Experimental Evidence for the Theoretical Condensation Isotherm on Spheres Arranged in the Closest Packing

By Izumi Higuchi, Yataro Ushiki
and Reiko Suzuki

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One of the contentions of the capillary condensation theory is that the shape of isotherms in the range of high relative pressure is determined by the pore distribution of the sorbent. Hitherto, however, we have not known any process to control precisely the pore distribution of sorbent in its preparation. Therefore the contention seems to have no experimental evidence.

In the former report[1,2] one of us calculated three types of theoretical capillary condensation isotherms which were given by spheres of the sorbent when they were arranged linearly, or two dimensionally, or in the closest packing. A number of experimental isotherms given by corpuscular sorbents, consisting of non-porous particles, exhibited unquestionably the capillary condensation in the range of relative pressure, which was anticipated from the theory and the size of particles, arranged in the two dimensional closest packing. If we can get a corpuscular sorbent of which packing type is previously known, the theoretical condensation isotherms will be confirmed experimentally. Experimental isotherms of benzene and methanol at 0°C on the porous Vycor glass are shown in Figs. 1 and 2. The shape of sorption and desorption isotherms are very similar to what we can theoretically obtain for the corpusclar sorbent if the elementary spheres are arranged in the closest packing. Porous Vycor glass, considering from its preparation process and

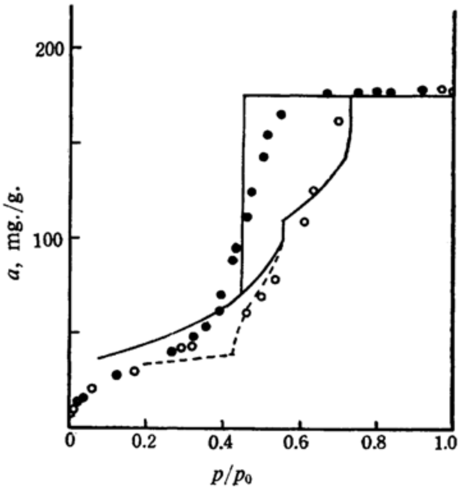

Fig. 1. Sorption isotherm of benzene at 0°C on porous Vycor glass. Circles, sorption data; solid circles, desorption data; the solid line, the theoretical condensation isotherm; the dotted line, the theoretical one, taking into account the vapor pressure correction.

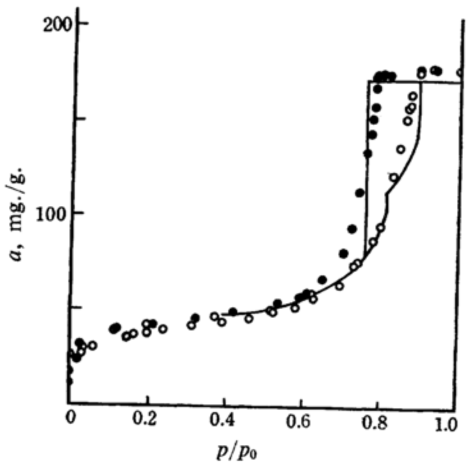

Fig. 2. Sorption isotherm of methanol on porous Vycor glass at 0°C. Circles, sorption data; solid circles, desorption data; the solid line, the theoretical condensation isotherm.

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its hardness, seems to be the most suitable sorbent which is idealized to be consisting of spherical silica particles arranged in the closest packing. The average diameter of elementary particles assumed to be spherical can be calculated from BET area, which is obtained experimentally with benzene isotherm. Then, theoretical condesation isotherms for benzene or methanol can be calculated from the $V(y)$-y relation given in the previous report$^{2)}$, wherein $V(y)$ denotes the condensed liquid volume per the unit volume of sorbent and y is the radius of curvature of the condensed liquid surface divided by the radius of spherical particles.

The theoretical ones, exhibited by solid lines in the figures, are in good agreement with the experimental values. This is a more satisfactory agreement than expected, because the packing model used in the calculation is quite an idealized one.

From the success mentioned above, we can draw a number of important conclusions for the sorption phenomena : (1) The structure of porous Vycor glass is idealized to be consisting of almost spherical particles arranged in the closest packing. (2) Both sorption and desorption isotherms in the range of high relative pressure are due to the capillary condensation of the sorbate. (3) Kramer-McBain mechanism for the hysteresis$^{3)}$ in isotherms is confirmed experimentally to be very reasonable.

Both works of Barrer et al$^{4)}$. and Kiselev et al.$^{5)}$ seem to be excellent extensions from the similar standpoint for the capillary condensation theory and hysteresis mechanism. Barrer et al. calculated various theoretical condensation isotherms for a number of single pores different in their shapes and gave a reasonable formula to compute the isotherm for the contact zone between spheres. According to our precise numerical estimations, it is not adequate to calculate the condensed liquid volume between contact spheres by their scheme because the difference in volume between their model and ours is so minor as to be practically negligible. On the other hand, calculations of vapor pressure of the sorbate by our approximation using the usual Thomson equation is rather serious for the linear packing of spheres. Fortunately, however, it is not so serious, as mentioned previously$^{2)}$ for the closest packing wherein true two dimensional concave meniscus is prevalent between spheres. The correction for this effect is shown by the dotted line in Fig. 1, indicating that our approximation adapted previously may not essentially influence the theory.

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College of Arts and Sciences
Tohoku University
Sendai

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