** bottom row: from desorption branch

As easily expected from Fig. 6, in which the results on the porous samples were depicted, though, the pore distributions could be obtained from the moisture content curves by employing $t$-curve of water vapor adsorption which had the different value of BET-C. The distributions were reasonable as shown in Table 7, and agreed with those obtained from isotherms of water vapor adsorption. Furthermore, in our previous papers, it was shown that the pore distributions in Figs. 7 and 8 agreed well with the ones measured by the mercury penetration method, and by the nitrogen adsorption method.

From these results, we concluded that values of $R_c$ and $M$ shown in Tables 2 to 4 were also useful for the equilibrium moisture content curves.

5. Conclusion

Investigations on the calculation and the measurement of the pore distribution were carried out, and it was shown that pore volume could be easily evaluated by Eq. (5). The equation contains two coefficients, $R_c$ and $M$, which can be calculated by the aid of $t$-curve.

The values of $R_c$ and $M$ obtained for the water vapor adsorption were applicable also to the determination of the pore distributions from the equilibrium moisture content curves.

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Nomenclature

- $C$: BET's constant [-]
- $f(t)$: $t$-curve [-]
- $M$: coefficient defined by Eq. (4) [-]
- $M_v$: molar volume of adsorbate [nm$^3$/mol]
- $R$: gas constant [J/(mol·K)]
- $r$: pore radius [nm]
- $R_c$: coefficient defined by Eq. (3) [-]
- $S$: specific surface area [m$^2$/kg]
- $T$: temperature in measurement [K]
- $t$: thickness of adsorbed layer in a pore [nm]
- $t_f$: thickness of adsorbed layer on the flat surface [nm]
- $V$: pore volume [l/kg]
- $v$: adsorbed volume [l/kg]
- $V_{cum}$: cumulative pore volume [l/kg]
- $V(r)$: distribution function of pore volume [l/(kg·nm)]
- $W$: adsorption amount of water vapor [kg-H$_2$O/kg-solid]
- $W_e$: equilibrium moisture content [kg-H$_2$O/kg-solid]
- $x$: relative pressure [-]
- $\gamma$: surface tension of adsorbate [J/nm$^2$]
- $\Sigma S$: total pore volume [l/kg]

Subscripts

- $\text{H}_2\text{O}$: adsorption of water vapor
- $\text{N}_2$: nitrogen adsorption

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